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PREVIEW

**MICROSCOPIC ELASTIC CONSTANTS OF STYRENE AND
METHYL METHACRYLATE COPOLYMERS**

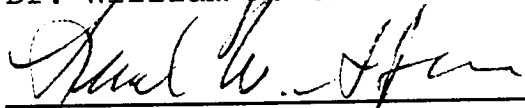
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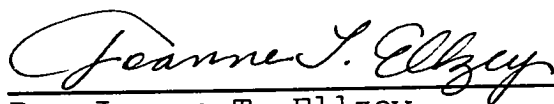
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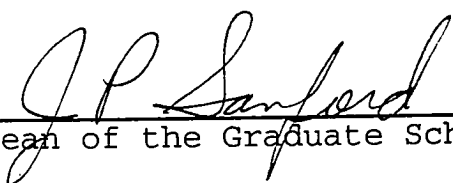

Dr. Carl W. Dirk, Chair


Dr. William R. Cabaness


Dr. Leo TerHaar


Dr. Joanne T. Ellzey


Dr. M.L. Ellzey


Dean of the Graduate School

To the memory of my beloved father

To my beloved mother

To Sudha, Suresh, Nandu, Vinay

MICROSCOPIC ELASTIC CONSTANTS OF STYRENE AND
METHYL METHACRYLATE COPOLYMERS

by

SAVITHA B. DEVANATHAN, B.Sc, M.Sc

THESIS

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ABSTRACT

In the present thesis the structural information at the microscopic regime has been obtained by a nonlinear optical technique namely Electric Field Induced Second Harmonic (EFISH) for a copolymer system of styrene and methyl methacrylate.

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CHAPTER 1

1.1 INTRODUCTION

Nonlinear optics is emerging in the frontier of science and technology due to its utilization in optical switching and logic operations in optical computing, optical sensing and optical fiber communications. As a result, the search for new nonlinear optical materials is very active, with intensive efforts in this field having been made for the last twenty years [1]. Four major categories are receiving attention : electrooptic crystals (inorganic and organic) [2,3], bulk semiconductors [3], polymeric organic materials [4] and molecular assemblies [5] each exhibiting a different mixture of advantages and disadvantages.

Another area of particular interest is the field of rheology, or flow, of materials. There is great interest in such properties of polymers because of the obvious commercial importance of plastics. The physical states and properties of polymeric materials are different from those of small-molecule materials due to their macromolecular nature. However, the macro or bulk properties depend in some intimate way on the microscopic structure. There are currently many methods to measure bulk rheological properties, and few available to

assay the microscopic rheological properties. This thesis presents a new technique, using nonlinear optics, to assay microscopic rheology, specifically the microscopic elastic constant of polymers.

1.1.1 CLASSICAL RHEOLOGY

Normally, when a thermoplastic material is stressed it responds by exhibiting viscous flow (which dissipates energy) and by elastic displacement (which stores energy). The elastic response presumes a return to the unstrained state following removal of the stress. The viscoelastic response involves some irreversible change in the material's state following removal of the stress. However, the viscoelastic response may still contain some elastic component to its overall response. Polymers have been found to display unique mechanical properties.

The elastic response is far simpler to deal with from the physical standpoint. Under the right conditions, most polymeric materials can be measured in a state that is primarily elastic rather than viscoelastic. However, the bulk response is normally never as simple as a Hookean model. According to Hooke's law the force of an elongated spring is directly proportional to the displacement x within the elastic limits. If stretched beyond this limit the force becomes

nonlinear.

$$F = -kx$$

The true bulk response is often a combination of physical stress-strain elongation-compression models [6].

1.1.2 NONLINEAR OPTICAL RHEOLOGY

Recently, a new nonlinear optical procedure [7] has been reported that provides microscopic molecular scale elastic constants of polymer systems. This measurement is rather unique in providing elastic information at unusually small wavelengths. Bulk elastic measurements, such as dynamic mechanical analysis are normally made on samples of dimensions of tens of centimeters with frequencies of deformation typically no larger than a few hundred hertz. This corresponds to an elastic measurement wavelength of meters. Even high frequency ultrasonic measurements provide information no more accurate than an elastic response wavelength of 0.1-1 mm [8]. Electric field induced index ellipsoid rotation [9] will provide information at the microscopic level, although this cannot be unambiguously interpreted in terms of an elastic constant due to the imprecise knowledge of the polarizability tensor ellipsoid.

The nonlinear optical process, i.e the second harmonic generation (SHG), can provide a direct measure of the

alignment of molecules with an electric field. Since the electric field induced SHG measurement (EFISH) directly measures a vectorial component of the molecule, rather than a tensorial component, it is unambiguous with respect to the electric field induced displacement of the molecule. Hence, the new nonlinear optical elastic constant procedure is unambiguous in that we can directly measure the actual polymer deformation as it relates to the field dependent dipole vector rotation of a probe molecule.

For many materials, the relationship between stress and strain can be expressed by Hooke's law which for low strains suggests that stress is proportional to strain and gives us Young's modulus

$$E = \text{stress/strain}$$

for simple uniaxial expansion or compression. However, this is not universal, and for complex systems this relationship has to be modified.

Previous nonlinear optical results on the microscopic elasticity of poly(methyl methacrylate) have shown that in the microscopic regime the response is purely elastic for short duration forces [7].

1.2 BACKGROUND:

What follows is a general discussion of the field of nonlinear optical measurements and materials followed by an introduction to the nonlinear optical elastic constant measurement reported in this thesis.

1.3 HISTORY OF NONLINEAR OPTICS

Historically, the earliest nonlinear optical (NLO) effect discovered was the electro-optic effect. The linear electro-optic (EO) coefficient, r_{ijk} , defines the Pockel's effect, discovered in 1906, while the quadratic EO coefficient, s_{ijkl} , relates to the Kerr's effect, which was discovered even earlier (1875). Of course, all-optical NLO effects were not discovered until the advent of the laser.

The second harmonic generation (SHG) was first observed in single crystal quartz by Francken et al [10] in 1961. They used a quartz crystal to frequency double the output of a ruby laser (694.3 nm) into the ultraviolet (347.15 nm) with a conversion efficiency of only about $10^{-4}\%$ in their best experiments.

Many other NLO effects were rapidly discovered [11]. The early discoveries often originated in two- or multiphoton spectroscopic studies. Parametric amplification was observed

in lithium niobate (LiNbO_3) by two wave mixing in temperature-tuned single crystals in 1965 [12]. The first observation of SHG in an organic material was made in benzopyrene by Rentzepis and Pao [13]. Hexamethylenetetramine single crystal SHG was examined by Heilmair in the same year, 1964 [14].

Two other organic materials followed rapidly: hippuric acid and benzil. Benzil was the first material which proved relatively easy to grow into large single crystals.

At the end of the 1960's, the Kurtz and Perry powder SHG method was introduced [15]. For the first time, rapid, qualitative screening for second order NLO effects was possible [16].

Much more recently, there has been active interest in polymer guest/host systems where a nonlinear optically active guest molecule is dissolved in a polymer matrix. Currently there is great excitement with poled polymer (electric field oriented guest molecules in a rigid polymer matrix) materials that display broad band electro-optic modulation properties [17].

1.4 BASIS AND PRINCIPLES OF NONLINEAR OPTICS

When a medium is subject to an intense electric field such as that due to an intense laser pulse, and assuming the

polarization of the medium (bulk) to be weak compared to the binding forces between the electrons and nuclei, the polarization can be expressed in a power series of the field strength E . Nonlinear optical effects arise when the movement of charge in a material is nonlinear with respect to the applied electric fields. The dipole per unit volume, or polarization density is the lowest order measure of charge distribution and is sufficient to describe a large number of nonlinear optical processes. In the dipole approximation, assuming a Taylor series expansion, the polarization density, vector P , is related to the electric field, E , through

$$P_i = P_i^{(0)} + \chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \dots$$

where, P_i is the i th component of P , E_i the i th component of E , $\chi^{(n)}$ the n th-order nonlinear optical susceptibility tensor. Summation notation is implied.

The first term in Eq.(1) is the spontaneous zero-field polarization and the second term describes linear optics including propagation of light in dielectric media, absorption and surface reflection. The third term leads to second harmonic generation, parametric mixing and the linear electro-optic effect, while the fourth term results in third harmonic generation and self-focusing. The susceptibilities, $\chi^{(n)}$,

depend on the frequencies of light present in the material.

If the electric fields are decomposed into Fourier components labeled by frequency, ω , the n th order susceptibility will lead to mixing of $n+1$ fields. For example, the second-order contribution to the polarization, $P_i^{\omega_3}$ at frequency ω_3 is given:

$$P_i^{\omega_3} = \chi_{ijk}^{(2)}(-\omega_3; \omega_1, \omega_2) E_j^{\omega_1} E_k^{\omega_2}$$

where energy conservation requires that $\omega_3 = \omega_1 + \omega_2$. The susceptibility quantifying the second harmonic intensity corresponds to the susceptibility $\chi_{ijk}^{(2)}(-2\omega; \omega, \omega)$ where two field quanta at frequency ω combine through the nonlinearity to form a field at the second harmonic frequency 2ω .

Similarly, the linear electro-optic effect results from the mixing of one optical field, $\omega_1 = \omega$, and one dc field, $\omega_2 = 0$, resulting in a phase change in the output optical beam, $\omega_3 = \omega$.

1.5 MICROSCOPIC NONLINEARITY

Organic systems consist of molecular units (molecules or polymers) that in the absence of net charge or intermolecular charge transfer interact only weakly. An oriented-gas model

[4] is often used to relate the molecular properties to the corresponding bulk properties. This model has also been used to relate the molecular optical nonlinearity to the bulk nonlinearity. In this model the optical nonlinearity of the organic medium is determined primarily by the nonlinear optical properties of the molecular unit.

1.6 SECOND-ORDER NONLINEAR OPTICAL PROCESSES

There are two ways of visualizing second-order nonlinear processes. In the first, the field associated with the first beam is viewed as altering the refractive index of the medium and the propagation characteristics of the second beam are then modified appropriately. This view is quite appropriate for the linear electrooptic effect where a dc field takes the place of the beam and alters the refractive index of the medium in proportion of the strength of the dc electric field. This can be written as $\chi_{IJK}^{(2)}(-\omega; 0, \omega)$. This effect results in interesting and useful applications.

The first-field component could also be at some frequency ω_1 and modulate the refractive index at that frequency. A second field passing through the medium at ω_2 would then be phase modulated and exhibit sidebands at the sum and difference frequencies. If the frequencies ω_1 and ω_2 are identical, then a harmonic overtone at 2ω is created. These

processes are often termed parametric processes because they result from modulation of the parameters of the medium.

A second method for viewing second-order nonlinearities utilizes nonlinearities in the polarization response to incident fields at various frequencies. The second-order nonlinear processes can be categorized according to the frequency, intensity, and phases of the field components. The second-order nonlinear tensor element can be written as

$$\chi_{IJK}^{(2)}(-\omega_3; \omega_2, \omega_1)$$

where $\omega_3 = \omega_2 \pm \omega_1$ and I , J , and K indicate the Cartesian components of the interacting fields and polarization waves.

Each Cartesian component is associated with a frequency component in the argument of $\chi^{(2)}$. When the nonlinear process is purely electronic in origin, Kleinman symmetry is applicable. Here, the frequency of light is far away from the absorption band of the molecule, and the Cartesian indices and frequency components can be freely interchanged. This is equivalent to assuming that there is no dispersion in the nonlinearity. For organic materials not having resonating structures this assumption is valid [18].

When, $\omega_3 = 2\omega$ and $\omega_1 = \omega_2 = \omega$ we have the second-harmonic generation, the highly utilized effects in nonlinear optics. In this process, energy is redistributed between the fields as a result of interaction of the waves with the medium and no energy is lost to the medium. To have efficient redistribution of energy by second-order nonlinear processes, momentum must be conserved. This is referred to as phase matching.

The processes of sum and difference generation occurs when the frequencies ω_1 and ω_2 are not identical. In the process of sum frequency generation under phase-matched conditions, the two lower frequency waves at ω_1 and ω_2 lose power to the sum frequency ω_3 . In difference frequency generation the source laser at ω_3 loses power not only to the difference frequency ω_1 (2nd) but also to the source at ω_2 .

1.7 SECOND HARMONIC GENERATION

Understanding second order nonlinearities in terms of simple well known physical-organic parameters requires starting from the standard perturbation theory expressions and then deriving the more limited expressions which can be related to simple physical observations [19]. Second harmonic generation (SHG) involves the mixing of two photons at frequency ω , and producing one photon at frequency 2ω .