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UMI®
A STUDY OF THE OVERALL INTERNAL DYNAMIC MODE
OF POLY(ETHYLENE OXIDE) IN METHANOL WITH
AND WITHOUT LITHIUM PERCHLORATE
(LiClO₄)

by

Gregory C. Piet

Bachelor of Science
Ramapo College of New Jersey
1996

A thesis submitted in partial fulfillment
of the requirements for the

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ABSTRACT

A Study of the Overall Internal Dynamic Mode of Poly(ethylene oxide) in Methanol With and Without Lithium Perchlorate (LiClO₄)

by

Gregory Piet

Dr. James Selser, Examination Committee Chair
Professor of Physics
University of Nevada, Las Vegas

It is shown that using PCS the detection and characterization of the overall internal relaxation mode of high molecular weight, narrow molecular weight distribution PEO in methanol with and without the presence of LiClO₄ is so difficult as to be impractical. Moreover, PCS analysis proved to be extremely sensitive to small differences in data quality which further decreased the reliability of measurements. Nevertheless, the results of the present study were sufficiently good to allow a meaningful comparison between experiment and theory and to reveal useful new information about the effect of LiClO₄ on PEO coil internal behavior in methanol solution. Sample preparation techniques and the equipment required to successfully make the measurements allowing for quantitative analysis of the overall internal mode are also described. Furthermore, the particular importance of the high molecular weight of the PEO sample of about one million Daltons combined with a narrow molecular weight distribution is presented and discussed. Restated, the results of this work while informative and useful show that using PCS investigations of PEO in methanol, regardless of the presence
if LiClO\textsubscript{4} is feasible but impractical for obtaining detailed, accurate and quantitative information relating to the overall internal relaxation mode of this linear, flexible polymer.
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CHAPTER 1

INTRODUCTION

As the uses of polymers increase everyday, the need to understand fundamental aspects of polymer behavior increases as well. With this greater understanding, improvements in current applications become possible and the efficiency of devising new applications is increased. Industrial applications produce a countless variety of polymers and polymer blends in the search for the optimal material for each application. In this work, learning more about the overall internal mode dynamics of PEO in solution with and without LiClO_4 addresses fundamental issues and provides insights on the behavior of a system of practical interest, i.e. on the mechanisms of charge transport through polymer electrolytes in polymer batteries. This information should assist in increasing the efficiency of polymer electrolyte charge transport thus allowing the manufacture of more efficient polymer batteries in the future.

In particular, the recent development of novel polymer batteries is a compelling reason for trying to learn about the overall internal mode of PEO, whether it be in the molten state or in dilute solution. The polymer electrolyte used in certain polymer batteries available today consists of an electrolyte salt dissolved into a polymer melt. It would seem that the behavior of a PEO melt would not directly relate to the behavior of PEO in dilute solution. In fact, there have been no attempts to correlate information about the internal behavior of PEO in solution with the behavior of PEO in the molten state. Considering the relatively dense environment in the interior of PEO coils in solution, it was felt that a correspondence between PEO
coil internal dynamic behavior in solution not only existed but might well provide valuable information about the behavior of PEO melts. So, one goal of this work is to assist in the development of polymer battery technology. Not only is learning about PEO behavior important for developing and improving existing industrial applications, but there is virtually no information available regarding the behavior of PEO internal mode dynamics demonstrating the need for additional information about PEO internal dynamic behavior as well.

Photon correlation spectroscopy (PCS) is an ideal method for analyzing polymer chain dynamic behavior (Berne, Pecora, 1990). A major advantage of PCS is that it is noninvasive, i.e. it does not perturb the sample being studied. By contrast, for the most part, other analysis techniques are invasive. Examples of commonly used invasive techniques include those that implement absorption of the probing radiation and those using a mechanical perturbation of the system to induce a measurable response. The noninvasive character of PCS recommends it for the task of determining the internal mode behavior of PEO in methanol.

PCS measurements are sensitive to motions of macromolecules in solution, i.e. to spontaneous, thermally activated dynamic behavior such as the Brownian motion (Berne, Pecora, 1990). PCS can provide information about the center-of-mass translational diffusive motion of the polymer in solution, and then about the polymer's hydrodynamic radius via the Stokes-Einstein relation (Einstein, 1957; Berne, Pecora, 1990; see also Chapter 2, Equation 6). In addition, PCS can provide information about the behavior of the overall internal relaxation of the polymer in solution (Berne, Pecora, 1990). This overall internal mode corresponds to the relaxation of polymer segments throughout the polymer coil in solution as the coil reconfigures from a nonequilibrium to an equilibrium conformation. For example, modeling the linear, flexible PEO coil as a string of "beads" and "springs" (see Chapter 2), Pec-
ora calculated the characteristic time of the overall internal relaxation mode of the (isolated) coil to be

$$\tau_1 = \frac{2R_g^2}{\pi^2 D}$$  \hspace{1cm} (1)

where $R_g$ is the coil gyration radius (See Chapter 2), and $D$ the coil center-of-mass translational diffusion coefficient. Roughly speaking then, $\tau_1$ is the time it takes the coil to diffuse a root-mean-squared distance of $R_g$, i.e. to diffuse across the coil. Detection of this mode requires that the magnitude of the probe length be smaller than the overall dimensions of the coil which is roughly when $qR_g > 1$. In turn, the length probed varies inversely as the magnitude of the scattering wave vector ($\vec{q}$) defined by equation 2 below and illustrated by Figure 1 where $\vec{k}_i$ represents the wave vector of the incident light, $\vec{k}_s$ represents the scattered light for this "quasi-elastic" scattering, ($k_s \approx k_i$), $n$ is the refractive index of the solvent, $\lambda_0$ is the incident vacuum wavelength, and $\theta$ represents the scattering angle:

$$q = \frac{4\pi n}{\lambda_0} \sin(\frac{\theta}{2}).$$  \hspace{1cm} (2)

Figure 1. Illustration of the scattering wave vector representation

Again, we have discovered that information on the overall internal mode of high molecular weight PEO is unusually difficult to obtain. This difficulty arises due to
physical limitations when manufacturing high molecular weight PEO, while at the same time ensuring small polydispersity, i.e. a sufficiently narrow molecular weight distribution. So, to make the necessary PCS measurements, a short wavelength CW (continuous wave) laser in the near ultra-violet was used at high scattering angle so that q was large and the probe length, $2\pi/q$, was about equal to or smaller than the span of the polymer coil in solution. These difficult-to-obtain conditions are the primary reasons why little information is available regarding PEO internal mode characteristics using the technique of PCS.

By varying the polymer and salt concentrations in a methanol solution, it is in principle possible, using PCS, to examine the effects of salt on the behavior of a neutral, very flexible, high molecular weight polymer in dilute solution. In particular, it should be possible to study these effects on the internal dynamic behavior of the PEO chain. This information would extend our fundamental understanding of the effects of salts on the dynamics of a neutral polymer, and act as a check on results obtained by previous experiments conducted in-house. Moreover, it would shed light on the effects of LiClO$_4$ on PEO in the molten state, i.e. on the state found in "solid" polymer electrolyte batteries because, in some sense, all relaxation modes in the melt are "internal".

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CHAPTER 2

POLYMERS IN DILUTE SOLUTION

Introduction

A linear polymer is composed of a string of monomers. Each monomer is in turn composed of a group of molecules and/or atoms. For a homopolymer, each monomer is identical in structure. When the monomers are joined end to end, normally by a chemical reaction, they produce a linear polymer. Depending on the number of monomers and the composition of each monomer, the polymer is typically described by its chemical name, molecular weight, and its molecular weight distribution. The molecular weight is determined by the monomer weight times the number of repeat units of the monomer denoted as X in Figure 2. The molecular weight distribution reflects the range of molecular weights present in a given polymer sample. An important parameter used to characterize this distribution is called the "polydispersity" which is a measure of the width of the molecular weight distribution about the mean molecular weight.

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 \\
\text{O} & \quad \text{X}
\end{align*}
\]

Figure 2. PEO monomer composition
PEO is a linear, flexible polymer that does not contain side groups along its backbone (Fig 2). Moreover, at the ether linkages (oxygenes), it is especially flexible. The dynamic behavior of PEO is oftentimes described using the bead-and-spring model (Berne, Pecora, 1990). By visualizing one such PEO configuration, it can be seen that there are a number of different spatial configurations the polymer could have. Since the polymer studied here has a high molecular weight, the number of possible configurations for a single PEO chain in solution is very large (See Figures 3, 4, 5).

Polymers behave differently depending on their surroundings. Oftentimes, these surroundings are either a solvent or other polymer chains (as in the molten phase).
Figure 4. Bead and Spring illustration of a flexible macromolecule. The beads represent the portion of the polymer that interacts with the impinging light while the springs represent the entropic restoring force which returns the system to equilibrium when a fluctuation takes place. (Berne, Pecora, 1990)

In solutions, chain behavior is influenced by polymer concentration. In particular, in binary solutions the solution regimes denoted as "dilute" and "semi-dilute" solutions are determined by the polymer chain concentration. In this work, only the dilute solution regime is considered. In the dilute regime, each linearly flexible polymer chain, or "coil" is only moderately influenced by the presence of other polymer coils in the solution. This interaction is generally a weak hydrodynamic interaction which occurs via the solvent. In the semi-dilute regime, polymer coils are close enough on average to directly interact with each other. Although not studied in this work, the molten phase of pure polymer without a solvent is referred to as a polymer melt. Just as these situations are described differently, the behaviors of such systems are also described differently. Due to the varying methods of description for each type of situation, it is necessary here to briefly discuss the general behavior of linear, flexible polymers in dilute solution.
Solvent Quality

The behavior of polymers in dilute solution can be treated in terms of three categories. These categories describe the solvent "quality" and are differentiated by the solvent's interaction with the polymer (Brown, Selser, 1996). These three categories of solvent "quality" are denoted as "good", "poor" and "theta". In the case of particular interest here, namely PEO and methanol (MeOH), the solvent can be classified as having any of these qualities depending on the temperature of the polymer solution. Measurements considered in this work were made in the "good solvent" regime and it was deemed that conducting measurements in the good solvent regime would provide relevant information for comparing dilute solution results with polymer melt studies.

When considering solvent quality, the primary consideration is the nature of the interaction between the solvent and polymer segments or the interaction between polymer segments. When polymer segments prefer to associate with solvent molecules rather than with other polymer segments, the solvent is denoted as a "good" solvent. A theta solvent quality is when polymer segments have no preference as to whether to associate with another polymer segment or the solvent. In the poor solvent case, polymer segments prefer to associate with other polymer segments, a situation often times preceding phase separation of polymer and solvent in the solution.

For the case of a good solvent, polymer segments avoid other polymer segments preferring solvent instead and the polymer coil swells. This swelling reflects a balance between the swelling osmotic action of the solvent and the retractive elastic force generated by expanding the polymer. It has been shown that the addition of LiClO₄ to PEO/methanol solutions at 30°C leads to further coil swelling (Banka et al, 1996). The dependance of the rms end-to-end distance of the polymer chain on molecular weight in good solvent can be described by the following power law expression where
M is the molecular weight and C is an arbitrary constant (Flory, 1953)

\[ R_{\text{rms}} = CM^{0.6} \quad (1) \]

In the case of a poor solvent, the interactions are such that the polymer segments prefer to interact with other polymer segments. This preference results in the chains' rms end-to-end distance decreasing so that the exponent in Eqn. 1 above decreases to 0.5. The rms end-to-end distance is defined as the rms distance between polymer chains ends in solution (see Figure 5)

Figure 5. Illustration of a polymer chain in solution and the rms end-to-end distance. a) Illustration of the polymer with the rms end-to-end distance equal to R. b) Illustration of the polymer confined to an rms end-to-end distance R

In the theta solvent case, the polymer does not preferentially interact with either the solvent or other polymer segments and the polymer is close to precipitating out of solution.
Radius of Gyration and Hydrodynamic Radius

With different techniques available to analyze the behavior and characteristics of polymer coils in solution, different information can be extracted. With light scattering, two closely related size parameters can be determined for coils. These parameters are the radius of gyration, $R_g$, and the hydrodynamic radius, $R_h$, determined using static light scattering and PCS, respectively. For a linear, flexible polymer in a good solvent, i.e. a coil, $R_g$ is directly proportional to $R_h$ as described in the following experimentally determined relationship for PEO in MeOH at 30°C (Banka et al., 1996),

$$R_g = 1.55R_h. \quad (2)$$

Although static light scattering was not used in the present work, the comparison of previous static light scattering results with those reported here proved useful. When determining the radius of gyration (Atkins, 1994), polymer segments on the outer portion of the sphere provide the dominant contribution to the size determination. The radius of gyration is measured using static light scattering to generate a "Zimm plot" (Berne, Pecora, 1990). A Zimm plot is a graph derived from scattering data obtained at varying scattering angles and varying polymer concentrations. The data on the graph are then extrapolated to zero concentration and to zero scattering angle. These extrapolations allow different properties of the system to be determined, one being the radius of gyration. Also, by determining the zero angle intercept of the zero-concentration curve, the weight-averaged molecular weight can be found. In addition, the slope of the above mentioned curve is proportional to the radius of gyration. In a static light scattering study, the radius of gyration $R_g$ can be found directly using the following equation where $n$ is the refractive index of the solvent and $\lambda_0$ is the vacuum wavelength of the exciting light with the slope and intercept as discussed.
above (Johnson, Gabriel, 1981):

\[(R_g)^2 = \frac{3\lambda_0^2}{16\pi^2n^2}\left(\frac{\text{slope}}{\text{intercept}}\right).\]  

(3)

The PEO coil hydrodynamic radius can be determined using the Stokes relation between the diffusion coefficient and the frictional constant \(f\) as shown by Equation 6 later in this chapter (Atkins, 1994). Unlike the determination of the radius of gyration, the inner polymer segments of the coil are the dominant contributors in determining the hydrodynamic radius. By using PCS to determine the diffusion coefficient \(D_0\), along with the Stokes relation (Equation 6), the hydrodynamic radius can be determined (Atkins, 1994).

The Diffusion Coefficient

One of the most useful parameters obtained from experiments on monodisperse samples of polymers in dilute solution is the polymer center-of-mass diffusion coefficient, \(D\) (Atkins, 1993). The diffusion coefficient is proportional to the mean-squared displacement of the polymer chain in solution in a given time \(t\):

\[< r^2 > = 6Dt \]  

(4)

\(D\) then corresponds directly to the center-of-mass autocorrelation function (ACF) relaxation mode measured in a PCS experiment and is determined by the following equation.

\[D = \frac{\Gamma}{q^2} \]  

(5)

Here \(\Gamma\) corresponds to the characteristic frequency or the "decay constant" of the coil center of mass ACF relaxation mode and \(q^2\) is the square of the scattering wave vector. To determine the diffusion coefficient, a linear fit of the experimentally determined \(\Gamma\) to \(q^2\) is made for data representing the center-of-mass mode only. By dimensional analysis it is apparent that the diffusion coefficient (with typical units of cm\(^2\)/second)
gives information about the size of the coil, $R_h$ (See Equation 6), as well as the relative motion of the polymer in solution.

**Viscosity**

Although viscosity is not directly measured in DLS experiments, the viscosity of the solvent is important in studying dilute polymer solutions. For dilute polymer solutions, viscosity is considered primarily in DLS when measuring the diffusion coefficient. Using the Stokes-Einstein equation it can be seen that the diffusion coefficient of the isolated coil, i.e. the coil at zero polymer concentration, varies inversely as the viscosity (Equation 6) where $\eta_0$ is the solvent viscosity, $k_b$ is the Boltzmann constant, and $T$ is the absolute temperature:

$$D_0 = \frac{k_b T}{6\pi \eta_0 R_h}.$$  \hspace{1cm} (6)

In a typical dilute polymer solution, the viscosity change upon addition of polymer to the solvent is small, but the addition of LiClO$_4$ does contribute noticeably to the solvent viscosity. When considering changes in relaxation modes with and without LiClO$_4$, the viscosity of the solvent must be accounted for. In this work the solvent viscosity of various methanol/LiClO$_4$ solutions was determined by previous experimental work in the laboratory and can be seen in Figure 6. As seen in Chapter 1 Equation 1, the overall internal mode is dependant on the diffusion coefficient, which is in turn dependant on the viscosity as shown above (Equation 6). Due to the viscosity dependance, it was possible to account for the viscosity changes when examining the center-of-mass translational mode by looking at the diffusion coefficient, as well as when examining the overall internal mode. This accountability made it possible to determine whether or not the presence of LiClO$_4$ affected the overall internal mode beyond the expected amount due to the change in viscosity alone.
The Bead-and-Spring Model and Normal Mode Analysis

For this work, experimental results were compared to the Bead-and-Spring model described in Berne and Pecora (Berne, Pecora, 1990). This model is one of the most simple theoretical treatments available that describes the dynamic behavior of a macromolecular coil in solution. This model has been specifically described by Pecora for a linear, flexible Gaussian coil in solution which will be discussed below. This model treats each "bead" as a light scatterer, and the "springs" between the beads provide the restoring force. This model then contains n+1 "beads" and n "springs" which make up one polymer coil. Solvent effects are only considered to the first order meaning the solvent inhibits the motion of a bead but any "wake effects"
(hydrodynamic interactions) which would affect another bead in a coil by the initially considered solvent/bead interaction are not addressed.

Due to the limited information available for high molecular weight PEO internal mode dynamics and the great complexity that arises from trying to model high monomer count polymer coils with more elaborate models available, the bead-and-spring model was a good starting point for comparison between experimental results and a theoretical prediction.

This model implements a normal mode analysis of the equation of motion for a linear flexible polymer in solution. The model itself considers three separate forces to create the equation of motion which is of the form below:

$$m \frac{d^2 \mathbf{x}}{dt^2} = F_x^{(1)} + F_x^{(2)} + F_x^{(3)} .$$

(7)

The first force considered is the frictional force by the solvent on n beads. This force is proportional to the velocity of the bead. In one direction this force is denoted as $F_x^{(1)}$ which is equal to $-\zeta \frac{dx}{dt}$ where $\zeta$ is the frictional coefficient.

The second force is an entropic restoring force which returns the beads to their equilibrium separation. In one direction this is denoted as

$$F_x^{(2)} = -\sigma \mathbf{A} \cdot \mathbf{x}$$

(8)

where $\mathbf{x}$ is a vector describing the position of each bead, $\sigma$ is the entropic force constant expressed in relation to the mean-square length of a segment $<l^2>$ as

$$\sigma = \frac{3k_BT}{<l^2>}$$

(9)
and $A$ is an $n+1$ second rank tensor of the (square matrix) form

$$
A = \begin{bmatrix}
1 & -1 & 0 & 0 & \ldots & 0 & 0 & 0 \\
-1 & 2 & -1 & 0 & \ldots & 0 & 0 & 0 \\
0 & -1 & 2 & 1 & \ldots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & \ldots & -1 & 2 & -1 \\
0 & 0 & 0 & 0 & \ldots & 0 & -1 & 1
\end{bmatrix}
$$

(10)

which corresponds to an effective force on bead $j$ in the Gaussian coil

$$
F_j = -\frac{3k_BT}{<\ell^2>} (x_{j+1} - 2x_j + x_{j-1})
$$

(11)

where $x_j$ is the position of the $j^{th}$ bead.

The third force considered in one direction is the stochastic Brownian force denoted as $F^{(3)}_x(t)$. Since we are only concerned with relatively slow, long-wavelength bead motions, we may ignore the left hand side of Equation 7, and after applying Newton's second law of motion to the beads, the equation of motion in the $x$ direction is the following (Berne, Pecora, 1990)

$$
\zeta \frac{dx}{dt} = F^{(3)}_x(t) - \sigma A \cdot x.
$$

(12)

Similar equations apply to $y$ and $z$, and then by conducting a Fourier series expansion, a set of normal coordinates may be found which may be represented as a normal coordinate vector $\mu_k \equiv (\mu^x_k, \mu^y_k, \mu^z_k)$. This leads to the equations of motion for the normal coordinate vectors to be written as.

$$
\zeta \frac{d\mu_k}{dt} = F^{(3)}_k(t) - 4\sigma \sin^2\left(\frac{\pi k}{2n}\right)\mu_k, \; k = 1, 2, \ldots
$$

(13)

Since in this work information is only sought regarding the translational center-of-mass mode and the overall internal mode, it is allowable to only consider low $k$ values. By setting this condition, namely $k \ll n$, the above equation can be rewritten in the following form (Berne, Pecora, 1990)

$$
\frac{d\mu_k}{dt} = \frac{1}{\zeta} F^{(3)}_k(t) - \frac{\mu_k}{\tau_k}.
$$

(14)
where \( \tau_k \) is the relaxation time of the \( k^{th} \) normal mode and for \( k = 1, 2, 3 \ldots \) is given by

\[
\tau_k = \frac{\langle l^2 \rangle n^2 \zeta}{3k_BT \pi^2 k^2}.
\]  

(15)

This equation can then be expressed in terms of measurable parameters which results in the form

\[
\tau_k = \frac{2R_g^2}{\pi^2 k^2 D}.
\]  

(16)

with \( n < l^2 >= 6R_g^2 \) and \( D = k_BT/n \zeta \) (Berne, Pecora, 1990). By transforming the normal modes to spatial coordinates by using a Fokker-Planck equation, the scattering function \( S(q, t) \) can then be written. Furthermore, after a suitable manipulation (Pecora, 1968) the scattering function can be written in the following form

\[
S(q, t) = S_0(x)e^{-q^2 D t} + S_2(x)e^{-(q^2 D + \frac{2}{\tau_1})t}.
\]  

(17)

where \( x \equiv q^2 R_g^2 \), and the \( S_0 \) term corresponds to the translational center-of-mass mode and the \( S_2 \) term corresponds to the overall internal mode. Specifically, since \( S(q, t) \) is proportional to the normalized field autocorrelation function \( g_1 \) (see Equation 12 Chapter 3), the value of the overall internal ACF relaxation mode value determined in PCS measurements, \( \Gamma_1 \), should be equal to \( (q^2 D + \frac{2}{\tau_1}) \) which enables a direct comparison between the experimental data obtained for \( \Gamma_1 \) and \( \tau_1 \) and the results expected using the bead-and-spring model.

As shown in the above equation, the terms \( S_0 \) and \( S_2 \) correspond to the scattering amplitude from each mode in Equation 17. It is further possible to predict the contribution from each mode on the overall scattering intensity (Pecora, 1968). This is shown for \( S, S_0, S_1, \) and \( S_2 \), in Figure 7 where the contribution of each mode is shown for varying \( x = q^2 R_g^2 \). It is then possible to examine the ratio \( S_0/S_2 \) and compare that to the ratio between the experimentally found amplitude ratios for the distinguishable modes. As may be noted in Equation 17, the \( S_1 \) term is not shown.
Figure 7. Normal mode analysis using the bead-and-spring model predicts the scattering amplitude contribution from each individual mode. Here $x = q^2 R_0^2$, $S$ corresponds to the total scattering amplitude, and each corresponding $S_i$ is the scattering amplitude of each individual mode.

By inspection of Figure 7, it is apparent that over the measured range of $x$ the $S_1$ term is very small compared to $S_0$ and $S_2$ and may be ignored (Pecora, 1968).
CHAPTER 3

PHOTON CORRELATION SPECTROSCOPY

Introduction

With several types of dynamic light scattering possible, whether photon correlation spectroscopy, Raman scattering, or Brillouin scattering, it is important to define which dynamic light scattering technique is being used. The experimental technique relevant to this work is photon correlation spectroscopy which will be described in detail later in this chapter. Secondly, the scattering process employed is referred to as quasi-elastic laser light scattering (QELLS). The term quasi-elastic is used because the light being used to study the system does not significantly perturb the system so that there is a negligible shift in wavelength of the scattered light compared to the incident wavelength provided by the laser (Δλ/λ₀ is very small). This negligible perturbation allows measurement of the system without affecting the system’s behavior unlike experiments such as absorption spectroscopy. In the dynamic light scattering technique, there is in-phase excitation of loosely bound electrons in the polymer sample creating oscillation dipoles. These oscillating dipoles emit light, and these emissions are the scattered light that is measured in the experiment. Since physical motions of polymers in solution is studied, this noninvasive technique can be used for retrieving useful information about the structure and dynamic behavior of the system.
Scattered Light

In order to describe the scattered light, classical electrodynamics is used. In the experiments discussed in this paper, the laser beam can be described as a monochromatic plane wave to a good approximation. This incident plane wave interacts with a non-absorbing medium with the detector far away from the region being probed (see Figure 8). Since the PEO system is nonmagnetic, the magnetic dipole contribution to the scattered light may be neglected leaving the electric dipole emission the dominant contribution to the scattering. Under these conditions, the incident electric field can be described by the following equation where \( \hat{n}_i \) is the incident polarization vector, \( \mathbf{k}_i \) is the incident wave vector propagating along \( x \) and \( \omega_i \) is the incident frequency (Jackson, 1999):

\[
\mathbf{E}_i = \hat{n}_i \mathbf{E}_0 e^{i\mathbf{k}_i \cdot \mathbf{x} - i\omega_i t}
\]  

The scattered electric field can also be described by the following generic equation where \( \mathbf{p}_i \) is the induced dipole field at the scattering point, and \( \mathbf{r} \) is the position on

Figure 8. Illustration of an individual scatterer and the corresponding vectors described below (Schaller, 1989).
the scatterer relative to its center (Jackson, 1999):

$$E_s = \frac{e^{i k_s \cdot r}}{4 \pi \varepsilon_0 r^2} \left[ (k_s \times p_i) \times k_s \right]$$

(2)

For a given scatterer the scattered electric field for a differentially small scattering subregion $d^3r$ is (See Figure 8)

$$dE_s = \frac{e^{i k_s \cdot (R-r)}}{4 \pi \varepsilon_0 |R - r| \times dp} \times k_s$$

(3)

where $R$ is the detector position and $dp$ is the dipole moment of an element $d^3r$ which can be expressed as

$$dp(r, t) = \alpha(r, t) \cdot E_i d^3r = \alpha(r, t) \cdot \hat{n} E_0 e^{ik_s \cdot r - i\omega t} d^3r$$

(4)

where $\alpha(r, t)$ is the polarizability tensor.

Since $r << R$, the total scattered field from the scatterer at the detector is of the form

$$E_s = \frac{E_0 e^{ik_s \cdot R - i\omega t}}{4 \pi \varepsilon_0 R} k_s \times \left\{ \int_{d^3r} d^3r e^{-i\omega t} \alpha(r, t) \right\} \times k_s$$

(5)

The polarizability tensor $\alpha(r, t)$ is described by (Equation 6) where $<\alpha>$ is an average value, $I$ is the identity tensor and $\delta \alpha$ represents the fluctuation of alpha from its mean value. It is the fluctuation $\delta \alpha$ that is responsible for the scattered light observed.

$$\alpha(r, t) = I <\alpha> + \delta \alpha(r, t)$$

(6)

Autocorrelation Functions

The fundamental idea behind an autocorrelation function is that by comparing a value of a function with a series of other values of the same function as some parameter is varied, it may be possible to determine some form of structure in the function being studied. This structure may then, for example, be interpreted in terms of the dynamic behavior (time is the parameter) of the system being studied. The
autocorrelation function in these PCS experiments is determined by comparing the scattered light intensity (the function) with the scattered light intensity at various later times (the varying parameter). The generic form of the autocorrelation function can be written as

\[ G(\tau) = \lim_{T \to \infty} \frac{1}{T} \int_t^{t+T} A(t)A(t + \tau)dt \]  

(7)

where \( A(t) \) is the signal, \( A(t+\tau) \) is a version of \( A(t) \) delayed by \( \tau \) and \( T \) is the measurement time. Since the signal analysis system being used is a digital correlator, by choosing sample times (\( \delta t \)) small compared to the behavior characteristic time(s), such as \( \tau_1 \), the integral is approximated by a finite sum of \( N \) products of integers stored in a buffer where each delay corresponds to a time shift \( \Delta t \).

The instantaneous intensity of light \( i(t) \) is proportional to the square of its electric field. Likewise, the measured scattered light intensity is proportional to the square of the scattered electric field. The fluctuating scattered light is incident on a photodetector and an output train of logic pulses is sent to a digital autocorrelator which then calculates the time autocorrelation function as described in Equation 8. Since the scattered light mixes only with itself on the photodetector, the detection technique is referred to as "self-beating" or "homodyne" light scattering spectroscopy. When the scattered light is mixed with the laser light on the photomultiplier, the technique is referred to as "heterodyne" light scattering spectroscopy. The homodyne intensity autocorrelation function is written as

\[ G_2(\tau) = \langle i(t)i(t + \tau) \rangle = \langle |E_s(t)|^2|E_s(t + \tau)|^2 \rangle. \]  

(8)

The corresponding field autocorrelation function is of the following form:

\[ G_1(\tau) = \langle E_s^*(t)E_s(t + \tau) \rangle. \]  

(9)

When the scattered field has a Gaussian distribution, \( G_1(\tau) \) and \( G_2(\tau) \) are simply

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related by the following equation:

\[ G_2(\tau) = B + A|G_1(\tau)|^2. \]  (10)

This equation is known as the Siegert relation (Chu, 1999) where \( B \) is the baseline value of \( G_2(\tau) \) equal to \(<i>^2\) and \( A \) is an experimental constant. Proper analysis of \( G_2(\tau) \) provides information regarding the structure and dynamic behavior of the system. This information is usually extracted by analyzing \( G_1(\tau) \). As can be seen in the above equations, \( G_1 \) and \( G_2 \) are not normalized. After baseline subtraction, the intensity autocorrelation function normalized by the baseline \( B \) and its field autocorrelation counterpart normalized by \(<i>\) are typically denoted as \( g_1 \) and \( g_2 \) (Kerker, 1969; Chu, 1999).

Data Analysis Techniques

Four programs were used to analyze ACF data obtained from PCS measurements. For the most part, one or two decay modes were extracted from \( g_1 \) functions, which were in agreement as expected from \( S(q,t) \) (Equation 17, Chapter 2). These computer programs attempted to fit the correlation function. Each program has its particular strengths, but to obtain useful information, all these programs were used. Ideally, each program would provide nearly identical results for a given data file, however autocorrelation function data are somewhat noisy and deviate from a perfect exponential or two exponential decay (depending on the experimental parameters), and each technique handles these variations somewhat differently so each analyzing technique provides slight variations of the fit values determined. Due to the expected similarity between results from each analysis program, consistency between analysis techniques was sought, thus providing "checks" to further reinforce the fact that the data obtained were not corrupted by an outside source during experimentation.
Cumulants

The method of cumulants is not unique to the Brookhaven program used, but the Brookhaven version will be emphasized since it is the program version used for all cumulants analyses for these experiments (Brookhaven Instruments Corp., BI-2030 Instruction manual). For quasiexponential ACF's, the method of cumulants is ordinarily useful in extracting the average decay rate of the relaxation function and a measure of the width of the relaxation function distribution, also commonly referred to as the "polydispersity".

The method of cumulants is used to fit the normalized first-order autocorrelation function which has the form below where \( t \) is now the time shift variable (\( \tau \) is also used) and \( w(\Gamma) \) is the frequency space relaxation mode distribution function:

\[
g_1(t) = \int w(\Gamma)e^{-\Gamma t}d\Gamma. \tag{11}
\]

The natural logarithm is then taken of both sides of the equation above and the exponential on the right hand side expanded in a Taylor series about the mean decay rate \( \bar{\Gamma} \) resulting in the following form.

\[
\ln g_1(t) = 1 - \mu_1 t + \frac{1}{2} \mu_2 t^2 - \frac{1}{3} \mu_3 t^3 + \ldots \tag{12}
\]

with \( \mu_1 = \bar{\Gamma} \) and \( \mu_2 = \langle (\Gamma - \bar{\Gamma})^2 \rangle \). Here \( \mu_1 \) corresponds to the mean value of the relaxation rate or decay constant of the ACF mode and \( \mu_2 \) corresponds to the width of the \( \Gamma \) distribution which is directly related to the decay constant polydispersity, \( \mu_2/\mu_1^2 = \mu_2/\bar{\Gamma}^2 \), of the system.

DISCRETE

DISCRETE is a powerful, flexible multiexponential analysis program widely used in the DLS community as it has minimal user input. DISCRETE is often times used as a preliminary analysis tool to determine input parameters for analysis using CONTIN.
(see following page). DISCRETE analyzes scattered light intensity autocorrelation functions by first extracting $g_1$ from $g_2$ and then fitting $g_1$, via the Siegert relation, to Equation 11:

$$
\sum_{j=0}^{n} \alpha_je^{-\Gamma_j \tau}.
$$

(13)

Each exponential decay mode detected has a corresponding decay constant $\Gamma_j$ and each mode amplitude corresponds to $\alpha_j$. DISCRETE can attempt to fit $g_1$ to a sum of at most nine discrete exponentials. In this work, at most two exponential decays were extracted from ACF's using DISCRETE.

This discrete sum of exponentials does not account for the presence of a continuous (narrow) distribution of different polymer molecular weights which adds to the complexity of determining the average relaxation mode. DISCRETE handles this by user input to determine the maximum number of relaxation modes, and treats each mode distribution in $\Gamma$ as a delta distribution at each mode maximum value, $\Gamma_j$. With the limited parameters considered in this program, when more than two exponential decays are found, fit values determined through these analyses typically deviate much more than the final output from CONTIN analyses. Nevertheless, this information can prove very useful in obtaining starting parameters for using the CONTIN analysis program.

CONTIN

CONTIN (Provencher, 1982) is perhaps the most robust and well-accepted PCS analysis program used today. CONTIN initially does a constrained Laplace transform inversion of the intensity correlation function, $g_2$ and then using the Siegert relation (Equation 11) fits the field correlation function $g_1$ to an expression of the form:

$$
g_1 = \int_0^\infty w(\Gamma)e^{-\Gamma t}d\Gamma.
$$

(14)

CONTIN has a number of parameters that must be set prior to an analysis of $g_1$. 

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These parameters are highly adjustable producing many possible modes of analysis. CONTIN fits $g_1$ to a continuous distribution of exponentials (Equation 15). This distribution in $\Gamma$ provides a relative width parameter which is the normalized variance, $\text{variance}/\Gamma^2$, for each distribution mode. The relative width parameter helps assess sample polydispersity as well as the presence of a second mode although this second mode may not be clearly resolvable.

KWW

The Kohlrausch-Williams-Watts (KWW) equation (Walkenhorst, Selser, Piet, 1998) was also used to analyze PCS results by fitting $g_2$ directly. The KWW equation was programmed into Microcal Origin to perform the fit calculations. The KWW is a stretched exponential, and $g_2$ functions were fit to a "double KWW" of the form of Equation 16 where $\beta_1$ and $\beta_2$ are the relaxation rate dispersion parameters which varied between zero and one which corresponded to the width of each exponential decay rate distribution. $B_o$ corresponds to the baseline value. Here, each of two modes is determined via the fit and a guess of the width of each mode must be inserted prior to the fit. Again, the reduced intensity autocorrelation function is fitted, whereas in other analysis fit methods fits to the field autocorrelation function were made. This method of analysis was used as a quick check after information was extracted using the previous analysis programs. The "double KWW" is of the form

\[
g_2 = (A_1e^{-(\Gamma_1 t)^\beta_1} + A_2e^{-(\Gamma_2 t)^\beta_2})^2 + B_o. \quad (15)
\]
CHAPTER 4

EQUIPMENT

Introduction

The equipment necessary to conduct dynamic light scattering experiments can be divided into five parts. The basic setup described herein is the light scattering setup devised by Brookhaven Instruments, Inc. exclusively for PCS. This Brookhaven setup is widely used in the PCS community. Along with the Brookhaven setup, some additional pieces of equipment have been incorporated into the setup to enhance the performance of the Brookhaven system as modified specifically for use in our laboratory. In addition, each part may also be modified depending on the sample to be examined while the general setup remains fixed for any dynamic light scattering measurement. These modified parts include the light source, the alignment optics, the sample holder assembly and sample cell, the detector optics, and the data storage and analysis devices. The key pieces of equipment are labelled in Figure 9 for clarification.

Light Source

The light sources used were the Innova 100 Ar-ion (Coherent Inc.) laser at selected emission lines of 5145, 4880, and 3511 Å, and the Innova CR-500K Kr-Ion laser (Coherent Inc.) using the emission line of 6471 Å retrofitted with an I-90 Innova ceramic plasma tube. Each continuous wave laser was running in the TEM\textsubscript{00} mode. The Ar-ion laser has a beam diameter of 2.0 mm and a beam divergence of 0.39 mrad and a maximum power output deviation of ±0.5%. The Ar-ion laser’s optical noise was also below 0.3% while in the light regulation mode (Innova-100 manual).

The Krypton laser did not have light intensity output regulation, per se, but after a sufficient warm up time of approximately 2 hours, the laser was measured to have a consistent output power which did not deviate more than 0.01 Watt during an entire experiment lasting well over 12 hours. This output power stability is essential for obtaining data with good statistics. According to the manufacturer and the specifications on the retrofitted tube, the Kr-ion laser has a beam diameter of 1.5 mm, a beam divergence of 0.8 mrad, power stability to within 0.5%, and optical noise output of less than 1.0%. Each laser has a coherence length of the order of 10 cm.
(much greater than the length of the sample volume being probed) and each was cooled using a dedicated in-house, closed-loop cooling system which reduced thermal variations which might have resulted in unacceptable output power variations.

Alignment and Optics

The alignment optics consisted of (see Figures 9 and 10) assorted apertures to assist the alignment process, reduce unwanted reflections and prevent backscattered light from re-entering the laser cavity causing unwanted output oscillations; neutral density filters were used to maintain the laser at a stable output power and simultaneously allow only the desired laser power entering the sample cell (avoiding damage to the sample), a polarizer to ensure that only vertically polarized light from the laser would enter the sample cell; and a beam focusing lens to concentrate light in the sample scattering volume. Depending on the wavelength or laser used, selection of these optics was varied to reduce unwanted propagating reflections, inhibit absorption in the optics, and maintain laser stability while keeping the laser power at the maximum level that wouldn't damage the sample being studied.

Figure 10. Alignment optics rail: 1) Rail 2) Neutral Density Filter 3) Neutral Density Wheel 4) Apertures 5) Beam Cutoff device (See Chapter 6) 6) Polarizer 7) Focusing Lens

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Light Scattering Spectrometer and Sample Cell

The Light Scattering Spectrometer was manufactured by Brookhaven Inc. specifically for conducting light scattering experiments (see Figure 11). It consists of a model BI-200SM automated goniometer which can vary the scattering angle observed by varying the angular position of the rail holding the detector optics. This is accomplished using a stepper motor which varies the angle between the detector rail and the incident laser beam. This scattering angle can vary in a plane parallel to the top of the optical table from 20 degrees to 150 degrees with an angular resolution of 0.01 degree with the laser beam representing the zero degree scattering angle. The sample cell assembly (See Figures 12 and 15) sits inside an index matching vat made of glass or fused quartz depending on the wavelength of laser light used. Each vat incorporated a black ertalyte(plastic) shield custom machined to rest in contact with the inside vat wall. The shield served to inhibit unwanted reflections inside the vat, and to limit the amount of light entering the cell from air/glass laser beam flare at the outer vat wall. The vat is filled with toluene index matched to the glass cell and to the vat to reduce reflections at the vat and flare at the exterior sample cell wall to acceptable levels. The vat/cell assembly was connected to a flow-through temperature controlled circulating bath which regulated the temperature of the index matching liquid and the sample to within 0.1 °C. This heating bath, manufactured by PolySciences, Inc., circulates a 50/50 mixture of ethylene glycol and water through two coils of copper tubing in the housing, one of which supports the vat at the bottom and the other immersed from above in the index matching liquid which is extended to a level below the top of the index matching vat. This heating system proved to regulate the sample temperature to 0.1 °C, an acceptable level.

The sample cell assembly itself (Figure 15) was custom fabricated in-house and represents an ongoing evolution from previous designs. The current sample cell in-
Figure 11. The various pieces of the goniometer (1) laser rail and mounts (2) base (3) turntable (4) rigid rotating arm (5) upright for 2mm aperture (6) detector rail (7A,B) center of rotation adjusting screws (7C) center of rotation locking screw (8) center of rotation table (9) beam focusing and steering assembly (10) sample cell surround (11) optional beam stop (12A,B) PMT lens adjustment horizontal/vertical (13A,B) Slit adjustment horizontal/vertical (14) mirror adjustment (15) eyepiece (16) pinhole wheel (17) Filter wheel (18) PMT housing (19) angle adjustment (20) clutch release (21) PMT housing support ring

corporates black teflon upper and lower pieces which fit into a glass or fused silica tube. These teflon pieces are first cooled and then inserted into the glass tube. Upon warming the teflon pieces, an interference fit which seals the sample cell is present. The interference fit was sufficient to prevent methanol evaporation, inhibiting the formation of bubbles in the sample cell which would produce unwanted reflections and alter the concentration of the sample being studied, thereby reducing errors in analysis. The top piece has input and output channels fitted with stainless steel needles allowing the sample solution to enter and exit the cell. Teflon (.2 and .5 micron nominal pore size) disposable filters manufactured by Millipore were fitted into the
needle hubs and used to eliminate dust in the sample solution as it was loaded into the sample cell. Valves on the cell inlet and outlet channels were used to seal the cell after the sample had been inserted. Before inserting the sample, a cell flushing sequence using toluene and methanol was developed to ensure that the sample cell itself was dust free.

![Diagram of upper teflon portion of sample cell assembly](image)

Figure 12. Upper teflon portion of sample cell assembly

Detection

The detection apparatus consists of beam guiding/filtering optics, the photomultiplier tube (PMT), and the amplifier/discriminator. Initially, scattered light reaching the PMT passed through a bandpass filter (Figure 13) centered at the laser output wavelength (FWHM 100 Å). This minimized the contribution to the signal at the detector due to light sources other than the laser. Behind the bandpass filter a (wheel selectable) pinhole limited the volume of the sample seen by the detector. This limiting factor maintains a balance between the maximum amount of photons impinging on the PMT, while at the same time ensuring that the photons impinging on the PMT...

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are within the central portion of the incident beam maintaining a tolerable signal to noise ratio. The pinhole selected for use is determined by setting the apparatus so that the coherence area defined by the following equation

\[ A_{coh} \approx \frac{\lambda^2}{\Omega} \]  

is approximately one, where \( \lambda \) is the laser light wavelength and \( \Omega \) is the solid angle subtended by the source (represented as a point) at the detector pinhole (Berne, Pecora, 1990). This area corresponds roughly to one "grain" in the dynamic speckle pattern associated with the scattered laser light. Light scattered from the sample was also guided through the post sample detection optics by a focusing lens which maximized the number of photons impinging on the photomultiplier tube (PMT), effectively guiding the scattered light onto the PMT. The PMTs employed were produced by Thorn EMI and distributed through Brookhaven under model numbers EMI-9863(Thorn) and BI-DS(Brookhaven). They were single photon counting, ambient temperature tubes with dark count rates of fewer than 40 counts per second. These PMT’s had S20 photocathodes with enhanced red sensitivity and with an effective diameter of 9mm. The PMT dynode configuration consisted of 14 BeCu dynodes in a linearly focused structure (see Figure 14). These PMT’s have a peak efficiency (Dennis, 1986) of 22\% in the visible light regime and a maximum gain of \( 5.0 \times 10^7 \). The rise time and electron transit time are 2.5 and 45 ns, respectively (Brookhaven manuals).

Once photons incident on the PMT photocathode had been converted into a pulse, the pulse was filtered and prepared using an amplifier/discriminator built into the rear of the PMT housing. This shielded internal design significantly reduced noise from external sources. Here the electrical pulses which correspond to incident photons registered by the PMT were amplified, and the width of these pulses with respect to time are set to a uniform value. This allows the correlator to interpret these standardized

TTL (transistor-transistor logic) pulses as photon counts so that digital correlation analysis of the scattered light intensity could be conducted. The discriminator also analyzed the pulse height before pulse standardization and correlation analysis to help reject pulses originating from thermionic emission, cosmic rays and thereby preferentially accepting photons scattered from the sample (Hamamatsu Photonics, 1994). Thus, pulses that were present and produced by something other than light scattered from the sample were mostly rejected and not sent to the correlator.

Data Storage and Analysis Devices

The signal processing devices used were the Brookhaven models BI-2030 and BI-9000 digital correlators. These units were used to compute the real-time intensity autocorrelation functions (ACF's) of light scattered from PEO solutions. The model 2030 uses 256 linearly spaced time delay channels. These 256 channels are divided into 3 groups, with each group having the same or different selectable sample times. In addition to these 256 channels, 8 more channels are present after the 256 chan-
Figure 14. Dynode Configurations (Dennis, 1986)

Channels of the correlator (which are determined by the correlator) and are delayed much later in time space than the other 256 channels. These 8 channels are used to determine the baseline of the ACF. To effectively extract correlation information, the total autocorrelation function time span for all channels of the BI-2030 (excluding baseline channels) did not exceed three orders of magnitude. The model 9000 has 512 channels available, but the channels are logarithmically spaced. The log spacing allows a much broader time window to be examined, but it has a major drawback. The problem inherent in the 9000 design results because the system automatically selects the number of channels to be used for a given time window. This means that relatively few channels may be used for the first two orders of magnitude in the time span.
window. As it turned out, for my measurements, there were too few BI-9000 channels to adequately characterize faster behavior associated with PEO chain internal behavior. This resulted in BI-9000 fast time ACF statistics being inadequate for the internal mode studies conducted. Since all 256 BI-2030 channels could be employed in capturing the scattered light ACF decay or decays, the BI-2030 was used in this work.

Several programs were used during data taking and equipment setup. A software package called ISIN, modified in-house from an existing program for use with the BI-2030 correlator, was used for sample cell, goniometer, and detector alignment. This ensured that the area being viewed by the detector optics was in the center of the sample cell and in the central portion of the laser beam. This also allowed proper alignment of the entire system by ensuring that the angle selected for measurement of scattered light was accurate to within ±0.02°.

To analyze real-time autocorrelation measurements, in addition to other analysis software, packaged ACF analysis software developed by Brookhaven for use with their correlators was also used. These two programs use the "method of cumulants" (See Chapter 3) to analyze ACF’s, and are referred to as BI30x, and BI9kx with "x" specifying the version number. Both programs were customized in the lab to allow ACF analysis results to be sent to a remote computer for further analysis without altering the ACF analysis results via a serial port connection. This output consisted of the scattered light intensity ACF, along with a corresponding CRH (count rate history) for each data run which logged the effective number of photons impinging on the PMT every second during the total time taken for a measurement. This enabled data acquisition while analysis was being carried out thus reducing "down time". As data runs became longer and more frequent, these programs were modified to enable multiple data runs to be conducted without having to involve user commands in

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between runs. This automated system sent the final data for each run to the remote machine, adjusted pre-programmed analysis parameters if necessary, and monitored experiment outputs and provided added safety by helping prevent damage to the photodetector. This was achieved by monitoring PMT output in one-second intervals and halting an experiment if necessary (See Chapter 4, System Automation).

Once data was sent to the remote machine it was analyzed employing two well established programs widely used in PCS measurements analysis. These programs are "CONTIN" and "DISCRETE". Each program runs independently and extracts information from scattered light intensity ACF's to characterize ACF relaxation modes. DISCRETE treats each ACF relaxation mode as a delta function (see Chapter 3 Equation 11), while CONTIN assumes a continuous distribution of relaxation times (see Chapter 3 Equation 12). Of the two programs, CONTIN is a much more versatile program, but it also requires much more user input to obtain acceptable results. DISCRETE is commonly used to get a feel for the ACF relaxation mode structure and to establish starting parameters and these are then entered into CONTIN to obtain the most probable fit for each data set.

Experimental Techniques

In order to conduct experiments to examine PEO internal mode dynamic behavior in methanol solution, a number of factors were addressed before and during an experiment. Some of the items are described in the following sections and are specialized to allow measurements on samples using laser output in the UV regime with associated large $q$ values so as to be particularly sensitive to PEO overall internal mode dynamic behavior. In terms of measured parameters, use of the I-100 351.1nm emission satisfied the criterion $qR_g > 1$ (see discussion, top of page 3). In particular, the $qR_g$ range for these measurements was between and 2.4 and 3.4.
Sample Preparation

Without proper sample preparation, conducting any measurement is pointless. The most typical roadblock in successfully making a reliable measurement using light scattering is the presence of dust in the sample. To remove dust, and to maintain the purity of the sample, it is necessary to thoroughly clean and seal the sample cell. This is accomplished using custom built sample cell assemblies which seal via hermetic fits between a glass sample cell tube and upper and lower machined black teflon plugs (see Figures 12 and 15). Stainless steel needles (Hamilton Inc.) are used to fill and evacuate the sample cells both during the final cleaning of the cell and the insertion of the sample. The needles are sealed using teflon valves (Burdick and Jackson model 9429T). Virtually all dust is removed from the cell by running approximately 50 ml of MeOH through a 0.2 μm nominal pore size teflon filter manufactured by Millipore Corp. into the cell followed by 50ml of toluene, and then followed again by 50ml of MeOH.

Spectrophotometric grade solvents are used during the entire sample preparation procedure (Burdick and Jackson). To reduce the presence of bubbles forming in the sample cell during measurement, all solvents are de-gassed prior to use. Fortunately, PEO in dilute methanol solution is insensitive to trace amounts of water present, so it is not necessary to remove all traces of water from the polymer prior to preparing the solutions. PEO chain ends were not capped, which is a typical treatment of PEO of lower molecular weight. The capping of PEO chain ends adds a methyl group to the end of each chain eliminating hydroxyl end groups to prevent individual polymers from interacting with each other. For ≈ 1,000,000 molecular weight PEO, the large number of repeat units in the polymer chain and the fact that the sample is in dilute solution results in the binding of polymer chains not being a matter of concern.
Figure 15. Photograph of a fully functional sample cell: 1) 0.2 μm teflon filter 2) Inlet valve 3) Exit valve 4) Exit needle 5) Inlet needle 6) Upper Teflon assembly 7) Glass or fused-silica cylinder 8) Lower teflon stopper

Since all measurements were conducted at 30°C, solutions were stored in a temperature controlled oven at 30°C prior to analysis. To avoid degradation of the polymer prior to that, the polymer itself is stored in a freezer at -20°C to -30°C. Since PEO does have a tendency to degrade over long times at room temperature due to bacterial attack, samples are not prepared and stored for measurement until days prior to measurement. Although bacterial attack is not a problem in methanol, storage of samples after preparation was limited to reduce any other unforeseen contamination as well.
As the experiment was conducted at thermal equilibrium, temperature control was critical. Prior to measurement, the vat containing the refractive index matching liquid was heated to 30°C and allowed to stabilize. Since gas-ion lasers have a tendency to fluctuate in power output until the system operating temperature has stabilized, the lasers were turned on and "warmed up" for one to three hours prior to measurement. Prior to any measurements it was also necessary to peak the laser output. This provided the maximum power output for a given current and further ensured laser power stability during the experiment.

Before making PCS measurements, it was necessary to ensure that the light scattering photometer was aligned to have accurate knowledge of the scattering angle. This was accomplished using an in-house alignment program called ISIN which was a modification to a Zimm plot program provided by Brookhaven Instruments Co. This program checks the scattered light intensity at a number of angles and then checks to see if the intensity follows the expected sine-of-the-scattering-angle dependence of intensity. This procedure is conducted sequentially with and without the sample cell present in the index matching liquid vat and sequentially with both the index matching liquid and then MeOH in the sample cell. The program is sensitive to within one percent of the actual value of intensity as compared to the expected value using the 90 degree scattering angle as a reference intensity. Typically it was possible to obtain good alignment as the entire scattering regime agreed to within 2% of the intensity pattern expected.

During the measurement process, it is imperative to monitor the experiment. For example, dust introduced into or an air bubble forming in the sample cell during the measurement can ruin an experiment. Either of these could cause a sudden
spike in the scattered light intensity measured by the photodetector. This spike may only introduce error in the measurement, but it could also permanently damage the photomultiplier tube. To prevent such damage, a shutter was designed, built and installed to block the incident laser beam before entrance into the sample cell. This shutter was triggered by a predetermined high count registered by the scattered light detector greatly reducing the possibility of damaging the PMT system.

The laser output power is sensitive to temperature fluctuations. With temperature fluctuations in the laboratory, and particularly when working in the UV regime, the power output may drop drastically with a change in room temperature of only a few Centigrade degrees. With this in mind, the rear mirror of the laser was realigned whenever necessary to ensure maximum output power and minimum current input. This is not ordinarily a concern when operating the laser in the visible regime, but still needs to be checked occasionally even in the case of visible light output by the laser.

Because of the immersion of the temperature control heating/cooling coils into the index matching vat, contamination of the index matching liquid was a concern. This contamination is a particular problem in the UV regime as it diffused the focused laser beam prior to entering the sample thereby reducing power and introducing an uncontrolled beam profile and intensity variations not easily dealt with during analysis. To remedy this behavior, it was necessary to clean the index matching vat and replace the index matching fluid frequently. This frequency corresponded to every twelve to thirty six hours. This tedious procedure required removal of the vat, and required the system alignment to be re-checked after every cleaning.

System Automation

To reduce down time, it is desirable to take measurements continuously. Therefore, several remote monitoring systems were devised, as was a method for automatic
data collection. The data acquisition system was linked to the computer performing primary analysis of the PCS data. During an experiment, the computer received count rate history reports which could be checked remotely. These count rate history reports were created by sampling the number of photons incident on the PMT in one-second intervals. These intensities were logged into a data file which was in turn plotted with intensity on the ordinate and run time on the abscissa. Under normal operating conditions, the intensity would vary about some mean value within 10%. A large spike in the intensity (typically double the mean value or higher) would suggest that there was "dust" or a bubble present in the system which in turn suggested that the data run was influenced by some external source not anticipated in the experiment. Consequently, a count rate of near zero would suggest a failure in the laser output, or that the laser beam was blocked. In either case such results would inform the operator that the experiment needed to be examined to ensure stability of the experiment.

For a given sample, the data acquisition system was also modified to allow the user to pre-program the system to conduct a selected number of experimental runs. The user then determined the number of runs in the experiment, the angles to use for each measurement, and the parameters the correlator would use. The data acquisition system then sent the output of each data run to the primary analysis computer, which stored each run as a file for further analysis. Laser output, laser cooling water temperature and laser cooling water flow could also be monitored by a camera that was remotely viewable.
CHAPTER 5
DATA ANALYSIS AND DISCUSSION

Introduction

Two different polymers were examined in an effort to acquire information on the overall internal mode of high molecular weight PEO. Each polymer was sold by the manufacturer as a polymer "standard" and was supposed to have a narrow molecular weight distribution. The first sample examined was manufactured by Polymer Standards Service (PSS) with a putative molecular weight of 1.41 million and a polydispersity, i.e. $M_w/M_n$, of 1.13. The second polymer studied was manufactured by TOSOH Corporation and was sold as having a molecular weight of 0.92 million and a $M_w/M_n$ of 1.10. Typically a "narrow" molecular weight distribution has an $M_w/M_n$ ranging between 1.03 and 1.10. Ideally for this work one would want a linear flexible polymer like PEO to have a molecular weight on the order of five million Daltons. Generally, as a rule of thumb, when $qR_g$ is greater than one, PCS measurements are beginning to become sensitive to internal mode behavior. As, previously discussed, $R_g$ is proportional to the molecular weight (See Chapter 2 Equation 1). By having a larger molecular weight, $R_g$ is increased, thus allowing $q$ to be a smaller value when the initial signs of an internal mode becomes detectable. This increase in the molecular weight would ensure that the sensitivity of the apparatus would be well within the parameters required for internal mode detection. Unfortunately, the manufacturing of high molecular weight monodisperse PEO is a difficult task due to limitations during synthesis of the chains. By all accounts, when a PEO chain has a molecular weight around one million Daltons, the polymer synthesis process experiences prob-
lems. These problems lead to problematical results such as a much broader molecular weight distribution along with the introduction of cross linking of the polymer. Due to the high molecular weight of the PSS sample and the marginal $M_w/M_n$ value, it was believed that valuable information could still be obtained so studies were made with the PSS sample and are discussed later in this chapter. After exhausting all possible methods for analysis using DLS on the PSS sample and still without definitive results, the search for another, more acceptable PEO sample began. The next candidate for analysis was the TOSOH brand PEO which proved to be a much better candidate for analysis.

**PSS 1.41M Dalton Molecular Weight PEO**

**Initial testing**

Initial testing of each polymer had to be conducted in order to assess the sample's potential for further measurements and to ensure the quality of the sample. In this assessment, PEO/MeOH solutions are examined using light scattering in the visible regime and at low scattering angles (see Table 1). This low-angle measurement allows comparison of the PEO coil center-of-mass diffusion coefficient with earlier measurements (amplitudes for ACF relaxation modes other than the CM mode were negligible) from methanol solutions of PEO having different molecular weights. By conducting these measurements, it is possible to make a plot of the center-of-mass diffusion coefficient versus the polymer molecular weight for a series of different PEO samples (see Figure 22) for a given concentration, temperature, and scattering wave vector. By conducting this check it can be seen that a power law accurately predicts the change in the CM diffusion coefficient for increasing PEO molecular weight. The 1.41M Dalton molecular weight PEO falls on this line within a deviation of 15%. This deviation was deemed acceptable due to the extrapolation beyond the available
Table 1 PSS 1.41M Dalton MW Single Mode Data

<table>
<thead>
<tr>
<th>Concentration (mg/ml)</th>
<th>$q^2$ (1/cm²)</th>
<th>$\Gamma_0$ (1/s)</th>
<th>$D$ (cm²/s)</th>
<th>$\text{sd} \ \Gamma$ (1/s)</th>
<th>$\text{sd/mean \times 100}$</th>
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<td>1.82X10⁻⁷</td>
<td>3.460</td>
<td>0.429</td>
</tr>
</tbody>
</table>

Data points to estimate a value. This result also supports the manufacturer's claim that the weight averaged molecular weight was 1.41M Daltons.

To determine the polydispersity (Johnson, Gabriel, 1981) of the system, further testing was conducted. The testing consisted of more lower angle visible light measurements paying particular attention to the normalized second cumulant, $\mu_2/\Gamma^2$, determined in each fit to the data (see discussion, p. 23). The mean value of the normalized second cumulant at the lowest possible scattering angle was .110. From experience this value typically signifies at best only a moderately monodisperse sample. With a higher than desirable normalized second cumulant, the manufacturer's claim of the narrow spread of molecular weights was in question. Due to this high polydispersity, the possibility of obtaining reliable information on the overall internal mode of the PEO coil was not promising. The reason for this lack of promise was the
masking of the overall internal mode during analysis by the broader molecular weight distribution (see Figure 20).

In order to have the maximum signal possible, PEO solutions were tested at various polymer concentrations (see Figure 16) to determine where the system would no longer behave as a very dilute solution. This can be seen by the deviation of \( \Gamma \) from the linear fit of \( \Gamma \) vs polymer concentration. In order to remain conservative, all samples examined after these preliminary tests were at concentrations at or less than 75% of the critical concentration, i.e. the PEO concentration where deviation from the linear fit occurred.

![PSS 1.41 M mw PEO Concentration Study](image)

**Figure 16.** PSS Concentration Study: As can be seen, when the concentration is above 1.4 mg/ml, the system no longer behaves as a dilute solution.
Figure 17. PSS $q^2$ Dependence with Varying Polymer Concentrations: The experiment's sensitivity of the overall internal mode can be determined when Gamma is no longer predicted by the linear fit. Also note that as the concentration rises, the presence of the internal mode is apparent for larger $q^2$. 

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Figure 18. A typical PSS low angle $\Gamma$ distribution result using CONTIN: Note the symmetric shape and the SD/mean value corresponding to the normalized second cumulant (which equals the (SD/mean)$^2$) value of 0.10

Searching for the Overall Internal Mode

To begin the search for the overall internal mode in PEO coils, tests were conducted at long wavelength with an initial scattering wave vector, $q$, selected to be well within the regime where only the presence of the center of mass mode was detectable. The magnitude of $q$ was then increased and the method of cumulants was used to determine the "total" relaxation mode, that is the center-of-mass mode along with any internal mode contributions. When this mode deviates from linear behavior with respect to $q^2$, the apparatus is becoming sensitive to solution concentration fluctuations revealing the overall internal mode behavior of the system. The regime where the experiment was only sensitive to center-of-mass mode fluctuations can be
Figure 19. A typical PSS low angle correlation function and fit using CONTIN: Note the dramatic change in the data points around 0.0085 seconds. This drop is due to the correlator channel sub-sections and is well out of the regime where the center of mass mode is determined.

seen in Table 1. This sensitivity is because of the increase in q which corresponds to a smaller probe length (see page 2) in the scattering volume. As can be seen in Figure 17, the solution exhibits signs of the detection of an overall internal mode contribution. However, upon further analysis using CONTIN and DISCRETE, it was not possible to resolve the CM mode from the overall internal mode for the 1.41M molecular weight PEO sample.

In an effort to obtain information on the overall internal mode, the emission wavelength of the laser was reduced thereby increasing q and reducing the probe length in order to become more sensitive to PEO coil internal mode behavior. This wavelength was reduced from 6471Å, to 5145Å, then to 4880Å, and finally to 3511Å. This
Figure 20. A typical PSS high angle $\Gamma$ distribution result using CONTIN: Note the non-symmetric shape and the SD/mean value corresponding to the normalized second cumulant (which equals the $(SD/\text{Mean})^2$) value of 0.13.

reduction resulted in an improved ability to resolve multiple ACF relaxation modes, but the ability to resolve multiple modes was not reliable. From the data obtained, the most likely relaxation modes were determined by analyzing hundreds of separate experimental runs using only ACF data files that could be inverted using CONTIN and resolved into two relaxation modes. These modes were initially believed to be the center-of-mass mode and the overall internal mode of the system. However, upon further analysis, $\Gamma$ for both modes was found to be $q^2$ dependent and thus comparable to the CM modes of two different molecular weights of PEO at the corresponding scattering wave vector. Knowing that the CM mode should still fall on the linear $\Gamma$ versus $q^2$ fit for a given molecular weight, the higher than desired normalized second cumulant, and the $\bar{M}_w/\bar{M}_n$ provided by the manufacturer, it was concluded that the
Figure 21. A typical PSS high angle correlation function and fit using CONTIN: Note the scatter from the fit at long time. This scatter is in the baseline regime of the correlation function and outside the regime where the nonsymmetric mode is determined.

The sample was in fact a combination of two distinct molecular weight distributions of PEO whose CM diffusions were detected in these PCS measurements. As a result, valuable information relating to the overall internal mode of the system could not be obtained (see Figures 18 to 21).
TOSOH 0.92M Dalton Molecular Weight PEO

Initial testing

As with the PSS sample, initial testing was conducted to ensure that the characterization claimed by the manufacturer was valid. Upon initial analysis, the CM modes obtained agreed well with predictions based on data collected from previous samples to within 5% (see Figure 22). During the analysis, normalized second cumulants were also analyzed. Upon analysis, normalized second cumulants of these solutions yielded values ranging from 0.03 to 0.08. These values were comparable to very monodisperse samples and were significantly better than those for the 1.41M PSS sample (See Figures 18 and 23).

![Power Law Molecular Weight Dependence](image)

Figure 22. A collection of experimental diffusion coefficients for various molecular weight PEO samples. The squares represent previous work while the diamonds represent the systems examined in this paper. Note the agreement with the two samples from this paper with previous work and the closer agreement with the lower molecular weight sample corresponding to the TOSOH sample discussed.

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Figure 23. A typical TOSOH low angle \( \Gamma \) distribution result using CONTIN to invert the ACF from a sample without LiClO\(_4\) : Note the symmetric shape and the SD/mean value corresponding to the normalized second cumulant (which equals \((\text{SD}/\text{Mean})^2\)) value of 0.03

A series of concentration measurements conducted at low \( q \) was used to determine the concentration regime where the system could be considered to be very dilute (See Figure 25). As before, all subsequent measurements were at concentrations 75% or less than the critical value where the CM mode was observed to deviate from the linear dependence.

Searching for the Overall Internal Mode

Due to the lower molecular weight and smaller solution size of this polymer compared to the PSS sample, testing was conducted primarily at longer wavelength for CM determinations and at shorter wavelengths in the UV for detection of the overall...
Figure 24. A typical TOSOH low angle correlation function and fit result using CONTIN on a sample without LiClO₄ internal mode. This change allowed the experiment to be more sensitive to smaller length scales determined by the change in the scattering wave vector. As can be seen in Figure 26 the deviation from a linear fit exhibits signs of a contribution besides the center of mass mode in the system at high q values in the 6471Å laser output regime, however it was not possible to resolve two distinct modes. Because of the difficulty associated with conducting light scattering measurements in the UV, the sample concentrations were limited to 75% or less than the critical concentration limit in order to minimize any heating that might have occurred by absorption of the PEO, even though no such absorption was apparent. A series of measurements at different concentrations was conducted to resolve the CM mode alone (see Table 2) to produce a reference for further studies while searching for the elusive overall internal mode as
Figure 25. TOSOH Concentration Study: As can be seen when the concentration is above 2.0 mg/ml, the system no longer behaves as a dilute solution

well as provide a check that the polymer has not been adversely affected by prolonged exposure to the UV source.

Upon examination of the samples at shorter wavelength and the highest q possible for the equipment (see Table 3), the ability to distinguish two modes was barely possible (see Figures 27 to 30). Unlike the 1.41M Dalton molecular weight PSS sample, with the TOSOH 0.92M Dalton molecular weight sample these modes were more easily distinguished with a 40% to 50% chance of attaining two mode resolvability depending on the sample and experiment parameters. When two distinct modes could be resolved, the values determined for the CM and the overall internal mode were repeatable to within a 10% difference between the mean value and a given data run
Table 2 TOSOH 0.92M Dalton MW Single Mode Data

| PEO Concentration (mg/ml) | LiClO₄ Molarity (1/cm²) | q² (1/cm²) | Γ₀ (1/s) | D (cm²/s) | sd Γ₀ (1/s) | sd/mean X 100 |
|---------------------------|----------------------|-----------|--------|--------|------------|-------------|----------------|
| 0.10                      | 0.0                  | 4.43X10⁹ | 563.9  | 1.27X10⁻⁷ | 8.700      | 1.543       |
| 0.10                      | 0.0                  | 5.98X10⁹ | 757.9  | 1.27X10⁻⁷ | 3.951      | 0.521       |
| 0.50                      | 0.0                  | 4.43X10⁹ | 659.3  | 1.49X10⁻⁷ | 10.84      | 1.645       |
| 0.50                      | 0.0                  | 7.05X10⁹ | 1052   | 1.49X10⁻⁷ | 57.16      | 5.434       |
| 0.50                      | 0.0                  | 2.63X10¹⁰| 3787   | 1.44X10⁻⁷ | 80.54      | 2.127       |
| 0.50                      | 0.1                  | 7.20X10⁹ | 927.1  | 1.29X10⁻⁷ | 21.07      | 2.273       |
| 0.50                      | 0.1                  | 2.68X10¹⁰| 3480   | 1.30X10⁻⁷ | 103.8      | 2.983       |
| 0.50                      | 0.3                  | 7.44X10⁹ | 842.3  | 1.13X10⁻⁷ | 21.42      | 2.543       |
| 0.50                      | 0.3                  | 2.78X10¹⁰| 3024   | 1.09X10⁻⁷ | 90.20      | 2.983       |
| 0.75                      | 0.0                  | 7.05X10⁹ | 1125   | 1.60X10⁻⁷ | 32.74      | 2.911       |
| 0.75                      | 0.0                  | 2.63X10¹⁰| 4011   | 1.52X10⁻⁷ | 123.5      | 3.078       |
| 0.75                      | 0.1                  | 7.20X10⁹ | 1001   | 1.39X10⁻⁷ | 27.72      | 2.769       |
| 0.75                      | 0.1                  | 2.68X10¹⁰| 3559   | 1.33X10⁻⁷ | 80.55      | 2.263       |
| 0.75                      | 0.3                  | 7.44X10⁹ | 894.1  | 1.20X10⁻⁷ | 24.91      | 2.786       |
| 0.75                      | 0.3                  | 2.78X10¹⁰| 3171   | 1.14X10⁻⁷ | 68.48      | 2.159       |
| 1.00                      | 0.0                  | 4.43X10⁹ | 744.3  | 1.68X10⁻⁷ | 14.29      | 1.920       |
| 1.00                      | 0.0                  | 7.05X10⁹ | 1209   | 1.72X10⁻⁷ | 27.20      | 2.249       |
| 1.00                      | 0.0                  | 1.53X10¹⁰| 2457   | 1.61X10⁻⁷ | 105.5      | 4.295       |
| 1.00                      | 0.0                  | 1.65X10¹⁰| 2628   | 1.59X10⁻⁷ | 23.02      | 0.876       |
| 1.00                      | 0.0                  | 2.63X10¹⁰| 4211   | 1.60X10⁻⁷ | 105.2      | 2.498       |
| 1.00                      | 0.3                  | 7.44X10⁹ | 945.1  | 1.27X10⁻⁷ | 19.69      | 2.083       |
| 1.00                      | 1.0                  | 2.01X10¹⁰| 1525   | 0.76X10⁻⁷ | 10.50      | 0.689       |
| 1.25                      | 0.0                  | 7.05X10⁹ | 1247   | 1.77X10⁻⁷ | 23.89      | 1.915       |
| 1.25                      | 0.0                  | 1.53X10¹⁰| 2905   | 1.90X10⁻⁷ | 56.31      | 1.938       |
| 1.25                      | 0.0                  | 1.65X10¹⁰| 3584   | 2.17X10⁻⁷ | 16.82      | 0.469       |
| 1.25                      | 0.3                  | 7.44X10⁹ | 1004   | 1.35X10⁻⁷ | 26.76      | 2.667       |
| 1.25                      | 0.3                  | 2.78X10¹⁰| 3795   | 1.36X10⁻⁷ | 133.5      | 3.517       |
| 1.50                      | 0.0                  | 4.43X10⁹ | 795.0  | 1.80X10⁻⁷ | 3.162      | 0.398       |
| 1.50                      | 0.0                  | 1.53X10¹⁰| 2689   | 1.76X10⁻⁷ | 78.62      | 2.924       |
| 1.50                      | 0.0                  | 1.65X10¹⁰| 2820   | 1.71X10⁻⁷ | 9.899      | 0.351       |
| 1.50                      | 0.3                  | 7.44X10⁹ | 1114   | 1.50X10⁻⁷ | 40.79      | 3.662       |
| 1.50                      | 0.3                  | 2.78X10¹⁰| 3923   | 1.41X10⁻⁷ | 171.5      | 4.372       |
| 1.50                      | 1.0                  | 2.01X10¹⁰| 1747   | 0.87X10⁻⁷ | 53.28      | 3.049       |
for any individual sample (see Tables 2 and 3). The average value of the dominant mode for a particular concentration (the center-of-mass mode) agreed to within 20% of the predicted value inclusive for all samples at a given concentration range. This was determined by a linear extrapolation from the low angle longer wavelength measurements conducted earlier. With only a 40% to 50% two-mode resolvability rate (dependant on sample and UV output stability) in the high q regime with the dominant mode corresponding to the CM mode, it was found that the equipment was at the absolute detection limit for internal mode fluctuations. Not only was detection difficult, but results were extremely sensitive to variations of initial fitting parameters. The second mode detected did not exhibit the $q^2$ dependence expected for a CM mode which suggested that the second mode was the overall internal relaxation mode sought. A lack of any $q^2$ dependance for the second mode is further supported by theory and by earlier results with high molecular weight polystyrene (Schaller, Devanand, Selser, 1993). Upon the successful detection of two distinct modes, a series of different LiClO$_4$ concentrations were studied preliminarily to determine the effects of LiClO$_4$ concentration on the overall internal mode with only limited resolvability.
Figure 26. TOSOH $q^2$ Dependence with a Polymer Concentration of 0.1 mg/ml: The vertical line denotes where one would expect the experiment to be sensitive to the overall internal mode. Note that the data deviates as expected from the linear fit at that value supporting that there is a contribution from the overall internal mode. NOTE: Each fit line and the different symbols correspond to results obtained by the three major analysis techniques used.

for different LiClO$_4$ amounts. As an aid to understanding these results, a direct comparison was made between the bead-and-spring model and the PEO LiClO$_4$ systems studied. This comparison provides relatively good agreement and is therefore quite useful. In general, some factors contributing to deviations between experiment and theoretical predictions reflect constraints and limitations present in the bead-and-spring model. One assumption in this model is that the polymer coil in solution has a Gaussian segment distribution. In fact, it is known that PEO in solution does not have such a distribution, and that this non-Gaussian segment distribution is enhanced by the addition of LiClO$_4$ (Banka et al, 1996). Furthermore, the model does not take
Table 4 TOSOH 0.92M Dalton MW at 1.5 mg/ml VS bead-and-spring model

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</tbody>
</table>

into account hydrodynamic interactions between polymer chain segments, nor self-avoidance, i.e. two segments can't be in the same place at the same time. Prior to analysis, these two differences between the polymer and the model were assumed to result in relatively small discrepancies between the real-world experiment and the theoretical model. In the model, regardless of the qR₀ value, contributions of multiple modes are always present however small, as shown by predicted Sᵢ values (see Figure 7). As shown, the Sᵢ values that are not used for comparison between the experiment and the model are negligible in comparison to those being studied and compared, namely the S₀/S₂ ratios. Even though these other scattering contributions are believed to be extremely small, taken together they provide some deviation between the model and experiment. Furthermore, since CONTIN analysis does not treat each resolvable mode (CM or overall internal) as a delta contribution, but rather as a distribution of relaxation rates about a mean value for each distinguishable mode (see Figures 27 and 29 illustrating bimodal results: CM and internal), it was necessary to find the area under each mode profile, i.e. each mode amplitude, and compare the ratio of these areas to theoretical S₀/S₂ values (see Figure 7).

For the case where there was no LiClO₄ present, τ₁ determined experimentally was approximately two times faster than the predicted value using the bead-and-spring...
Figure 27. A typical TOSOH high angle $\Gamma$ distribution result using CONTIN on a sample without LiClO$_4$: Note the two modes able to be differentiated with the dominant amplitude mode corresponding to the center of mass mode exhibiting $q^2$ dependence and the other mode corresponding to the $q$ independent overall internal mode.

model (see Table 4). This factor of two discrepancy can be accounted for by a number of factors. The most likely reasons for the discrepancy are believed to be the lack of consideration of chain hydrodynamic interactions and not taking into account chain self-avoidance. This self-avoidance condition would reduce the number of possible chain configurations in the bead-and-spring model and would thus intuitively result in bead-and-spring model relaxations back to the equilibrium conformation faster than beads able to deviate further from its equilibrium state as described by the model. Comparison between the ratio $S_0/S_2$ determined experimentally and the predicted value using the bead-and-spring model shows that experimentally determined ratio
Figure 28. A typical TOSOH high angle correlation function and fit result using CONTIN on a sample without LiClO$_4$. Note: visual inspection of the correlation function does not exhibit two separate relaxation modes, and two modes can only be determined by mathematical analysis. The inset graph contains all data points showing a well defined baseline in the fit.

is approximately 3.15 times greater than predicted using the model (see Table 4). This signifies that in the experiment the center-of-mass mode is more dominant than predicted using the bead-and-spring model. This dominance is believed to be due to the non-gaussian segment distribution in the system studied, and also due to the general difficulty in resolving a second mode in the data analysis technique when the first mode is distinctly more pronounced than the second mode.

With the addition of LiClO$_4$ to the system, the deviation between the model and experiment was more pronounced. Before any comparison was made, it was necessary to account for the solutions change in viscosity along with the swelling of the coil that has been shown to occur upon the addition of LiClO$_4$ (Banka et al, 1996). The
Figure 29. A typical TOSOH high angle $\Gamma$ distribution result using CONTIN on a sample with LiClO$_4$: Note the two modes able to be differentiated with the dominant amplitude mode corresponding to the center of mass mode exhibiting $q^2$ dependence and the other mode corresponding to the overall internal mode. Compared to the same polymer concentration, after accounting for the changes in viscosity from the LiClO$_4$ the characteristic relaxation time of the overall internal mode is close to the predicted value.

The most pronounced change was with regards to $\tau_1$, where the experimentally determined value was approximately seven times faster than the theoretically predicted value (see Table 4). According to the model, the overall internal mode is affected by the coil's increase in $R_g$ and decrease in D. These deviations in $R_g$ and D were accounted for, but this correction alone was not sufficient to describe the behavior of PEO internal mode dynamics with and without LiClO$_4$. With the addition of LiClO$_4$, the system is believed to have been even more restricted in possible configurations thus resulting in an even faster than predicted relaxation time than in solution when no LiClO$_4$.
Correlation Function of TOSOH Sample at High Angle
1.0 mg/ml Concentration and 351.1 nm Laser Output
With 1.0M LiClO₄

Figure 30. A typical TOSOH high angle correlation function and fit result using CONTIN on a sample with LiClO₄. Note: visual inspection of the correlation function does not exhibit two separate relaxation modes, and two modes can only be determined by mathematical analysis. The inset graph contains all data points showing a well defined baseline in the fit.

This faster than predicted relaxation time is believed to be due to the LiClO₄ complexing along a PEO chain, which restricts the number of possible configurations a PEO coil can be in. The reduction in possible configurations is believed to limit the degree that a coil may deviate from its equilibrium configuration resulting in the coil having to move a lesser amount to return to the equilibrium conformation. This reduction in the coil displacement required to return to its equilibrium conformation is believed to result in a smaller amount of time to return to the equilibrium conformation. This reduction in configurations may necessitate accounting for hydrodynamic interactions and self-avoidance in PEO coils which appears to be more of a factor in modelling system behavior than the swelling of the coil. These
factors are likely the cause of the greater deviation between theory and experiment than for the case without LiClO$_4$. The comparison between $S_0/S_2$ shows that the experimentally determined ratio was 3.4 times greater than the theoretical prediction (see Table 4). This slight increase from 3.15 to 3.4 of the deviation between experiment and the model for $S_0/S_2$ is believed to arise from the additional deviation of the non-Gaussian segment distribution as shown by previous work (Banka et al, 1996). Also noted, but perhaps due to statistical variance, was the apparent increase in the resolution between two modes with LiClO$_4$ in the system (see Table 4). By introducing LiClO$_4$ and thereby causing the coil to swell (increasing the segment spacing in the coil), it is believed that the swelling allowed the equipment which was already using the minimum probe length to more readily detect the coil overall internal mode.

After considering the limitations of the bead-and-spring model, along with the lack of information available regarding the behavior of the overall internal mode of high molecular weight PEO, it was necessary to determine whether or not there was acceptable agreement between the model and experiment. The overall trend found experimentally shows evidence of some agreement between the system being studied and the model described, but at the same time it is apparent that the model does not account for variables that can affect the system such as the addition of LiClO$_4$. With further study, the bead-and-spring model may well be modified to be able to show general trends in the behavior of the coil overall internal mode for a particular LiClO$_4$ concentration. However, it is believed that the addition of varying LiClO$_4$ concentrations may add a degree of complexity that the bead-and-spring model cannot account for.
CHAPTER 6

CONCLUSIONS

As shown in this work, detecting an overall internal mode in a PEO/MeOH solution is extremely difficult. The most significant problem in this endeavor is the inability to obtain a high molecular weight polymer sample that also exhibits a low polydispersity. With current polymer synthesis limitations and the physical properties of PEO itself, two of the highest molecular weight samples available that also claimed a low polydispersity were studied in this work and resulted in limited but significant success. This success was only possible by using the equipment to its full capabilities, and requiring meticulous monitoring and adjustment of the apparatus well beyond the care required for a typical dynamic light scattering experiment. Even with the great care taken during experimentation, obtaining useful data proved to be extremely difficult. As shown in this paper, using this experimental technique makes it barely possible to even detect the PEO coil internal mode of a PEO/MeOH solution. With the results shown, great care was taken prior to claiming meaningful results. This caution is due to the difficulty of obtaining data, along with the difficulty of extracting any useful information from the data obtained.

Continued studies of this system may provide further information concerning the internal mode behavior of PEO/MeOH dilute solutions. However, the time required to conduct this work is great, with no guarantee of success. Because of the great amount of time that would be required to obtain data by this technique the automation systems described in this work proved to be an invaluable resource. Without such
systems, the time required for the data taking process could easily be extended by a factor of four.

Since PEO is one of the most flexible of polymer coils, modelling its behavior using the bead-and-spring model provided surprisingly good agreement considering the simplicity of the model and the difficulty in obtaining useful measurements. It is believed that the decrease of the overall internal mode relaxation time beyond the predicted change using the bead-and-spring model can be explained by recognizing that the model did not take into account the hydrodynamic interaction between beads, which appears to be even more of a factor once LiClO$_4$ is introduced to the system, and did not take into account bead self avoidance. The discrepancy between the predicted scattering intensities resulting from each mode is believed to be due to the coil itself not having a Gaussian segment distribution, as used in the model. The PEO coil is known not to have a Gaussian profile in a good solvent since the coil is swollen. Furthermore, swelling in the outer portion of the coil is exaggerated even more with the addition of LiClO$_4$ (Banka et al, 1996).

The systems studied here support previous work regarding the center of mass relaxation mode studies of dilute solution PEO/MeOH made by others (Banka et al, 1996) and has shown that the detection of the internal mode is possible, but extremely difficult. Measurements taken with LiClO$_4$ in the system also agree with previous work, but no new conclusions could be drawn from the limited amount of data obtained. Aside from the changes of the systems viscosity due to the increase in LiClO$_4$ along with the increase in the coil hydrodynamic radius due to LiClO$_4$, no new information regarding the presence of LiClO$_4$ was found beyond the significant fact that the overall internal relaxation time ($\tau_1$) was a factor of seven times faster than that predicted by the bead-and-spring model. Interestingly, $\tau_1$ was only two times faster than the predicted value without LiClO$_4$. Upon a lengthy study with a wide
range of different LiClO$_4$ concentrations on a series of different PEO/MeOH solutions, valuable information regarding polymer conformation and behavior related to the electrolyte of polymer batteries may be forthcoming. However, with the difficulty shown in detection of the internal mode discussed earlier, it is just as possible that no useful information will be obtained with a detailed study of the systems using this technique.

Overall, it is possible to detect the internal mode of high molecular weight PEO in MeOH solution both with and without the presence of LiClO$_4$, but in general this technique is not recommended. This recommendation is simply due to the difficulty in obtaining any useful data. Along with this difficulty, it is very easy to acquire data which appears valid on first analysis, but later proves to be useless after detailed studies of the system. With these problems inherent in the experiment, much caution must be taken before trusting any results and a great deal of time may be spent before realizing that the information being taken is not useful for the detection of the elusive overall internal mode of PEO in MeOH.
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