A STUDY OF THE EFFECTS OF LICIO₄ ON POLY(ETHYLENE OXIDE), (PEO) MELT DYNAMIC BEHAVIOR USING FABRY-PEROT INTERFEROMETRY

by

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ABSTRACT

A Study of the Effects of LiClO₄ on Poly(ethylene oxide), (PEO) Melt Dynamic Behavior Using Fabry-Perot Interferometry

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Poly(ethylene oxide)/lithium perchlorate (PEO/LiClO₄) complexes are widely studied as a prototype solid polymer electrolyte in rechargeable lithium-polymer batteries. Characterizing the structure and dynamics of the system in its molten state is important for understanding the role of the polymer environment in lithium ion transport and conductivity. We implement a fiber-optic coupled Fabry-Perot interferometer to investigate the electrolyte elastic properties and structural response times, which are both related to the intrachain local mobility and therefore to ion diffusion. We propose a simple and inexpensive fiber-optic experimental design combining two experimental techniques, Fabry-Perot interferometry and photon correlation spectroscopy. Our tests and evaluation show that the setup performs very well giving good resolution and numerous advantages to both techniques. We report Brillouin scattering results on PEO-1K melts and PEO-1K/LiClO₄ complexes at temperatures in the range from 40 to 80°C and salt concentrations from 0% to 31% (by weight). The temperature dependence for the no-salt samples revealed a monotonic decrease in the sound velocity and the longitudinal modulus in the medium. The system undergoes a glass transition in this temperature-frequency range. Upon addition of salt the longitudinal modulus increases significantly, which we interpret as stiffening and stabilization of the polymer network. That behavior is consistent with previous PCS results and should have great importance in optimizing the polymer electrolyte performance.

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CHAPTER 1

INTRODUCTION

Solid polymer electrolytes (SPEs) are an important class of conducting solid-state ionic materials having significant potential in a variety of electrochemical devices, especially in secondary (rechargeable) lithium/polymer batteries. Polymer electrolytes exhibit a number of advantages over conventional liquid electrolytes. For example, the viscoelasticity of polymers combines both solid-like and liquid-like properties making them particularly suited to commercial applications. Batteries based on SPEs are compact, lightweight, durable and safe. The prototypes and the first commercial units showed high-capacity, high power densities and good charge-discharge characteristics. It is hoped that batteries of this type will eventually serve as off-peak power storage and as light weight power supplies in electric and hybrid electric/internal combustion engine vehicles. Other important applications include portable electronic devices, backup power supplies, etc. An example of a working battery already on the market is the one developed by Avestor (Boucherville, Quebec, Canada) - a company created in a partnership of two major energy industry corporations, Hydro-Québec (Canada) and *Kerr-McGee* (USA).¹

In the search for the polymer electrolyte with the best performance and the greatest compatibility with battery electrodes, compositions based on poly(ethylene oxide) (PEO)

with lithium perchlorate (LiClO₄) were identified as worthy candidates. At room temperature, PEO is in a bi-phasic semi-crystalline state, well above its glass transition temperature of about -40° C and below the melting temperature of the crystalline phase (about 60°C for high molecular weigh PEO). It was shown that lithium ion transport occurs exclusively in the amorphous, non-crystallized regions of the polymer host.² It was also found that the conductivity of PEO/LiClO₄ electrolytes reaches practically useful values (of about 10^{-4} S/cm) only at temperatures of 60-80°C, or higher. Adding liquid plasticizers (to lower the operational temperature) promotes deterioration of the electrolyte's mechanical properties and increases its reactivity towards the lithium metal anode. These considerations have led to the concept of a "dry" (plasticizer-free) and "warm" (operating temperatures between 60° C and 80° C) polymer battery which is implemented in the battery by *Avestor* mentioned above.

Despite remarkable progress in the last decade toward designing lithium/polymer batteries and the considerable experimental and theoretical research in the area, there is still a lack of a understanding of the mechanisms that the polymer host plays in battery ion transport. We believe that a better understanding of the processes on a fundamental level will ultimately lead to higher performance and better design of polymer batteries. In recent years, our research group has been involved in extensive studies of the bulk properties of molten PEO and PEO/LiClO₄. Both the structure and dynamic behavior of these systems have been studied at various temperatures, for a range of salt concentrations, and for two different polymer molecular weights.^{3,4,5} The principal experimental techniques employed in our studies have been static light scattering (SLS), dynamic light scattering (DLS), and viscometry. Analysis of the light scattered by density

fluctuations in the molten PEO revealed long-ranged structure. It was identified as a transient physical network formed by the polymer in the melt. The structure persisted after the addition of LiClO₄ (at least for salt concentrations up to 28 weight percent). The results were interpreted in terms of the behavior of a random elastic PEO network immersed in a viscous PEO damping liquid (overdamped system). As a model system we used the "wet gel" model similar to that investigated by Tanaka, *et al.*⁶

In our recent PCS studies we collected a great amount of information. Even though we were able to construct an intuitive picture of the internal structure of the system, it proved to be very complex and there are still a lot of fundamental aspects and properties to be studied. In order to gain better understanding of the structure and dynamics in the bulk of the polymer electrolyte we initiated Brillouin scattering measurements implementing a Fabry-Perot (F-P) interferometer. This technique can be used to investigate the elastic properties of the polymer melt and polymer/salt complexes as well as structural response times, which are both related to the intrachain local mobility and therefore to the ion diffusion. As a previous study⁷ on poly(propylene glycol)/sodium triflate electrolyte suggested, this kind of measurement can provide valuable information linking the structural relaxation of the polymer backbone, the free-ion concentration and the observed conductivity of the electrolyte.

Although photon correlation spectroscopy (PCS) and Brillouin spectroscopy are both dynamic light-scattering techniques, they probe different physical phenomena at different timescales (Figure 1). PCS spans a very broad dynamic range and can be used to study processes such as the Brownian motion of particles in suspension and the diffusion of molecules in dilute polymer solutions or collective phenomena in concentrated polymer



Figure 1. Laser Spectroscopy

solutions and polymer melts. The accessible frequency range is typically from 10^{-3} to 10^{7} Hz, corresponding to characteristic times for the processes between hours to hundreds of nanoseconds. Naturally, the dynamics of the processes probed in this range are represented in time space. By using PCS we were able to study in detail the collective diffusion of the polymer network formed by the polymer in its melted state. The characteristic times for the collective diffusion in PEO (M_w=1060) were in the range from 0.1 to 1 seconds.

On the other hand, Fabry-Perot interferometry opens an additional dynamic range enabling us to observe faster processes with characteristic times ranging from microseconds to picoseconds and corresponding frequencies between 10^6 and 10^{12} Hz. In this sense, the two techniques are complementary, providing information about the dynamics of the system over a very broad time range. The natural representation for the F-P data is in frequency space. The observed spectra result from Rayleigh-Brillouin scattering which is considered in detail later in the thesis (see Sections 2.1 and 3.1). In the present work, we report measurements of some viscoelastic properties of melted PEO and PEO/LiClO₄ compositions with salt concentrations up to 31 weight percent and in the temperature range between 40 and 80°C. The characteristic times for the dynamic processes are in the picosecond range, corresponding to the gigahertz, or the so called "hypersonic" frequency range.

As far as determining the viscoelastic properties of the network component is concerned, we already mentioned the pioneering work of Tanaka, Hocker, and Benedek.⁶ They were able to demonstrate that the overdamped motion of the polymer network will give rise to broadening of the central Rayleigh line of the Rayleigh-Brillouin spectrum (see Section 2.1, Figure 5), which can better be resolved in the time domain by the technique of photon correlation spectroscopy. Marqusee and Deutch⁸ argued that the density fluctuations that propagate through the medium as sound waves will be scattered by the elastic polymer network. That scattering will lead to a shorter lifetime for the phonons and hence, to broadening of the Brillouin peaks. They extended the Tanaka theory for light scattering from gels and polymer networks to include Brillouin scattering. The theory of Marqusee-Deutch was further developed in the work of Ng and Li⁹ to include a revised relationship between the speed of sound in the network and its polymer volume fraction. They considered two limiting cases. The first case occurs for small frictional damping between the network and the fluid and essentially predicts the observation of two pairs of Brillouin peaks, one for the liquid and one for the network component. The other limiting case is for strong frictional damping. It predicts a single

pair of Brillouin peaks at frequencies determined by the average sound speed in the gel. In practice, all experimental results fall in the second category. Reported measurements of poly(vinyl acetate) (PVA), poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA) and polyurethane gels (see Ref. 9) show the presence of only a single pair of Brillouin peaks. Our work on PEO melts and PEO/LiClO₄ solutions showed that these systems behave similarly. Combined PCS and viscosity measurements published earlier⁵ revealed that the network and the liquid component are strongly coupled. Indeed, the diffusive motions of the network component are strongly damped by the viscous liquid component. Thus, it is not surprising that in our Brillouin scattering measurements we also observe a single pair of Brillouin peaks in the spectra (see Section 3.3). In fact, we observe a substantial increase of the sound speed in the medium upon the addition of salt, which is a result of the increase in crosslink density and elastic modulus in the network component induced by the increased concentration of the dissociated free ions.

An interesting possibility arose during the initial stages of designing and building the experimental setup for Brillouin spectroscopy: the use of fiber-optic coupling of the scattered light signal into both the Fabry-Perot interferometer and the PCS setup allowing simultaneous or consecutive measurements with both techniques, conducted without changing the conditions or disturbing the sample. It combines both instruments in one experimental setup which can be used to study a very broad dynamic range – some 15 orders of magnitude in frequency.

Since the late 1980s, significant effort has been put into incorporating fiber-optic detection into dynamic light scattering experiments. In his pioneering work,¹⁰ Brown made an intriguing observation: he found that the collection efficiency of a single-mode

fiber seemed to match or even surpass that of a classical two-pinhole detection optics in PCS experimental setups. After a short debate in the community, it was shown both theoretically and experimentally by Rička¹¹ that with single-mode fiber detection one can achieve the theoretical limit of 1 for the PCS experiment coherence factor (see the discussion in Section 2.1) while maintaining high light-collection efficiency.

To the best of our knowledge, single-mode fiber detection has not yet been used as a coupling scheme for high resolution F-P interferometry. There are only a few reports on using multimode fiber setups in similar experiments. Pakulski and Holuj¹² describe an experimental setup using a 200 μ m fiber along with a triple-pass F-P, but they focus their attention on the automated stabilization procedure they developed. Another report by Skinner¹³ describes the use of a multimode fiber and an F-P spectrometer to resolve the emission lines of H_a, D_a and T_a in a D-T plasma which implies an entirely different frequency range (the resolution they used was 0.2Å or ~14GHz) and therefore is not relevant to our discussion since we concentrate on higher instrumental resolutions (on the order of few hundred MHz).

Combining the two techniques by implementing a fiber-coupling scheme will offer numerous advantages in terms of flexibility and convenience in the experiment as well as substantial improvements for both instruments. In the case of the Fabry-Perot interferometer, it makes possible accessing a broad range of scattering angles entirely avoiding the difficult and tedious realignment of detection system components associated with the classical pinhole setup. In the case of PCS, the single-mode fiber detection has the intrinsic advantage of selecting signal from a single coherence area in the scattering volume while accepting sufficient amount of light for measurement. Therefore, with this setup it is easy to achieve very high quality in the measured autocorrelation function.

This thesis is structured as follows: In the next chapter we describe the fiber-optic approach in the experimental setup. In Section 2.1 we offer a brief description of the theory of operation of both the F-P and PCS systems. We limit the discussion to the relevant characteristics of the two techniques which allows us to make a comparison between the classical and fiber-optic configurations and to address the performance of the proposed experimental setup. In Section 2.2, we introduce the fiber-optic experimental setup and discuss some of the advantages and disadvantages that arise from the use of fiber-optic coupling. Section 2.3 offers qualitative and quantitative comparisons between the fiber-optic and classic system performances. We also study the effect of the multimode structure on the resolution of the F-P interferometer. Chapter 3 is devoted to the properties of the PEO melts and PEO/LiClO₄ solutions as studied by Brillouin spectroscopy. In Section 3.1 we give a brief account of the thermodynamic and elastic properties of polymer melts and relate them to the properties of PEO based electrolytes. We also give a description of the observed Rayleigh-Brillouin spectra in polymeric systems and the relation of their characteristic features to the elastic and dynamic properties of the polymers. Section 3.2 describes the experimental procedure used and we present the results, followed by discussion in Section 3.3. Our findings are summarized in Chapter 4.

CHAPTER 2

FIBER-OPTIC SETUP FOR SIMULTANEOUS PHOTON CORRELATION SPECTROSCOPY AND FABRY-PEROT INTERFEROMETRY

2.1. Theory and Background

2.1.1. Fabry-Perot Interferometer

Interference effects due to waves successively reflected between two parallel surfaces have been studied for centuries. In fact, the first simple theoretical description of the phenomenon was given by George Airy¹⁴ in 1831, in his *Mathematical Tracts*. Some



Figure 2. Classic (pinhole) geometry of a F-P interferometer. The first lens, L_1 with focal length f_1 , collimates the scattered light from the sample. The two parallel F-P mirror plates have adjustable spacing d. The second lens, L_2 with focal length f_2 , images the signal onto the pinhole of the detector. The diameter of the pinhole, a determines the scattering volume in the sample.

68 years later (1899), Alfred Perot and Charles Fabry¹⁵ described an interferometric device based on the same concept. Since then, it has been widely used in spectroscopic measurements and is referred as the Fabry-Perot (F-P) interferometer.¹⁶

The classic F-P interferometer is schematically shown in Figure 2. The sample is illuminated by a laser beam in a typical light scattering geometry. Single mode operation of the laser is essential, and it is usually achieved by introducing an F-P etalon inside the laser resonator. The scattered light from the sample is collimated by the first lens, L_1 and then passed through the two parallel F-P mirror plates with adjustable spacing, *d*. The second lens, L_2 collects the light and the output signal is detected through a pinhole, *a*. The diameter of the pinhole determines the scattering volume in the sample.

Between the two plates the light undergoes multiple reflections and multiple-beam interference is observed (Figure 3). The transfer function of the device is derived in standard textbooks.¹⁷ Light of intensity I_i , wavelength λ and wave vector \vec{k} with magnitude $k = 2\pi/\lambda$ is incident on the plates with separation d at incidence angle φ from the normal to the surface. We assume the space between the plates is filled with air with refractive index n=1. The two surfaces are characterized by reflectance R and transmittance T=1-R (assuming negligible absorption), defined for light intensities.



Figure 3. Multiple-beam interference at a plane-parallel configuration

The reflected and transmitted intensities are given by:

$$\frac{I_r}{I_i} = \frac{Q_R \sin^2 \frac{\delta}{2}}{1 + Q_R \sin^2 \frac{\delta}{2}} \tag{1}$$

$$\frac{I_{t}}{I_{i}} = \frac{1}{1 + Q_{R} \sin^{2} \frac{\delta}{2}}$$
(2)

where

$$\frac{\delta}{2} = \frac{2\pi d}{\lambda} \cos \varphi \tag{3}$$

The quality factor for the reflectivity Q_R is often denoted as the finesse coefficient (or coefficient of finesse):

$$Q_R = \frac{4R}{\left(1-R\right)^2} \tag{4}$$

A plot of the transmittance function is shown on Figure 4 for different values of Q_R (different reflectivity). It is periodic with maxima occurring when δ is an integer multiple of 2π . Two adjacent interference orders are separated by a frequency interval called the



Figure 4. Transmittance function I_t/I_i of a plane-parallel Fabry-Perot interferometer for different reflectivities *R* of 0.1, 0.42, 0.75, 0.91 (quality factors 0.5, 5, 50, and 500, respectively).

free spectral range (FSR, measured in Hz):

$$\Delta v_{FSR} = \frac{c}{2d} \,, \tag{5}$$

where *c* is the speed of light in vacuum. Two properties are characteristic for the transmission function: the full-width at half maximum, Δv_{FWHM} and the suppression of light between the maxima, measured by the contrast, $C=I_{max}/I_{min}$:

$$C = Q_R + 1 = \frac{(1+R)^2}{(1-R)^2}$$
(6)

The ratio of the peak distance to the peak half-width defines the finesse of the instrument

$$F = \frac{\Delta V_{FSR}}{\Delta V_{FWHM}} \tag{7}$$

In the ideal case considered so far, assuming no absorption, perfect flatness of the two reflecting surfaces and perfectly collimated illumination, corresponding to infinitely small aperture *a* and ideal lens system, the finesse depends only on the reflectivity. It is often referred to as reflectivity finesse

$$F_R = \frac{\pi}{2}\sqrt{Q_R} = \frac{\pi\sqrt{R}}{1-R} \tag{8}$$

In a real instrument one has to consider the effects of imperfect reflecting surfaces, finite aperture size, monochromatic aberrations of the collimating optics, etc. All of the effects listed above have negative effect on the finesse and lower the instrument's resolution. The total or effective finesse is given by

$$\frac{1}{F_{eff}^2} = \frac{1}{F_R^2} + \frac{1}{F_M^2} + \frac{1}{F_a^2} + \dots$$
(9)

The two most significant corrections are given by the flatness finesse

$$F_M = \frac{M}{2} \tag{10}$$

with *M* being the flatness figure for the mirror's surface with rms flatness λ/M , and the aperture (pinhole) finesse:

$$F_a = \frac{\lambda}{d} \frac{4f_1^2}{a^2},\tag{11}$$

with f_1 being the focal length of the collimating lens. In practice, one could measure the observed half-width and free spectral range and use Eq. (7) to calculate the actual finesse for a given F-P interferometer.

The term *instrument resolution* is used here in its most general sense; i.e. as the broadening imposed on the spectral line by the instrument, which in practice is represented by $1/\Delta v_{FWHM}$. From Eq. (7) it is evident that greater finesse directly leads to greater resolution. Therefore, these two terms will be used interchangeably throughout this discussion.

2.1.2. Rayleigh-Brillouin Spectrum

In spectroscopic measurements, the spectral range of the interferometer is scanned in most cases by changing the spacing *d* between the plates using piezoelectric actuators. A typical Rayleigh-Brillouin spectrum observed in a simple system is schematically shown in Figure 5. The central Rayleigh peak *R* with half-width Γ_R is centered at the laser frequency ω_0 . The two Brillouin peaks labeled *L* corresponding to longitudinal acoustic waves are shifted by frequency $\Delta \omega_l$ and are characterized by half-width Γ_l .



Figure 5. Generic Rayleigh-Brillouin spectrum. The Rayleigh component R with halfwidth Γ_R is centered at the laser frequency ω_0 . The two Brillouin peaks, L corresponding to longitudinal acoustic waves, are shifted by frequency $\Delta \omega_l$ and are characterized by half-width Γ_l . In some occasions, the peaks T corresponding to transverse acoustic waves can be observed.

On certain occasions, the peaks labeled *T* corresponding to transverse acoustic waves can be observed. In principle the longitudinal components can be decoupled from the transverse components by making polarization dependent measurements. While both anisotropic and isotropic scattering contribute to the I_{VV} spectrum, the spectrum due to transverse phonons is entirely anisotropic and occurs only in the $I_{VH}=I_{HV}$ spectrum (see Section 3.1).

Generally speaking, for a simple viscoelastic liquid, the following information is contained in the Rayleigh-Brillouin spectrum: the Brillouin frequency shift is directly related to the speed of sound in the medium and carries information about the compressibility modulus; the linewidth of the Brillouin peaks is related to the medium viscosity; the width of the central peak is related to the thermal conductivity of the medium; the ratio of the central peak intensity to the Brillouin intensity is called the "Landau-Placzek ratio" and it is related to the ratio of the specific heat at constant pressure, C_p and constant volume, C_V . A detailed description of the spectrum in the case of light scattered by viscoelastic liquids is given in Section 3.1. For a broader discussion, the reader is referred to an excellent review by Patterson.¹⁸

2.1.3. Photon Correlation Spectroscopy

The dynamic light scattering (DLS) technique of photon correlation spectroscopy (PCS) is a standard technique for measuring the dynamics of suspensions and liquids. PCS assesses fluctuations in the random interference pattern created by coherently illuminated, randomly moving scatterers. Fluctuations in the intensity of the scattered light provide a signature of the dynamics of the system. For example, from the scattered-light autocorrelation function (ACF), one can deduce the diffusion coefficient of particles in suspension.

A correlator forms in real time the autocorrelation function between the scattered light intensities at time *t* and at some later time t+t' (Figure 6), where *t*' is called the lag time or time shift:

$$G^{(2)}(t') = \left\langle I(t)I(t+t') \right\rangle \tag{12}$$



Figure 6. Dynamic light scattering examples: I(t) vs. t and $g^{(2)}(t')$ vs. t'.

Normalized to its baseline at large correlation lag times, normalized autocorrelation function is formed (Figure 6 – right):

$$g^{(2)}(t') = \frac{\langle I(t)I(t+t')\rangle}{\langle I(t)\rangle^2}$$
(13)

Fluctuations can be observed only if the detection optics provides sufficient angular resolution to resolve the interference pattern. Ideally, the initial value of the autocorrelation function amounts to twice its limiting value at large values of t' (solid line). In practice, the amplitude of the dynamic part of the correlation function decreases with decreasing angular resolution (Figure 6, dashed line).

We will limit ourselves to a few brief points relevant to our discussion. For comprehensive treatment, the reader referred to some of the classic sources in the field.^{19,20}

For Brownian motion of non-interacting identical particles in suspension with diffusion coefficient, D

$$g^{(2)}(t') = 1 + e^{-2q^2Dt'}$$
(14)

A more general property of the autocorrelation function is expressed by the Siegert relation

$$g^{(2)}(t') = 1 + f \left| g^{(1)}(t') \right|^2$$
(15)

with $g^{(1)}(t')$ being the ACF for the scattered electric field. The factor f in front of the dynamic part of the autocorrelation function is called the coherence factor, $0 \le f \le 1$. In a classical setup which consists of two circular apertures and an imaging lens, the value of f depends on the area of the pinhole f = f(A) and is typically in the range of 0.5 - 0.8.

Generally speaking, when the scattered light has low intensity one is forced to work with larger pinholes, which in turn leads to lower coherence factors *f*.

If the scattering is strong, it is possible to use a smaller size pinhole thus improving the coherence factor. The signal-to-noise ratio is high when both a high coherence factor and a high light-collection efficiency are achieved.

As already mentioned, Rička¹¹ was able to show both theoretically and experimentally that by using a single-mode fiber to collect and transport the light to the detector, one can achieve the theoretical limit of 1 for the coherence factor while maintaining high light-collection efficiency. In order to understand his argument, one has to realize that the single-mode fiber is not simply a convenient way to collect the signal and transmit it to the detector, but it acts as a filter as well. A single-mode waveguide can transmit only one transverse mode of the electromagnetic field (ignoring the two polarizations). Regardless of the monochromatic field illuminating the fiber entrance, the field propagated through the fiber always has the same transverse spatial structure resulting from the boundary conditions imposed on the electromagnetic field by the fiber geometry, and it is called the fiber mode.

To compare the classical (pinhole) setup with a fiber-optic detection setup one can define the light-collection efficiency as $\langle J \rangle / J_e$, where $\langle J \rangle$ is the average signal at the detector and J_e is the power of the excitation beam. Comparison of the two schemes assuming equal values of J_e leads to¹¹

$$\langle J \rangle_{pinhole} = N \langle J \rangle_{SM \ fiber},$$
 (16)

where *N* is the ratio of the area of the detector pinhole $A_{detector} = \pi a_D^2$ to the coherence area A_{coh} that is due to a circular source with radius a_s at a distance R:

$$N = \frac{A_{detector}}{A_{coh}}$$
(17)

$$A_{coh} = \frac{\lambda^2 R^2}{\pi a_s^2} \tag{18}$$

The number of coherence areas, N is conveniently expressed in terms of the coherence factor:

$$N = \frac{1-f}{f} \tag{19}$$

This simple result shows that opening the detector aperture a_D in order to increase the light-gathering power will at the same time decrease the coherence factor and thus the dynamic part of the autocorrelation function will become less visible. In effect, uncorrelated contributions from different areas of the detector aperture will add up incoherently and will average out. Let us consider a few examples (using Eq. (16) and Eq. (19)):

$$f = 0.5 \quad \rightarrow \quad \langle J \rangle_{pinhole} = \langle J \rangle_{SM \ fiber}$$
$$f = 0.8 \quad \rightarrow \quad \langle J \rangle_{pinhole} = \frac{1}{4} \langle J \rangle_{SM \ fiber}$$
$$f = 0.9 \quad \rightarrow \quad \langle J \rangle_{pinhole} = \frac{1}{9} \langle J \rangle_{SM \ fiber}$$

The light-collection efficiency of both detection schemes is equal when f = 0.5, which in practice is considered rather small. For f = 0.8, which for classical pinhole detection is considered close to optimum, the single-mode fiber offers four times larger light-collection power and for f = 0.9 it rapidly increases to nine times larger signal.

A similar analysis of the performance of a multimode fiber setup shows that increasing the number of modes (choosing fibers with larger core diameter) will result in an increase of the signal at the detector; however it will reduce the coherence factor. In the limit of very large number of modes across the fiber aperture, the result will converge to the case of a uniformly illuminated pinhole of the same diameter as the fiber. Overall

$$f_{pinhole} < f_{MM \ fiber} < f_{SM \ fiber} \tag{20}$$

2.2. Experimental

2.2.1. Experimental Setup

The experimental setup we designed and built is schematically shown on Figure 7. We used an argon-ion laser (*Coherent*, Palo Alto, California) operating at single longitudinal and transverse mode at λ =514.5 nm. The typical output power of the laser was in the range between 0.1 to 0.8W depending on the sample and the technique used. The laser output was vertically polarized and moderately focused at the center of the sample cell. The goniometer assembly along with the sample holder and temperature control are part of a standard light scattering setup, BI-200SM from *Brookhaven Instruments Corp.* (Holtsville, New York). The angle of the goniometer arm is adjusted by a stepper-motor. To couple the scattered light into the receiver end of the fiber we used a microscope objective with 10x magnification and compact five-axis spatial filter assembly both from *Newport Corp.* (Irvine, California), modified to accommodate standard fiber connectors in place of its pinhole. The spatial filter assembly was mounted

on the goniometer arm and it provided sufficient degrees of freedom for precise alignment. The microscope objective effectively couples the signal into a single mode fiber. The optimal microscope objective is determined by the best possible match with the numerical aperture of the fiber and the desired dimensions of the scattering volume in the sample. There are a variety of other coupling solutions for use with multimode fibers.

If necessary, a second polarizer can be used in front of the optical assembly in order to make polarization dependent detection. It is essential to resolve the polarization of the scattered light before it is coupled into the fiber since a standard optical fiber scrambles the polarization dependent information in the signal. There are polarization preserving



Figure 7. Experimental setup

fibers that can be used to avoid such an effect, but they have additional problems. For example, to resolve the polarization at different directions, the fiber has to be rotated around its axis which might be practically difficult and there is a great chance the alignment of the system will be affected.

In order to keep the setup as versatile as possible it has to allow easy and quick substitution between different fibers. A list of the fibers that we tested along with some of their basic characteristics are presented in Table 1. The first three fibers (SM-3.5, MM-4 and MM-6.6) used standard FC connectors whereas the rest of the fibers used standard SMA connectors. It should be noted that most of the fiber-optic vendors allow specifying the connectors used, therefore allowing for a system design with fully interchangeable fibers. Once the scattered light is coupled into the receiving fiber, it can be directed to either of the two instruments, PCS or Fabry-Perot interferometer, and then detected, analyzed and stored by the appropriate electronic and computer equipment.

In the case of the Fabry-Perot interferometer, the light leaving the receiver fiber is collimated by the first lens system, L_1 which is only schematically shown in Figure 7. Better collimation directly results in better resolution; therefore a good quality achromatic doubled or more refined lens system is necessary. The lens used in our setup was a 2 inch, achromatic doubled from *Thor Labs Inc.* (Newton, New Jersey). After the light passes through the Fabry-Perot interferometer it is collected by the second lens, L_2 and focused into a multimode fiber with large core diameter (typically 600µm) and directed to the PMT optics which consisted of a band-pass filter and an imaging lens. This last fiber is used only for convenience and does not have any effect on the interferometer characteristics.

Fiber	SM – 3.5	MM – 4	MM - 6.6	MM - 8	MM - 50	MM - 100	MM - 200	MM - 400
Core Diameter	3.5 μm [*]	4 µm [*]	6.6 μm [*]	8 μm [*]	50 µm	100 µm	200 µm	400 µm
Specified cutoff wavelength	430 nm	620 nm	950 nm	850 nm			_	
Numerical aperture	0.13	0.12	0.13	n. a.	0.22	0.22	0.22	0.22
Number of modes @ 514.5 nm	1	3	6	n. a.	\sim 2,260 [†]	$\sim 9{,}000^{\dagger}$	$\sim 36{,}000^{\dagger}$	$\sim 145,000^{\dagger}$
	single mode	e "few modes"			"true" multimode			
Connector	FC	FC	FC	SMA	SMA	SMA	SMA	SMA
Supplier	Nufern (ThorLabs)	3M (ThorLabs)	3M (ThorLabs)	Ocean Optics	Ocean Optics	Ocean Optics	Ocean Optics	Ocean Optics

Table 1. Single-mode and multimode fibers used

* MFD – mode field diameter $(1/e^2 \text{ fit} - \text{near field})$ † estimated

n. a. – information not available

In Figure 8, we show the scattering geometry defined by the excitation (laser) and the receiver (fiber) beams, which does not differ from a standard light scattering geometry. It is worth noting that it can be easily visualized by coupling laser light at the back end of the receiver fiber. That can be very helpful for initial alignment where by using the controls on the optical assembly one can intersect both beams at their waists and at the center of the sample. In the region where the excitation and receiver beams intersect, they are very well approximated by Gaussian beams and have well defined scattering vectors \vec{k}_e and \vec{k}_s inside the scattering volume. An angle θ between the excitation and the observation beam determines the scattering vector $\vec{q} = \vec{k}_s - \vec{k}_e$ with amplitude

$$\left|\vec{q}\right| = \frac{4\pi n}{\lambda} \sin\frac{\theta}{2} \tag{21}$$



Figure 8. Scattering geometry. The excitation and the receiver beams are approximated by Gaussian beams intersecting at their waists in the center of the scattering volume with well defined wave vectors \vec{k}_e and \vec{k}_s at that point. Angle θ between the excitation and the observation beam determines the scattering vector $\vec{q} = \vec{k}_s - \vec{k}_e$.

where *n* is the refractive index in the sample.

The Fabry-Perot interferometer used in this experiment is model RC-110 from *Burleigh Instruments* (now *EXFO Burleigh Products Group Inc.*, Victor, New York). It is worth noting that when the interferometer was purchased, many of its otherwise standard components were not available. Thus a number of accessories had to be reverse-engineered and custom built in our machine and electronic shops. Some of the most important additions include the kinematic base, the thermal enclosure, the multi-pass feature, custom electronic components, etc. In addition, many of the optical mounts had to be modified or redesigned to incorporate the fiber-optic approach.

2.2.2. Samples and preparation

In order to test the proposed fiber-coupled experimental setup we used two simple organic solvents, toluene and n-hexadecane, with well known Brillouin spectra as well as the molten polymer poly(ethylene oxide) (PEO). High purity toluene (99.9% min. by GC) was supplied by *Burdick & Jackson* (Muskegon, Michigan). High purity n-hexadecane (99.9% min. by GC) was supplied by *Tokyo Chemical Industry (TCI) America Inc.* (Portland, Oregon). A low molecular weight PEO sample (M_w=1060), designated here as "PEO-1K sample", with a narrow molecular weight distribution (M_w/M_N=1.03) was custom synthesized by *Polymer Standards Service (PSS)* (Mainz, Germany). PEO chain ends were "capped" with methyl groups to avoid complicating behavior associated with chain hydroxyl end-groups. Based on rheological measurements, the PEO-1K sample is unentangled in the melt (the critical value for the melt entanglement molecular weight is about 3500) and the melting temperature is about 38°C. After receiving the samples they were further purified using multiple dissolution rinses with methanol and diethyl ether,

each rinse followed by precipitation at -40°C. After the final rinse and filtration, the PEO samples were dried in a desiccator under high vacuum, and than handled inside a dry-box filled with dried and purified nitrogen, with the moisture level maintained below 10 ppmV. Keeping PEO samples dry is essential; PEO is highly hygroscopic and even small amounts of absorbed water can dramatically affect its properties. The absence of water in PEO prepared this way as well as the complete capping of PEO chains were previously verified by infrared absorption spectroscopy of representative samples. The LiClO₄ used in this work was a highly purified grade (Fluka, Buchs, Switzerland) initially dried in a vacuum oven and then further dried under high vacuum in a desiccator. Both the neat PEO samples and the PEO/LiClO₄ solutions were prepared by controlled evaporation of methanol from PEO/LiClO₄/methanol solutions. All samples were filtered through 0.2 micron pore-size Teflon membrane filters (Millipore, Bedford, Massachusetts) into dustfree 5 mm square spectrofluorometer cuvettes (Starna, Atascadero, California). During measurements, the sample cell assembly was thermostated maintaining sample temperatures within 0.1°C of set values. The temperature range was between 40 and 80°C. The lower limit was determined by the melting temperature of the polymer, while on the high end of the range the temperature was limited by the sample cell assembly design.

2.3. Results and Discussion

2.3.1. PCS with single-mode fiber receiver

We performed a series of PCS measurements to verify that by introducing the singlemode fiber detection the performance is not affected in a negative way and to determine whether or not the quality of the autocorrelation function follows the prediction outlined in the theoretical section. In Figure 9 we compare measurements of a PEO-1K sample in the melted state at a temperature of $T = 60^{\circ}C$ and a scattering angle of $\theta = 90^{\circ}$ done by using both the fiber-optic and the conventional pinhole setups. The normalized autocorrelation functions are represented on a log-linear plot which has the advantage of providing easy comparison of the relaxation rates. On the graph, the function represented by open circles was taken using the classical pinhole setup. In fact, it was selected among many measurements because of the very good value of its coherence factor, $f_{pinhole} \approx 0.78$. The second autocorrelation function, represented on the graph by filled



Figure 9. Classic vs. fiber-optic light detection used in PCS. The sample was PEO-1K melt at $T = 60^{\circ}C$, scattering angle $\theta = 90^{\circ}$ and collection time about 1½ hours. The open circles represent the classical (pinhole) measurement and the filled diamonds – the single-mode fiber detection setup. $\Gamma = q^2D$ – relaxation rate; β – dispersion parameter; f – coherence factor

diamonds, was measured using the single-mode fiber setup and showed a coherence factor of $f_{SM fiber} = 1.0$ in excellent agreement with the prediction. Both autocorrelation functions were collected for about 1 ½ hours accumulation time.

In order to extract the coherence factor and the rest of the parameters from the experimental data we used Kohlrausch-Williams-Watts (KWW) fits, also known as "stretched exponential" fits²¹

$$g^{(2)}(t') = 1 + \frac{A}{B_0} e^{-2(q^2 D t)^{\beta}}, \qquad (22)$$

with fitting parameters: A – amplitude, B_0 – baseline, $\Gamma = q^2 D$ – relaxation rate, and β – dispersion parameter, $0 < \beta \le 1$. The dispersion parameter provides a measure of the width of the distribution of decay rates, Γ . A β value of 1 corresponds to single-exponential relaxation, for example, in the ideal case of identical, non-interacting particles in suspension (Eq. (14)). Smaller values of β indicate broader distributions. In our analysis the parameter β was always very close to 1.

By comparing Eqs. (15) and (22) it is clear that coherence factors can be extracted using the KWW fits

$$f = \frac{A}{B_0} \tag{23}$$

One can also use the graph and visually compare the amplitudes of the autocorrelation functions. It is evident that the ACF measured using the single-mode fiber setup converges to an intercept of 2 for small values of t' while the one taken with the conventional (pinhole) setup converges to somewhat lower intercept of about 1.8.

Comparing the values of the extracted relaxation rates, Γ , we see that they agree very well within the experimental error.

Our comparison between the results of the classical setup and the single-mode fiber setup shows that the latter provides essentially the same qualitative and quantitative physical information about the sample along with substantial improvement in terms of higher coherence factors. It is also confirmed that the fiber-optic setup has stable performance in terms of very good reproducibility of the results between different measurements.

2.3.2. Brillouin scattering with single-mode fiber receiver

One of our goals was to assess the performance of the described setup as a Fabry-Perot interferometer using a single-mode fiber receiver. As a reference system we used high purity toluene at room temperature ($T = 21^{\circ}C$) for which the Brillouin shift is known with good accuracy.²² The scattering angle was set at $\theta = 90^{\circ}$. The Brillouin spectrum we obtained is shown on Figure 10-a. The Brillouin peaks are well resolved. The observed instrument resolution was $\Delta v_{FWHM} \approx 300MHz$. We used the published values for the Brillouin frequency shifts to calibrate the free spectral range of our F-P interferometer. We determined $\Delta v_{FSR} \approx 17GHz$. Therefore, the experimentally determined finesse (using Eq. (7)) was about 55-56. We used the calibration value for the free spectral range in the measurements discussed below and shown in Figure 10 and Figure 11.

As a second reference system we used high purity n-hexadecane. It has been very popular in a series of papers by Patterson (see Ref. 18 and references therein) and it has been referred to as classic, "textbook" example of the Brillouin spectrum from a simple



Figure 10. Brillouin spectra of simple organic liquids obtained with the single-mode fiber detection setup: a) toluene and b) n-hexadecane

liquid. The measurement we performed using our single-mode detection setup at room temperature ($T = 21^{\circ}C$) is shown on Figure 10-b. Again, the Brillouin spectrum was very well resolved with resolution similar to that of toluene.

After we confirmed that the fiber-coupled F-P interferometer performed as expected, we initiated measurements on PEO-1K melts. In Figure 11, we show two measurements performed at different temperatures. The Brillouin spectra are well resolved and the measured frequency shifts are 6.1 GHz at T=55°C and 5.7 GHz at T=70°C. They agree very well with previous measurements reported in the literature²³. Furthermore, the decrease in the shifts with increasing the temperature agrees with theoretical predictions and experimental observations (see Ref. 18 and Section 3.1).

The above series of measurements demonstrates clearly that introducing a singlemode fiber detection scheme in place of the classical pinhole detection does not degrade the performance of the instrument. We were able to achieve the same finesse and


Figure 11. Brillouin spectra of molten 1K-PEO at different temperatures: a) $T=55^{\circ}C$ and b) $T=70^{\circ}C$

resolution as in a classical Fabry-Perot interferometer. This is a strong indication that fiber-optic coupling the scattered signal into an interferometer is a viable option introducing numerous practical advantages to the instrument without diminishing its performance. A possible improvement will be to incorporate a multi-pass feature in order to further increase the contrast and resolution.

2.3.3. Effects of multimode fibers on the resolution of

the Fabry-Perot interferometer

In some experimental situations the scattered light from the sample has very low intensity and the detection becomes problematic. As examples, this could be the case in very dilute solutions or in small molecule liquids. Therefore, in order to collect as much signal as possible, it would be preferable to use multimode fibers with larger core diameter in place of the single-mode fiber described in the previous section. Therefore, it is important to address the question of the possible effects of the fiber mode structure on the resolution of the Fabry-Perot interferometer. It can be easily shown that going to larger core-size fibers will unavoidably lead to reduction in the resolution. Indeed, the fiber exit aperture acts as an entrance aperture for the Fabry-Perot collimation optics. Therefore, the core size of the fiber will affect the aperture (pinhole) finesse of the interferometer according to Eq. (11). For fixed free spectral range it will directly reduce the resolution by making the instrument's line wider:

$$\Delta v_{FWHM} = \frac{c}{8\lambda f_1^2} a_{fiber}^2, \qquad (24)$$

where a_{fiber} is the fiber core diameter. The numerical aperture of the fiber and the diameter of the Fabry-Perot mirror plates impose a limit on the maximum focal length, f_1 , of the collimating lens, therefore that parameter cannot be used to minimize the broadening of the linewidth resulting from the increase in the fiber core-size.

In this measurement, we used a He-Ne laser operating at $\lambda = 632.8$ nm, the focal length of the collimating lens was $f_1 = 10$ cm and the mirror spacing was d = 12 cm, which resulted in $\Delta_{FSR} = 1.25$ GHz. The fiber aperture limit on the resolution was calculated using Eq. (24) with the appropriate experimental parameters and is shown in Figure 12 (dashed curve). As is evident from the plot, this is the major limiting factor on the instrumental linewidth for fiber core diameters of about 100 μ m and larger. For sizes smaller than 30 μ m, the primary limiting effect is the combined reflectivity and the flatness finesse which was found to be about 50. And finally, there is a "cross-over" region between 30 μ m and 100 μ m where both effects contribute. The solid line represents the limit with all factors combined. The points on the graph represent measurements of the actual instrumental linewidth for a few of the fibers selected from



Figure 12. Effect of the fiber core diameter on the F-P interferometer resolution. The solid line represents the resolution limit imposed by the instrument (see text) and the points are the measured linewidths for fibers with core diameters of $8\mu m$, $50\mu m$, $100\mu m$ and $200\mu m$

Table 1. Most of them are in very good agreement with the prediction. The only point that is slightly off is the 50 micron fiber. But even in this case, the measured and the predicted resolutions differed by less than a factor of two. The most likely reason for the discrepancy is the fact that while this is still a fiber with a relatively small diameter, it has a large numerical aperture. As a consequence, the collimating lens L_1 (Figure 7) was used at its entire diameter and thus the monochromatic aberrations were appreciable. The lens used in our setup was a 2 inch, achromatic doublet from *Thor Labs Inc.* (Newton, New Jersey), which reduces the aberrations somewhat, but in this case a better optimized optical system is needed.

There are several important points to be made:

(1) Increasing the core diameter of the fiber does broaden the instrument linewidth as predicted by Eq. (24). Apparently this is due to the increased diameter of the effective entrance aperture of the interferometer and not to the mode structure of the fiber.

(2) If one needs to use larger fibers in order to collect more light, it can be done only at the expense of lowered resolution. Diagrams similar to the one shown on Figure 12 can be used as a good initial estimate of the limitations.

(3) If one is forced to operate in the cross-over regime (i.e. with 50 micron fiber), it is important to take into account the monochromatic aberrations of the collimating optics. The requirements on the optics will be higher.

(4) Even the 200 micron fiber shown in Figure 12 results in resolution of about 250 MHz which is considered very good for a typical Fabry-Perot interferometer. It can be adequate for a large number of applications. For example, the instrument linewidth in all of the Brillouin spectra shown in Figures 10 and 11 was 300 MHz. Therefore, we could have used any of the multimode fibers (up to 200 μ m) in place of the single-mode fiber in that series of measurements to achieve essentially the same result.

2.3.4. Advantages and Disadvantages of Fiber-Coupling

A. Photon Correlation Spectroscopy and Single Mode Fiber.

In this case the coherence factor f is equal to 1. Therefore, by using a single-mode fiber receiver, one can achieve the theoretical limit where the amplitude of the dynamical part of the autocorrelation function amounts to twice its baseline. That leads to the best possible quality of the autocorrelation data. In essence, the high coherence factor is achieved due to the property of the single mode fiber to select light strictly from one coherence area in the scattering volume. In Section 2.3 we offer yet another demonstration of that remarkable property. In the last decade the advantage of using single mode fiber detection was widely recognized. Moreover, there is at least one commercial system (*ALV-Laser Vertriebsgesellschaft mbH*, Langen/Hessen, Germany) implementing the idea.

B. Photon Correlation Spectroscopy and Multimode Fiber.

As we discussed, there is no real advantage in substituting the single-mode with multimode fiber. Presumably the light-collection efficiency will increase with increasing the core diameter of the fiber but at the same time the coherence factor is significantly degraded, resulting in lower overall quality of the autocorrelation function.

In many occasions, however, it is desirable to use the same experimental setup for static light scattering (SLS). In this case, the coherence factor is not essential but the amount of collected light is important and thus the use of multimode fiber with a large core diameter is preferable. Due to the widespread use of optical fibers in telecommunications, a great number of standardized elements are available including standard connectors, 2-way splitters, 2-way switches, etc. Therefore, one can easily switch between single mode and multimode fibers without disturbing the optical alignment of the system or the state of the sample.

C. Fabry-Perot Interferometer and Single-mode Fiber

In contrast with PCS, selection of a single coherence area in this case is not essential. On the other hand, the small core diameter of a single mode fiber (typically 3-4 microns), which acts as an input aperture for the F-P interferometer, results in high degree of collimation even when using a single collimating lens. That can be easily seen from Eq. (11).

D. Fabry-Perot Interferometer and Multimode Fiber

Increasing the size of the fiber core diameter automatically leads to quadratic increase of the collected light intensity. For weakly scattering samples that might be the only way to ensure adequate signal. On the other hand, increasing the size of the core diameter, according to Eq. (11), leads to quadratic decrease in the aperture finesse which lowers the angular resolution. Moreover, typical multimode fibers have numerical apertures about twice those of single-mode fibers. In order to achieve the maximum possible collimation, one needs to replace the single lens L_1 with a system of lenses optimized for minimal monochromatic aberrations.

It is obvious from the arguments above that there is a trade-off between the intensity of the signal and the resolution. It can be decided on a case-by-case basis which of the two regimes is more suitable. Once again, the abundance of standardized connectors and other elements for fiber optics makes the swapping of different fibers easy.

E. Common Advantages of Using Fiber-Coupling

One of the biggest practical advantages benefiting both techniques is the ability to perform measurements at different scattering angles and thus at different values of the scattering vector \vec{q} . In the case of PCS experiments, detection at different scattering angles has been accomplished by mounting the detector along with the detecting optics on a goniometer arm which allows varying the detection angle in a controllable fashion. While heavy and bulky, the system performs quite well. On the other hand, using the goniometer design for the F-P interferometers is impossible since they are very large and massive by design (in order to ensure stability). In addition to the interferometer itself, it requires collimating optics, a detector along with detection optics, a thermal enclosure, and in many cases additional components such as multi-pass optics, an iodine filter, etc. Ideally, the whole system associated with the F-P interferometer is assembled on an optical table to reduce any vibrations. Changing the angle involves moving the whole system to a new position and complete realignment. As a result of the difficulties of that procedure, most experimentalists limit themselves to detection only at 90 degrees scattering angle. In rare cases, where detection at different angles was attempted, the authors were limited only to a few angles (usually 30 and 150 degrees). There are some examples were the excitation laser beam was redirected with the use of clever optical arrangements. These techniques, though, are not widespread due to their difficult alignment and the fact that they also can access only a limited range of angles.

Using fiber-coupled detection offers a very elegant and inexpensive solution to this major problem. The front end of the fiber detector consists of an optical mount which accommodates a microscope objective, a standard fiber optics connector and has a number of degrees of freedom to allow fast and easy optical alignment. Such units are inexpensive and are offered as a standard item by most of the major suppliers of optical equipment. They are light and small in size and can be easily mounted on the goniometer arm to allow instant access to various scattering angles without any additional complications. The fiber-optic connector allows interchanging different fibers without disturbing the sample or the optical alignment in any way.

The second major advantage of using fiber-coupled detection is the built-in ability for switching between PCS and F-P interferometry, or even using both in simultaneous measurements. This is very easily achieved since the system uses standard connectorized fiber-optic cables. Once the scattered light is coupled into the receiver fiber, it can be redirected to either instrument simply by reattaching the back end of the fiber to the desired port. An even more elegant solution is to use a 2-way fiber-optic switch to redirect the signal. If the detected signal is strong enough, a 2-way fiber-optic splitter can be introduced allowing for simultaneous measurements. In principle, the system could be easily expanded to include other experimental techniques as well. All necessary elements such as connectors, adapters, switches, splitters, etc. are well developed due to their widespread application in fiber-optic communications. They introduce minimal loss and are readily available and inexpensive.

There are numerous other advantages of using fiber-coupled detection. The optical alignment of the detector side is fast, easy, robust, and is completely independent of any changes or modifications introduced in other parts of the system. The actual instruments along with all necessary components and accessories may be arranged at convenient location and distance. If the measurement is performed in a harsh environment with levels of dust, temperature variations, vibrations, etc., intolerable for the proper operation of the instrument, it can be easily isolated in a different room. Another appealing possibility is that the instrument can be assembled on a platform and used at different locations by connecting the appropriate fiber to the front port.

CHAPTER 3

RAYLEIGH-BRILLOUIN SPECTROSCOPY OF PEO-1K MELTS AND PEO-1K/LiClO₄ SOLUTIONS

3.1. Theory and Background

In the following section we introduce the thermodynamic equation of state of PEO as well as some important physical quantities defined in the standard way through thermodynamic derivatives. Later, in our discussion of the experimental results we will make use of both experimentally determined and calculated values for the density, specific volume, thermal expansion coefficient, isothermal compressibility, specific heat capacity, etc. In Section 3.1.2 we introduce the complex longitudinal modulus and in Section 3.1.3 we relate its dispersion in the hypersonic frequency range and the glass-rubber transition in the amorphous phase of the polymer. In Section 3.1.4 we consider the temperature dependence of the elastic properties which is required to explain the observed data. In Section 3.1.5 we describe the features of a typical Rayleigh-Brillouin spectrum observed in polymeric systems. The analysis of the Brillouin frequency shift and linewidth and their relation to the elastic and dynamic properties of the polymer melt is done in more detail since it is directly applied to the experimental results. Some other features such as the Rayleigh and the Mountain peaks are only briefly mentioned for

completeness. In Section 3.1.6 we give a very brief account of two publications in the literature which are closely related to our discussion.

3.1.1. Equation of state and thermodynamic properties of PEO

There are many theoretical models^{24,25} describing the thermodynamics of polymers in the liquid state leading to a number of different forms for the equation of state relating the canonical variables pressure *P*, volume *V* and temperature *T*. For a wide variety of polymers including poly(ethylene oxide), the pressure-temperature dependence of the volume is given in the following semi-empirical form, which is known as Tait equation

$$V(P,T) = V(0,T) \left\{ 1 - C \ln \left[1 + \frac{P}{B(T)} \right] \right\}.$$
 (25)

Here we accept the common system of units in which the volume in given in cm^3 , the pressure in *bar* and the temperature in ${}^{o}C$, unless otherwise stated. In terms of density, ρ (in g/cm^3) the equation of state is given as

$$\rho(P,T) = \frac{\rho(0,T)}{1 - C \ln\left[1 + \frac{P}{B(T)}\right]}.$$
(26)

In the above equations, V(0,T) and $\rho(0,T)$ are respectively the volume and the density at zero pressure, as functions of temperature. In the case when the coefficient of thermal expansion, $\alpha = \alpha_0$ (to be defined later) is a constant at zero pressure, they can be expressed as

$$V(0,T) = v_{sp}(0)e^{\alpha_0 T},$$
(27)

$$\rho(0,T) = \rho_0 e^{-\alpha_0 T} \,. \tag{28}$$

In general, the thermal expansion coefficient is not necessarily constant, however for PEO at constant atmospheric pressure and in the temperature range considered it is essentially constant and Equations (27) and (28) provide a good description of the experimental observations. The rest of the parameters in Equations (25) to (28) are as follows: *C* is an unitless constant; ρ_0 is the limiting value of the density at zero pressure and temperature; $v_{sp}(0)$ is the same limit for the specific volume (by definition $v_{sp}(0) = 1/\rho_0$), and B(T) is a temperature dependent parameter given by the expression

$$B(T) = b_0 e^{-b_1 T}, (29)$$

where b_0 and b_1 are empirical constants specific for a given substance.

Using the equation of state and standard notation for the thermodynamic derivatives, we can define the following thermodynamic quantities:

- coefficient of thermal expansion, α

$$\alpha = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_{P} = \frac{1}{v_{sp}} \left(\frac{\partial v_{sp}}{\partial T} \right)_{P}, \qquad (30)$$

where $v_{sp} = 1/\rho$ is the specific volume.

- isothermal compressibility, β_T

$$\beta_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T = -\frac{1}{v_{sp}} \left(\frac{\partial v_{sp}}{\partial P} \right)_T.$$
(31)

If we use Eq. (26) to calculate β_T at zero pressure, we get

$$\beta_T = \frac{C}{b_0} e^{b_1 T} \quad \text{(at zero pressure)}. \tag{32}$$

The compressibility (bulk) modulus is defined as $K_0 = \frac{1}{\beta_T}$, or

$$K_0(T) = \frac{b_0}{C} e^{-b_1 T} \quad \text{(at zero pressure)}. \tag{33}$$

Here the subscript "0" in K_0 denotes the "zero frequency" or static value, or the so called thermodynamic limit.

- thermal pressure coefficient, γ_V

$$\gamma_{V} = \left(\frac{\partial P}{\partial T}\right)_{V}.$$
(34)

The values of the parameters and constants discussed above are usually determined by fitting the equation of state to experimental PVT data and are tabulated for a wide variety of polymers.^{24,25,26,27} Some of the experimental methods include dilatometry, density gradient column methods and other specialized PVT methods.²⁸ For poly(ethylene oxide) some of the parameters discussed above are summarized in Table 2. Later in the discussion we use the empirical equations for the density of PEO at ambient pressure and the expression for the compressibility modulus, K_0 . Any comparison with our measured data have to be done with the understanding that the literature data are typically reported for highly entangled polymers, where some of these quantities are independent of the polymer molecular weight. Our PEO sample with molecular weight M_w =1060 is unentangled, since it is well below the critical entanglement molecular weight of about M_c =3500.

$v_{sp}(0) = 0.8766 \ cm^3 / g$ $\rho_0 = 1.142 \ g / cm^3$ $\alpha_0 = 7.087 \times 10^{-4} \ (^{\circ}C)^{-1}$	$V(0,T) = 0.8766 \ e^{7.087 \times 10^{-4}T}$ $\rho(0,T) = 1.142 \ e^{-7.087 \times 10^{-4}T}$
$b_0 = 2077 \ bar$ $b_1 = 0.003947 \ (^{o}C)^{-1}$ C = 0.0894	$B(T) = 2077 \ e^{-0.003947T}$ $\beta_T = \frac{0.0894}{2077} e^{0.003947T}$ $K_0 = \frac{2077}{0.0894} e^{-0.003947T}$
$\gamma_V = 15.79 - 0.0250T + 1.532 \times 10^{-4} T^2$	

Table 2. Empirical parameters for the equation of state for poly(ethylene oxide), (PEO)

3.1.2. Viscoelasticity of polymers

Viscoelastic materials simultaneously exhibit a combination of elastic and viscous behavior.^{29,30} While all substances are viscoelastic to some degree, this behavior is especially prominent in polymers. The description of the elastic properties involves some mechanical terms, such as: the Young's modulus, *E*, the shear modulus, μ , the compressibility modulus, *K*, and the Poisson's ratio σ . These quantities are related by the familiar relationships

$$K = \frac{E(1-\sigma)}{3(1+\sigma)(1-2\sigma)}$$
 and $\mu = \frac{E}{2(1-\sigma)}$. (35)

The longitudinal modulus, *M* is defined as

$$M = K + \frac{4}{3}\mu \,. \tag{36}$$

In a Brillouin scattering experiment, where the propagation of longitudinal thermal acoustic phonons in the fluid media is observed, the longitudinal modulus, M is of primary interest. In dynamic experiments it is convenient to define dynamic mechanical moduli. Following the typical convention, subscript "0" will indicate the low frequency limit and subscript " ∞ " will indicate high frequency limit. For example, $K_0 = 1/\beta_T$ and $\mu_0 = 0$. The complex longitudinal modulus is defined as

$$M^* = M' + iM'', (37)$$

where M' is the storage modulus and it is a measure of the energy stored elastically during deformation, and M'' is the loss modulus – a measure of the energy dissipated as heat. Both the real and the imaginary parts are functions of frequency, temperature and pressure. Similar definitions hold for the other moduli.

The loss tangent (sometimes called the loss factor) is defined as

$$\tan \delta = \frac{M''}{M'}.$$
(38)

If the system has a purely elastic response, the modulus is constant and real, and $\tan \delta = 0$; if the response is purely viscous, the modulus is purely imaginary and $\tan \delta = \infty$; when the storage and the loss parts of the modulus are of comparable order of magnitude, the response is called viscoelastic.

3.1.3. Glass-rubber transition and behavior of the loss factor

The transition that separates the glassy state from the viscous state in polymers is known as the glass-rubber transition. It exhibits properties similar to those of a secondorder transition at very slow rates of heating or cooling, however, strictly speaking it is not a second order transition. Below the glass transition temperature, T_g , the Young's modulus is constant. In the transition region it drops substantially. Often the glass transition temperature is defined as the temperature where the thermal expansion coefficient undergoes a discontinuity. After the sharp drop during the transition the modulus becomes almost constant again in the rubbery plateau where the polymer exhibits long-range rubber elasticity. If a polymer is semicrystalline (like PEO), the amorphous portions go through the glass transition, but the crystalline portions remain hard. The modulus (the height of the rubbery plateau) depends on the degree of crystallinity. The crystalline plateau extends until the melting point of the polymer. At the melting temperature, the modulus drops rapidly to that of the corresponding amorphous material, now in the so called liquid flow region. The melting temperature is always higher than the glass-transition temperature.

In the case of poly(ethylene oxide), the properties below the melting point including the glass-rubber transitions (often called "relaxations") are largely influenced by the degree of crystallinity of the polymer, which depends on the molecular weight of the samples and also on their thermal history. The polymer displays multiple relaxation processes, which have been studied by mechanical, dielectric loss, nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC) and other methods.³¹ The static (zero frequency) values for the temperature of the glass-rubber transitions are usually obtained by DSC measurements. For high molecular weight PEO there are number of such relaxations reported anywhere in the range between -60° C and -20° C and they are strongly dependent on the thermal history of the samples.

When the polymer undergoes transitions between different states, tan δ goes through maxima. As the mechanical disturbance (for example, a phonon) travels through the fluid, the pressure, temperature and shear stress are changed, thus driving the system to a new equilibrium state. The peak in the loss factor occurs when the driving frequency is in resonance with the system's characteristic frequency for the relaxation process. The loss peaks can be determined as a function of frequency. Traditionally, the log of the peak frequency, *f* is plotted against $1/T_{max}$ where T_{max} is the temperature at which the maximum occurs, to obtain the so-called "transition maps" (an example is shown in Figure 13). The data measured by mechanical, dielectric, and NMR methods agree very well and group onto discrete transition lines. Transition maps for most linear amorphous polymers are characterized by at least two transitions. The primary glass-rubber relaxation data follows the WLF (Williams-Landel-Ferry) equation

$$f = f_0 \exp\left(-\frac{E_a}{R(T - T_0)}\right),\tag{39}$$

while the secondary data displays an Arrhenius temperature dependence

$$f = f_0 \exp\left(-\frac{E_a}{RT}\right),\tag{40}$$

with E_a being the apparent activation energy for the process, R is the molar gas constant and T_0 is the "true" glass transition (absolute) temperature extrapolated to zero frequency and infinitely slow heating rate. At high frequencies the two main chain transition lines often merge and only a single maximum in tan δ is observed experimentally.

The characteristic frequencies associated with Brillouin scattering from polymers are in the gigahertz range. Therefore, the technique can provide valuable information about the behavior of the transition line above the point where the relaxations merge, which can be fundamental to the understanding of the glass-rubber relaxation. The loss tangent can be directly determined from a Brillouin scattering experiment by measuring the splitting and the width of the Brillouin peaks (as discussed later in this section).

Figure 13 (from Ref. 23) shows the transition map for poly(ethylene oxide). The solid line corresponds to the primary glass transition measured by dielectric measurements. The maximum loss found by Brillouin scattering agrees perfectly with the dielectric measurements confirming that the relaxation process observed in the hypersonic frequency range is indeed the primary glass-rubber transition.



Figure 13. Transition map for PEO-1K: comparison of dielectric and Brillouin scattering results [Ref. 23]

3.1.4. Temperature dependence of the sound velocity; determination

of the longitudinal modulus and the hypersonic loss

In general, the complex adiabatic longitudinal modulus can be represented as a function of frequency

$$M^{*}(\omega) = \gamma K_{0} + M_{R} \int_{0}^{\infty} \frac{w(\tau)i\omega\tau}{1+i\omega\tau} d\tau, \qquad (41)$$

where M_R is the total relaxation strength for all processes that couple to the longitudinal stress, τ is the relaxation time and $w(\tau)$ is the distribution of relaxation strengths for these processes. The integration is over all relaxation times, i.e. over all contributing relaxation processes. The longitudinal sound velocity, $V_l(q)$ for waves of wave vector magnitude q is determined by the real part of the adiabatic longitudinal modulus

$$V_l(q) = \sqrt{\frac{M'}{\rho}} \,. \tag{42}$$

The hypersonic sound velocity can be experimentally determined by measuring the Brillouin splitting, $\Delta \omega_l$ and using the relationship $\pm \Delta \omega_l = qV_l(q)$. The behavior of the sound velocity as a function of temperature changes through three distinct regions³² (see Figure 14 – solid curve): the relaxation times for the dominating processes are (1) short, (2) comparable, and (3) long relative to the inverse Brillouin frequency, $1/\Delta \omega_l$ which defines the experimental time scale.

In the first case (high temperature limit) the sound velocity is close to its zero frequency (thermodynamic) value $\sqrt{\gamma K_0 / \rho}$. In this region, the relaxation strength of the other processes is small relative to γK_0 and they have only a negligible effect on the measured hypersonic velocity.

In the second region, where the characteristic relaxation times are comparable to the reciprocal of the Brillouin frequency, a maximum hypersonic loss is observed (Figure 14 – dashed line) and the hypersonic velocity shows different characteristic behavior. As the temperature is decreased the characteristic relaxation times associated with the glass-rubber relaxation in the polymer fluid increase. This leads to an increase in the hypersonic velocity above its zero frequency value. With decreasing temperature, initially there is only a small increase in the hypersonic sound velocity since the value of M_R is only a fraction of K_0 . As the sample is cooled further, the relaxation modulus, M_R increases and the hypersonic velocity increases more rapidly than $V_1(0)$ eventually approaching its high frequency limiting temperature behavior which is close to linear for temperatures well below the temperature of maximum hypersonic loss. The high



Figure 14. Brillouin splitting and linewidth as a function of temperature for 2,4,6 trimethylheptane

frequency limiting value goes like $\sqrt{M_{\infty}/\rho}$. The crossover region between the high frequency limiting velocity and the zero frequency regime is rather narrow and quite smooth with temperature.

In the third region, the relaxation times become longer compared to the experimental time scale and the sample eventually will approach its nonequilibrium glass state. Since our study focuses on the properties of the poly(ethylene oxide) melt, the glassy state will not be discussed here.

3.1.5. Rayleigh-Brillouin scattering

In homogeneous, non-absorbing liquids, light is scattered by density fluctuations. The spectrum of the scattered light reflects spontaneous, thermal fluctuations in the dielectric tensor of the medium which are averaged over the scattering volume. Thus, Rayleigh-Brillouin scattering will yield only highly averaged information about the local structure of the medium. Furthermore, the length scales that are probed by light scattering are of the order of 1/q and are typically greater than 100 nm. Nevertheless, the magnitude and the frequency of the fluctuations can be used to infer structural information. There are many types of fluctuations that couple to the local dielectric tensor and lead to light scattering, but the most important contributions are from pure compression, pure shear, temperature and collective orientation. Information about each of them and various combinations can be obtained by measurements using different polarization geometries. Polarization perpendicular to the scattering plane is denoted as vertical and polarization parallel to the scattering plane in denoted as horizontal. If the recorded spectrum is obtained when both the incident and the detected light are vertically polarized (I_{VV}) , it will be determined by fluctuations in the longitudinal stress, temperature and orientation.

In the case when the incident and the scattered light have mutually perpendicular polarizations ($I_{HV}=I_{VH}$) the spectrum depends on fluctuations from shear and orientation. It is often referred to as depolarized scattering. The V-V spectrum results from isotropic and anisotropic contributions which can be resolved if both I_{VV} and I_{VH} are measured

$$I_{VV} = I_{iso} + \frac{4}{3} I_{VH} \,. \tag{43}$$

The following discussion is limited only to I_{VV} spectra since the measurements presented in this work did not involve use of the depolarized scattering geometry. A linear viscoelastic theory of Rayleigh-Brillouin scattering has been developed by Rytov³³ and extended by Patterson¹⁸ to include scattering from systems where the relaxation times are long, such as amorphous polymers near the glass transition. The theory of the Rayleigh-Brillouin spectrum of a pure monatomic fluid and molecular liquids including relaxation processes is developed in detail in Sections 10.4 and 10.5 of Ref. 20.

The spectrum (see Figure 5) of the scattered light from a simple purely viscous liquid is characterized by a central Rayleigh peak and two shifted Brillouin peaks due to scattering by propagating density fluctuations (sound waves). The total intensity is proportional to $\rho k_B T / K_0$, where k_B is the Boltzmann's constant, T is the absolute temperature. The relation for the total intensity remains true for viscoelastic liquids. The ratio of the central peak intensity to the Brillouin intensity in the purely viscous limit is equal to $\gamma - 1$ where $\gamma = C_P / C_V$ is the ratio of the specific heats at constant pressure and volume. That ratio is called the Landau-Placzek ratio. The linewidth of the central Rayleigh peak is given by

$$\Gamma_R = \frac{\kappa q^2}{\rho C_p},\tag{44}$$

where κ is the thermal conductivity, and q is the magnitude of the scattering vector. The thermal diffusion process is present in all liquids and is a weak function of temperature. The central Rayleigh peak is usually too narrow to be resolved (~10MHz or less) using Brillouin spectroscopy. Thus the influence of the thermal conductivity/diffusivity can be ignored in most of the cases.

The Brillouin intensity is proportional to

$$I_B \propto \frac{\rho k_B T}{M'} \tag{45}$$

The increase in the value of M' as the liquid becomes viscoelastic (more elastic) leads to a decrease in the Brillouin intensity. A new spectral feature called the Mountain peak³⁴ is present in this range. It is centered at the laser frequency and its relative intensity is given by

$$I_M = \frac{\rho k_B T}{\gamma K_0} \frac{M' - \gamma K_0}{M'}.$$
(46)

In the region of the glass transition where the dispersion in M' is quite large, the Mountain peak has a significant contribution to the spectrum.

The Brillouin shift is determined by the adiabatic sound velocity

$$\Delta \omega_l = q V_l(q) \,. \tag{47}$$

For purely viscous liquids the static sound velocity is given by

$$V_l(0) = \sqrt{\frac{\gamma K_0}{\rho}} . \tag{48}$$

The Brillouin linewidth Γ_l can be represented as

$$\Gamma_l = \frac{q^2}{2\rho} \left(\eta_v + \frac{4}{3} \eta_s \right), \tag{49}$$

where η_v and η_s are the volume and the shear viscosities. Because the sound waves are adiabatic there is a temperature change associated with the compression, and the volume viscosity will contain contributions from both the relaxing specific heat and from volumetric structural relaxation. In the case of simple liquids it is assumed that all the relaxation times that determine the viscosities are fast compared to $1/\Delta\omega_l$. As the liquid is cooled, the viscosity increases, and the relaxation time becomes comparable to the inverse of the Brillouin splitting. A more general expression for the Brillouin linewidth in this region is

$$\Gamma_l = \frac{M'' q^2}{2\rho\omega}.$$
(50)

If the imaginary part of M^* as given by Eq. (41) is used in Eq. (50) the result is

$$\Gamma_l = \frac{q^2}{2\rho} M_R \int_0^\infty \frac{w(\tau)}{1 + \Delta \omega_l^2 \tau^2} d\tau \,.$$
(51)

As long as $\Delta \omega_l \tau \ll 1$ (high temperature limit) for all τ , the Brillouin linewidth is determined by the average relaxation time

$$\Gamma_{l}(0) = \frac{q^{2}}{2\rho} M_{R} \langle \tau \rangle.$$
(52)

In the case when $\Delta \omega \tau \gg 1$ (low temperature limit) the linewidth is proportional to the average frequency $\langle 1/\tau \rangle$.

A qualitative description of the effects can be obtained by considering single relaxation time instead of distribution of relaxation times. In this case Eq. (41) reduces to

$$M = \gamma K_0 + \frac{M_R i \omega \tau}{1 + i \omega \tau}.$$
(53)

53

Introducing the high frequency limiting longitudinal modulus $M_{\infty} = \gamma K_0 + M_R$, Eq. (53) can be written also in the equivalent form

$$M = M_{\infty} - \frac{M_R}{1 + i\omega\tau}.$$
(54)

If we regard the thermal diffusivity and the thermal expansion as negligible, the dispersion equation determining the Brillouin spectral features takes the simple form

$$Mq^2 - \rho \omega^2 = 0. \tag{55}$$

There are three roots of the dispersion equation:

$$\omega_1 = i\Gamma_M, \qquad \omega_{2,3} = i\Gamma_l \pm \Delta\omega_l, \qquad (56)$$

where, using the expression (54) for M

$$\Gamma_M = \frac{1}{\tau} - 2\Gamma_l \tag{57}$$

$$\Delta \omega_l = \sqrt{\frac{M_{\infty}q^2}{\rho} + 3\Gamma_l^2 - \frac{2\Gamma_l}{\tau}}$$
(58)

$$\Gamma_{l} \approx \frac{M_{R}q^{2}/2\rho\tau}{1/\tau^{2} + M_{\infty}q^{2}/\rho}$$
(59)

and the Brillouin spectrum takes the form*

$$S_B(q,\omega) \propto \frac{2\Gamma_l \Delta \omega_l^2}{\left(2\omega\Gamma_l\right)^2 + \left(\Delta \omega_l^2 - \omega^2\right)^2}.$$
(60)

In the short relaxation time limit the Brillouin linewidth is approximately given by

$$\Gamma_l = \frac{q^2}{2\rho} M_R \tau \,, \tag{61}$$

in agreement with Eq. (52) when single relaxation time τ is used.

^{*} For treatment of the complete Rayleigh-Brillouin spectrum the reader is referred to Chapter 10 of Ref. 20 or the discussion in Ref. 18.

If we substitute that approximate relation in Eq. (57) the linewidth of the Mountain peak becomes

$$\Gamma_{M} \approx \frac{1/\tau^{3} + \gamma K_{0}q^{2}/\rho\tau}{1/\tau^{2} + M_{\infty}q^{2}/\rho},$$
(62)

which has the correct limits at both short and long relaxation times and in both cases the linewidth goes as $1/\tau$.³²

If the relation (61) is substituted into Eq. (58) we get an expression for the Brillouin splitting

$$\Delta \omega_l = q \sqrt{\frac{\gamma K_0}{\rho} + 3 \left(\frac{M_R \tau q}{2\rho}\right)^2} .$$
(63)

Of course, the temperature dependence of $\Delta \omega_l$ is the same as the one described earlier for the hypersonic velocity V_l since the two quantities are directly proportional.

We note, once again that Eqns. (53) - (63) are valid only with the simplifying assumption that a single relaxation time τ is involved. These expressions correctly predict the short time limit and the fact that the linewidth goes through a maximum when $\Delta \omega_i \tau \approx 1$. For temperatures well below the linewidth maximum the full description allowing for distribution of relaxation times should be used. Even for a simple anisotropic molecular liquid there must be at least two relaxation times: translational and orientational relaxation time. For chain molecule liquids, the orientational relaxation time is usually more than an order of magnitude longer than the translational relaxation time and there are other relaxation processes corresponding to various degrees of freedom.

Finally, we express the loss tangent in terms of the Brillouin splitting and linewidth

$$\tan \delta = \frac{2\Gamma_l \Delta \omega_l}{\Delta \omega_l^2 - \Gamma_l^2} \,. \tag{64}$$

The measured values of $\tan \delta$ are usually plotted vs. temperature. The important quantities are the temperature, T_{max} and frequency $\omega_{l,max}$ at which the maximum loss occurs. The average relaxation time for the process can than be found as

$$\left\langle \tau \right\rangle = \frac{1}{\omega_{l,\max}}.$$
(65)

Instead of using the loss tangent, some authors prefer to define the acoustic absorption or acoustic loss via the ratio of the Brillouin linewidth to the sound speed

$$\alpha_{B} = \frac{\pi \Gamma_{l}}{V_{l}(q)}.$$
(66)

3.1.6. Related experiments with PEO and PPG

In 1977, Patterson²³ reported a Rayleigh-Brillouin study on poly(ethylene oxide) M_W =1000 in the temperature range between 40°C and 110°C. It was observed that the Brillouin frequency decreased and the Brillouin linewidth went through a maximum in agreement with the arguments above. He found a maximum in the loss factor at a temperature 60°C and frequency 6.06 GHz. The loss process was confirmed to be the glass-rubber transition in the gigahertz range. The result was compared to previous data from dielectric measurements³⁵ and the agreement was very good (Figures 13 and 15).

An interesting study on poly(propylene glycol) (PPG) and sodium triflate (NaCF₃SO₃) complexes was done by Sandahl, Torell, Stevens, *et. al.*⁷ in 1989. The temperature range studied was from room temperature to about 230°C where the polymer started to degrade. Similarly to PEO, they observed that in PPG the Brillouin frequency decreased monotonically with increasing the temperature, while the Brillouin linewidth went through a maximum at about 143°C. Addition of salt had very interesting effects. They found that the frequency shifts increased as the salt content increased. The dispersion curves of the various salt concentrations differed more on the low temperature side while they seemed to converge at higher temperatures. From the widths of the Brillouin component it was found that maximum absorption occurred at higher temperature for complexes than for the neat PPG and the absorption peak shifted



Figure 15. Brillouin frequency and tan δ for poly(ethylene oxide) M_W=1000

monotonically to higher temperatures with increasing salt concentrations. Furthermore, that increase was found to correlate very closely with the increase of the glass transition temperature investigated earlier³⁶ by DSC measurements. They concluded that the uncomplexed polymer relaxes more rapidly with temperature than the complexes. On the high temperature side, the sound velocity data for the complexes approaches those of the uncomplexed polymer implying similar zero frequency velocity, V_0 independent of the salt concentration. At the other extreme, the infinite frequency velocity, V_{∞} (the velocity of the unrelaxed system) at the low temperature range was found to depend strongly on the salt concentration.

3.2. Experimental

We used the experimental setup described in Section 2.1 to measure the Rayleigh-Brillouin spectra of the PEO melt and PEO-melt/LiClO₄ solutions. The Fabry-Perot interferometer was scanned using a ramp generator RG-93 supplied by *Burleigh* as part of the interferometer configuration. The duration of each scan was 100 ms. The data was accumulated using a multichannel scaler (MCS-pci) from *Ortec* (Oak Ridge, TN) with accompanying software package MCS-32 (ver.2.12). In a typical measurement the dwell time was 100 μ s, the number of channels was 1,000 and the spectra were averaged for 3,000 to 6,000 passes corresponding to collection times from 5 to 10 minutes. The PMT dark count was very low – typically less than 10 counts per second. For 10 minutes accumulation time the dark counts in any individual channel rarely exceeded 3-4 counts. Our F-P interferometer lacks an automated self-adjusting system to keep perfect alignment of the mirror plates, therefore we had to make manual adjustment before each series of measurements. In order to have reliable calibration of the measured frequencies we recalibrated the free spectral range using toluene following each manual adjustment. Thus, all the data taken within a series of measurements or between different series were adjusted to the same reference spectra. The accuracy of the frequency calibration was estimated to be \pm 0.05 GHz. Occasionally, we used an iodine filter in order to suppress the strong Rayleigh scattering and get better resolved Brillouin lines in the spectra.

The data collected by the MCS were exported to *Origin* (OriginPro ver.7.0, *OriginLab Corp.*, Northampton, MA), where its peak fitting procedure was used to fit the data with the expected line profiles. The spectra were fit using four Lorentzians – two for the Brillouin peaks and two for the central feature. At this point, reliable results are obtained for the peaks positions, therefore only the Brillouin shifts are reported. We are in the process of improving the fitting algorithm and implementing a deconvolution procedure which will allow us to deconvolute the instrumental function from the measured spectra. That in turn will lead to reliable values for the Brillouin frequency shifts provide valuable information about the sound speed in the medium and the behavior of the longitudinal modulus of the system.

The samples of neat PEO-1K melts and PEO-1K/salt solutions were prepared as described in Section 2.2. Here we report results for 0%, 16%, 26.5% and 31% salt concentrations (by weight). The free spectral range as determined by toluene calibration was 16.5 GHz for the no-salt sample, 18.9 GHz for the 16% sample and 21.3 GHz for the 26.5% and 31% samples.

3.3. Results and Discussion

3.3.1. Neat PEO-1K melt

Typical results for neat PEO-1K melts were already shown in Figures 11, a) and b). In Figure 16 we show the temperature dependence of the Brillouin frequency shift $\Delta \omega_l$ determined in our experiment for the no-salt sample. The values of the frequencies monotonically decrease with increasing temperature as expected in excellent agreement with previously published results²³ (Figure 15).

Using the measured values of $\Delta \omega_l$ and Eq. (47) we calculated the sound velocity in the medium and the corresponding values for the real part of the longitudinal modulus, M' according to Eq. (42):

$$(I) = (I) = (I) + (I)$$

$$M' = \rho V_l^2 \tag{67}$$

Figure 16. Brillouin frequency shift for PEO-1K sample (no-salt)

The values of the density ρ used in this calculation are taken from Ref. 26 and extrapolated using the empirical equation shown in Table 2. In this range the average density is about 1.1 g/cm³ and it is weakly dependent on temperature (with variation over the range of about 2.8%).

In Figure 17 we show the longitudinal modulus M' (in kbar) vs. temperature. It is represented by open circles and the line is just to guide the eye. We also note that in this range, where the maximum in the hypersonic loss is observed, the value of M' is a result of two contributing terms: static and relaxing

$$M' \sim \gamma K_0 + M_R \tag{68}$$

In the same graph we plot the product γK_0 (filled diamonds) and an extrapolation of that quantity over the temperature range (dashed curve) calculated according to the empirical equations given in Table 2. The values for the thermodynamic (zero frequency) bulk modulus K_0 are taken from Ref. 26 and the values of the heat capacity ratio γ are calculated using thermodynamic relationships and known quantities.^{*}

The temperature dependence of M' can be qualitatively explained as follows: at the high temperature limit, where the relaxation time is short compared to $1/\Delta\omega_l$, the value of M' will converge to its thermodynamic limiting value γK_0 . Even though our apparatus has a high temperature limit of 80°C it is evident that M' tends to converge to its relaxed value at high temperature. As the temperature is decreased, the relaxation part

* To calculate $\gamma = C_p / C_V$ we used the thermodynamic expression $C_V = C_p - \frac{\alpha^2}{\beta_T} VT$; the values for C_p were taken form Ref. 27 and the values of α , β_T and V = V(0,T) were taken from Ref. 26 and Table 2. All quantities were calculated per gram substance and the temperature is in K.



Figure 17. Temperature dependence of the real part of the longitudinal modulus M' for PEO-1K sample (no-salt)

 M_R of the longitudinal modulus becomes comparable in magnitude to γK_0 and its effect becomes appreciable in the region of the transition, were $\Delta \omega_l \tau \approx 1$. In this range, the value of M' increases much faster compared to the value of γK_0 .

We already mentioned that the maximum of the hypersonic loss as reported by Patterson²³ is centered at about 6 GHz, corresponding to relaxation times for the process in the range of 150 - 200 ps. These characteristic times are attributed³⁷ to relaxations arising from long-range segmental motion of the polymer chain in the melt and are some 10-11 orders of magnitude faster than the cooperative relaxations in the bulk of the polymer melt (observed by PCS).

3.3.2. PEO-1K/LiClO₄ solutions

The results for the Brillouin frequencies shifts measured in PEO-1K/LiClO₄ samples with different salt concentrations are summarized in Figure 18. It can be seen that the



Figure 18. Brillouin frequency shift vs. temperature for PEO-1K samples with different $LiClO_4$ concentration

frequency shifts increase as the salt concentration increases. This implies higher values for the sound speed and the real part of the longitudinal modulus M' in the medium. The structural relaxation manifests itself as dispersion in the sound velocity. Also, the general form of the curve changes as salt is added to the polymer.

The observed monotonic increase in the sound velocity and the modulus can be interpreted as stiffening of the polymer network due to cross-linking of adjacent polymer chains, which as it has been suggested for other polymer electrolytes³⁸ occurs via the dissociated salt ions. Increasing the salt concentration results in an increased density of transient crosslinks with an overall stabilization of the network. This result correlates very well with our previous observation by PCS measurement made for much larger length and time scales,⁵ where from measurements of the diffusion coefficient and the

viscosity it was concluded that the network became stiffer. Observations in the behavior of the glass transition temperature T_g by DSC measurements³⁹ also show a monotonic increase in T_g with increasing salt concentration (Figure 19). Similar observation in poly(propylene glycol) based electrolytes was interpreted by some authors³⁸ as a result of "consolidation" of the polymer network by increased crosslink density facilitated by the increased concentration of free ions.

The dependence of the sound velocity on the salt concentration is revealed better on the next plot (Figure 20). Data for only three temperatures are shown for clarity. The results for the rest of the temperatures in the range behave similarly to those chosen here. It seems that initially the sound velocity increases at a faster rate with increasing salt concentration. That effect is more pronounced at the lower end of the temperature range. With further increase in the concentration (above 20% wt.) the dependence becomes weaker and looks like eventually it will level off. This is consistent with some Raman results in similar polymer electrolyte systems showing that the concentration of dissolved free ions first increases with salt content and thereafter decreases when the salt



Figure 19. Glass transition temperature T_g as a function of salt concentration for PEO/LiClO₄ complexes as measured by DCS [Ref. 39]



Figure 20. Sound velocity vs. salt concentration in PEO-1K/LiClO₄ samples for different temperatures

concentration becomes high enough for ion-ion associations and ion aggregates formation to become appreciable.

In the case of PEO-melt/LiClO₄ solutions we do not calculate the value of the longitudinal modulus M' since reliable mass density data for such complexes at various concentrations are not available. Nevertheless, a rough estimate of the density can be made easily: by knowing the mass of the LiClO₄ added to the polymer and assuming the volume is changing only slightly upon addition of salt, we calculate that the densities increase with increasing the salt concentration. These figures are somewhat overestimated since it is known that the polymer melt expands slightly upon addition of salt. Following this argument we conclude that the density varies between 1.1 g/cm³ in the no-salt sample to 1.4 g/cm³ in the highest concentration sample (31% wt.) and it is a

weak function of temperature. Therefore, the density values are not expected to have any appreciable effect on the real part of the longitudinal modulus M'. Its behavior is expected to follow closely that of the square of the sound velocity.

Another important feature of the Brillouin shifts shown in Figure 18 is that the form of the dispersion curve changes as salt is added to the polymer. As the data for the no-salt sample is slightly curved (this is even more evident in the scale of Figure 17), addition of salt appears to reduce the curvature and for the samples with the highest salt concentrations the data appears more or less linear. This is an indirect indication that the loss maximum is shifting to higher or lower temperature upon increasing the salt content. The shift is most probably toward higher temperatures as already observed in PPG based electrolytes by Sandahl, et al. Of course, it is desirable to have direct measurement of the dependence of the loss peak on the salt concentration. Improvements in our experimental system as well as in the data reduction procedure currently under way will allow us to perform reliable measurements of the widths of the Brillouin peaks and to calculate the frequency and the temperature of the absorption maximum. Again, the loss mechanism is attributed to the relaxation arising from long range segmental motion in the polymer melt. In this case, the relaxation is likely to involve cooperative motion of the dissociated ions with the polymer segments.

The results presented above show changes in both the elastic properties (M') and the local dynamics (the shift of the absorption peak and the related shift in the structural relaxation time) as the salt concentration is increased in the polymer. In the first case, the density of the transient crosslinks in the polymer network increases leading to stiffening and stabilization of the network with direct effect on the ion diffusion. This effect is
expected to become weaker at higher temperatures where the sound speed and the modulus are expected to converge to their relaxed (thermodynamic) limits V_0 and γK_0 , respectively, independent of salt concentration. Thus the mobility of the polymer network at higher temperatures is expected to become independent of salt concentration. That regime is well outside our temperature range and it could not be investigated. It is not clear if that limit can be reached for temperatures below the decomposition point for the polymer. On the other hand, the shift of the absorption curve with increasing salt concentration is a result of a change in the relaxation time for the process. For example, if future measurements confirm our expectation that the maximum absorption shifts to higher temperatures, that will imply a slowing down of the intrachain motions, which may negatively affect the ionic conductivity in the electrolyte.

CHAPTER 4

SUMMARY AND CONCLUSIONS

A fiber-coupled system for light scattering experiments was designed and tested. The setup combines Fabry-Perot interferometry and photon correlation spectroscopy allowing simultaneous or consecutive measurements with both techniques, conducted without changing the conditions or disturbing the sample. The fiber-optic coupling approach introduces a great amount of flexibility and convenience in the experiment. On the other hand, it also offers some substantial improvements for both instruments. In the case of the F-P interferometer, it makes possible accessing a broad range of scattering angles entirely avoiding the difficult and tedious realignment of the system components associated with the classical pinhole setup. In the case of PCS, the single-mode fiber detection has a significant intrinsic advantage of selecting signal from a single coherence area in the scattering volume. Therefore, with this setup it is easy to achieve the theoretical limit of 1 for the coherence factor and hence very high quality in the measured autocorrelation function.

We offer a simple and inexpensive experimental design which combines components of an existing commercial light scattering setup, a commercial F-P interferometer and a system of optical fibers along with the accompanying optics. The two experimental techniques complement each other allowing experiments over an extremely broad dynamic range, spanning some 15 orders of magnitude in frequency space. The system is very flexible and easily expandable – it may accommodate any number of additional instruments if needed.

The system was tested using toluene, n-hexadecane and molten poly(ethylene oxide) and its performance was excellent in both PCS and F-P modes. In the case of PCS, we were able to confirm that the fiber-coupled setup provides essentially the same qualitative and quantitative physical information about the sample as the classical setup with additional substantial improvement in terms of the increased coherence factor. In the case of the F-P interferometer, we were able to achieve the same finesse and resolution as with the classical setup, which confirmed that introducing fiber-coupled detection does not reduce the instrument performance. In addition, we tested several different multimode fibers with the F-P interferometer and we showed that the reduction in the resolution was due to the increased size of the effective entrance aperture of the instrument and not to the mode structure of the fiber. This measurement also provides a quick estimate of the practical limitations on the resolution which may be useful in designing similar systems.

Next we performed a series of Brillouin scattering measurements on PEO-1K melts and PEO-1K/LiClO₄ complexes at various temperatures and salt concentrations. Our nosalt results were in excellent agreement with previously published data for the Brillouin frequency shifts in the same system. The temperature dependence for the no-salt samples revealed a monotonic decrease in the sound velocity and the longitudinal modulus in the medium with increasing temperature. Comparison with relaxed (thermodynamic) data for the bulk modulus showed clearly that the system undergoes transition in this temperaturefrequency range which was identified as the primary glass-rubber relaxation in the hypersonic frequency range.

Upon addition of salt the sound velocity and the longitudinal modulus increased significantly. This result is similar to the effects observed in other polymer electrolyte systems. The interpretation proposed here is that the increase in the elastic modulus in the medium results from stiffening and stabilization of the physical network formed by the polymer molecules in the melt. This interpretation and the observed network consolidation with increasing salt concentration correlates nicely with our previous observation of the collective diffusion effects by PCS in the same system as well as with the observed dependence of the glass transition temperature on salt concentration reported earlier. It was also observed that initially the elasticity increases faster with increasing the salt concentration and then the dependence becomes weaker. That effect is more pronounced at the lower end of the temperature range.

The findings summarized above should be important when trying to explain the mechanism of ion transport in the polymer electrolytes. It is believed that the diffusion of the charge carriers through the polymer host is directly affected by the local segment mobility along the polymer chains. The formation and the elastic properties of the transient polymer network in the melt will directly affect these motions. On one hand, the local segment mobility of the polymer chains will be hindered by the network and it will be more restricted with increased salt concentrations due to the stiffening effect of the dissolved ions. On the other hand, the formation and stabilization of the network, which as we showed earlier spans the bulk of the polymer, will provide continuous pathways for

the free ions between the two electrodes in a battery configuration, which will facilitate the conductivity.

A number of improvements in the experimental setup and the data analysis procedure are under way, which will allow us to measure directly the dependence of the maximum absorption in the medium as a function of salt concentration. That will add another important piece of information about the system by revealing the effects of salt on the characteristic relaxation times in the PEO-melt/LiClO₄ electrolyte. Our future studies will be extended to include higher molecular weight PEO (50,000 Daltons) which will allow us to address the elastic and dynamic properties in a highly entangled polymer system. Those systems are of even greater practical importance since they are closer to the high molecular weight polymers used in typical battery applications.

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