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Poly(ethyl acrylate) and Poly(γ-benzyl-L-glutamate): An Interpenetrating Polymer System

CPT Peter Rene Gibson
HQDA, MILPERCEN (DAPC-OPA-E)
200 Stovall Street
Alexandria, VA 22332

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The rigid rod polymer poly(γ-benzyl-L-glutamate) (PBLG) dissolves in ethyl acrylate (EA) at elevated temperatures. Upon cooling to room temperature, a gel is formed. Phase separation occurs on a submicron level. The PBLG forms a continuous submicron network. The sample is homogeneous to the eye. With the addition of an initiator to the EA, the vinyl monomer may be polymerized to form poly(ethyl acrylate) (PEA). When the polymerization initiated by photochemical initiator occurs from the EA-PBLG gel state, no gross change in the PBLG network occurs. A polymer film of linear PEA and PBLG is formed. With the addition of an initiator and crosslinker to the EA, EA may be crosslinked upon polymerization from the EA-PBLG gel state. An interpenetrating polymer network (IPN) of crosslinked PEA and PBLG is formed. Rheologically, the storage and loss moduli variations due to changes in frequency, strain, and PBLG concentration are examined for each type of sample. Additionally, the effects of crosslinker concentration is examined for IPN's. The characteristics of the PEA made in the laboratory are compared to commercial PEA samples by nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC). The swelling and leaching traits of the PEA-PBLG samples are investigated using methanol. Methanol is a good solvent for PEA but a non-solvent for PBLG. The results in all areas are related into an understanding of the structural and dynamic properties of the EA-PBLG gel, linear PEA-PBLG film, and crosslinked PEA-PBLG IPN.

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POLY(ETHYL ACRYLATE) AND POLY(γ-BENZYL-L-GLUTAMATE): AN INTERPENETRATING POLYMER SYSTEM

A THESIS
SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL
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BY
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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
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CHAPTER ONE: BACKGROUND

1.1 INTRODUCTION

Since World War II, when American scientists developed styrene-butadiene rubber (SBR) as a substitute for natural rubber, research on polymer synthesis and properties has blossomed. As it became accepted that these macromolecules existed, studies of their properties began and theories on the mechanisms of synthesis were developed.

Today, polymers are accepted, yet still intriguing, molecules. It is hard to imagine our world without plastics. As a slew of polymers were studied, the concensus on the structure of polymers was that of a random coil. More study lead to the discovery of a rigid rod or stiff-chain structure. Investigations continued as the uses of polymers increased. The versatility of polymers amazed scientists as the varying properties of individual polymers became known.

As efforts were turned to controlling the physical properties of polymers, various synthesis techniques were developed by altering reaction conditions. Mixtures of polymers became commonplace and their interactions, mechanisms, and physical properties were investigated. The growing interest in combining polymers to obtain polymer blends with different properties lead to a barrage of related terms. These various terms for polymer combinations are based on the way in which the polymers interact with themselves and each other.

1.2 NOMENCLATURE

A polymer blend can be considered a combination of two polymers without any chemical bonds between them. A graft copolymer has chemical bonds between the two homopolymers. A graft copolymer can be made when a monomer is in the intimate presence of a polymer and the monomer is polymerized. The actual extent of the grafting between the homopolymers of the copolymer formed may be very small. An interpenetrating polymer network (IPN) also involves the polymerization of a monomer in the intimate presence of a polymer; however, at least one of the resulting polymers is crosslinked. So, IPN's may be considered a special type of graft copolymer.

But, confusion still exists. The term interpenetrating polymer network was first introduced in the chemical literature in 1960 by J. R. Millar [1]. Primary, secondary, and tertiary networks were formed. The primary network was a conventional crosslinked network of a solution of 50 % divinylbenzene (DVB), by weight, in ethylstyrene and styrene. To make the secondary network, Millar swelled the primary network with the same styrene and 50 % DVB solution, then crosslinked and polymerized the solution. The procedure was repeated to form the tertiary network.

From Millar's work, other scientists developed variations in sequencing of polymerization and crosslinking, in which polymer was crosslinked, and in the compatibility of the individual polymers. Klempner et al. [2] suggested three methods of classifying IPN's. They used IPN as a general term to denote a polyblend with permanent entanglements made by homocrosslinking of the two polymers with no covalent bonds between the polymers.

The first method, based on morphology, considers completely interpenetrating polymer networks (CIPN) as the ideal case where no phase separation is present. However, due to the incompatibility of most polymers, most IPN's are only partially interpenetrating and are more appropriately called phase separated IPN's (PSIPN). Some systems are semicompatible or partial IPN's (PIPN). The final distinction in this classification scheme is the quasi IPN (QIPN) which shows a single glass transition temperature, as a CIPN would, but no proof of complete miscibility has been established.

The second method of Klempner et al. is predicated on the IPN synthesis technique. A latex IPN (LIPN) is made by emulsion polymerization of individual monomers which are then combined, coagulated, fused, and crosslinked. Simultaneous interpenetrating networks (SIN) are combined in bulk or solution. A SIN may be made by combining two different monomers with crosslinking agent and catalysts. The monomers must be chosen so that no coreaction occurs allowing each monomer to be homopolymerized. A sequential IPN (SIPN) is formed by proceeding through the synthesis steps in order. This means that one polymer is completely polymerized and crosslinked while the other is still a monomer. The foamed IPN (FIPN) has cellular structure as it is blown into a foam.

The third method presented by Klempner et al. is the non-topological scheme. It deals with interpenetrating homopolymer networks (IHPN) similar to Millar's IPN's where the same polymer or copolymer is swollen with its monomer. Also, joined IPN's (JIPN) consider the situation where significant intramolecular crosslinking exists. Finally, when two polymers form an IPN while only one is crosslinked, a pseudo IPN (PDIPN) is made.

The PDIPN has also been referred to as a semi- IPN [3]. A semi-IPN of the first kind (semi-1-IPN) is where the initial polymer is crosslinked. A semi-IPN of the second kind (semi-2-IPN) is where the monomer being polymerized to form the IPN is crosslinked.

As Klempner et al.'s systems hint, there are thousands of different combinations of possible synthesis steps, crosslinking performed, and actual modes of grafting. Sperling [4] suggested a qualitative and quantitative approach to organizing possible structures. Then, Sperling and Ferguson [5] developed a system based on group theory to describe these combinations. Since morphology of the materials formed, and hence physical and mechanical properties, are strongly influenced by synthetic sequence, a way to singularly describe a particular combination is important. However, this system has not been universally accepted. Sperling et al. [6] offered a variation of the earlier group theory system based on mathematical rings. This system uses two binary operations; one involves polymeric combinations without bonds and the other represents combinations with bonds.

1.3 POLYMER PHASE BEHAVIOR

The phase behavior of a polymer-diluent system depends on the structure of the polymer. A random coil polymer in solution has phase behavior that differs vastly from the phase behavior of a rigid rod polymer in solution.

1.3-1 RANDOM COIL POLYMER PHASE BEHAVIOR

Flory [7-11] investigated the thermodynamics and phase equilibria in various polymer-solvent systems. Consider a standard temperature versus composition phase diagram for a random coil polymer solution. The phase diagram (Figure 1.1) for a given molecular weight polymer has two regions. Region I is a one phase polymer-solvent region, while region II represents a two phase polymer-solvent region. The two phases of region II both contain polymer and solvent, however, one phase is polymer rich while the other is polymer poor [12].

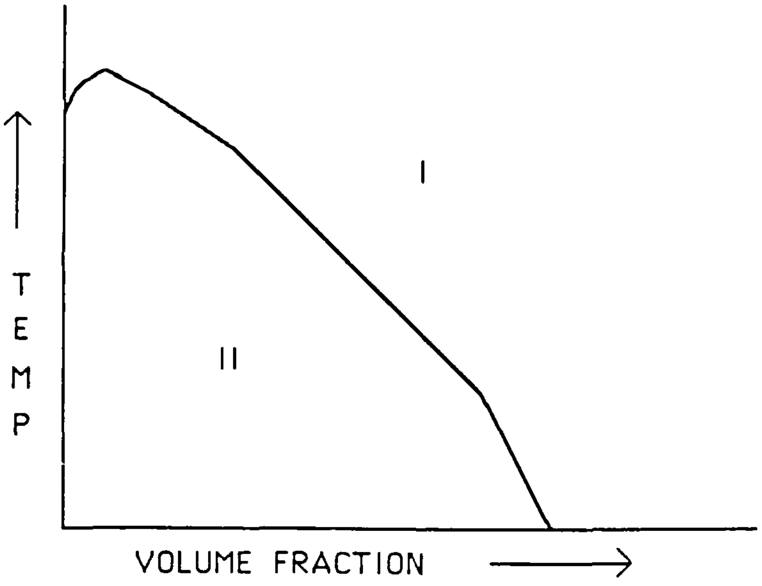


Figure 1.1. Phase Diagram (Temperature vs. Volume Fraction) for a Random Coil Polymer-Diluent System.

(adapted from [7])

1.3-2 RIGID ROD OR STIFF-CHAIN POLYMER PHASE BEHAVIOR

With rigid rod polymers, phase behavior is distinctly different from that of random coil polymers. The phase diagram (Figure 1.2) has four regions.In dilute solutions, an isotropic (I) phase exists. At higher concentrations, but low temperatures, a two phase (isotropic and liquid crystal (LC)) region exists. As the temperature increases, the solution passes through a region with two liquid crystalline phases to a region of one liquid crystalline phase.

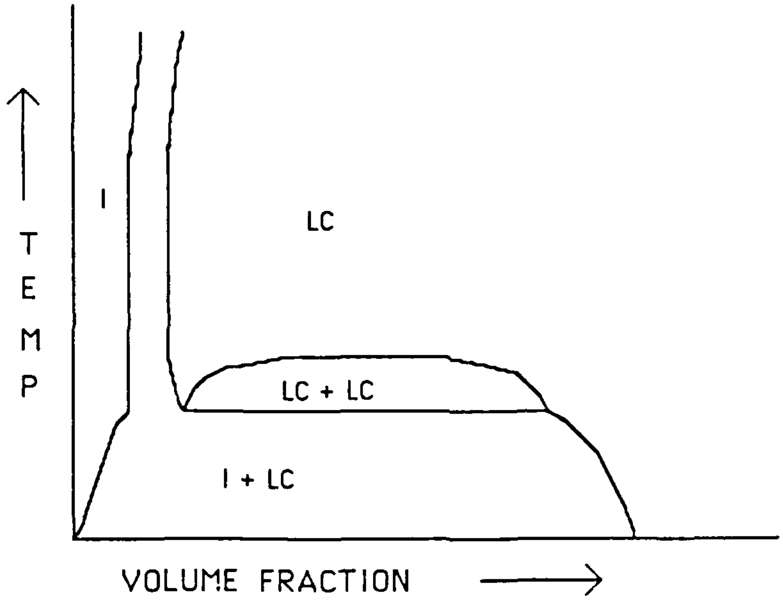


Figure 1.2. Phase Diagram (Temperature vs. Volume Fraction) for a Rigid Rod Polymer-Diluent System. (adapted from [13])

1.4 LIQUID CRYSTALLINITY

One of the most interesting characteristics of rigid rod polymers in a diluent is their ability to form a single liquid crystalline phase or a two phase liquid crystalline region depending on conditions. The liquid crystalline state is characterized by long range as well as short range orientationally ordered molecules. The molecules are either nematic, smectic, or cholesteric. Nematic structure allows for translational mobility of constituent molecules, while the molecular layers of the smectic structure limits translational movement. If optical chirality exists, the nematic phase has a twist and is referred to as cholesteric.

1.4-1 FORMATION OF LIQUID CRYSTALS

Liquid crystallinity, or mesomorphism, is usually induced in one of two ways. The first method is enantiotropic or heating from a solid phase. The second method is monotropic or supercooling of the isotropic liquid phase below the melting temperature. Enantiotropic liquid crystals are thermodynamically stable and can be obtained on both heating and cooling cycles. Monotropic liquid crystals are metastable with respect to the solid and are seen in the cooling regime only [14].

As with most rules in life, there are exceptions. Lyotropic polymer liquid crystals spontaneously form a fluid having long-range order when in the presence of a solvent [15]. This state results from selectively weakening specific crystalline lattice sites [14].

In studying the formation of the lyotropic mesophase, viscosity dramatically increases when the concentration of the rod-like solute is increased. This trend continues until a critical concentration is reached where a sharp decrease in viscosity accompanies the formation of the lyotropic mesophase [14].

1.4-2 A RIGID ROD POLYMER IN LIQUID CRYSTALS: POLY(γ-BENZYL-L-GLUTAMATE) - PBLG

Poly(γ -benzyl-L-glutamate) (PBLG) (see Figure 1.3) is a rigid rod polymer. Polymerization can be achieved by solution polymerization of the monomer, the N-carboxyanhydride of the benzyl glutamate, using base initiation. PBLG provides an opportunity to study a material whose order is well defined in both the solid and liquid states. The order is incumbent upon the conformational structure known as the α-helix. This trait is not a unique structure; it may vary with changes in environment [16].

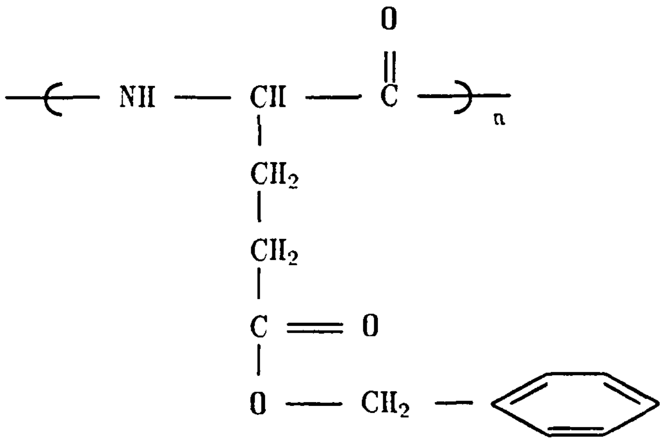


Figure 1.3. Poly(γ - benzyl-L-glutamate) (PBLG).

In the mid 1950's, Lundberg and Doty [17] studied the synthesis and structure of PBLG in different solvents as part of a series of investigations on polypeptides. Since then, PBLG has been studied extensively in dimethylformamide (DMF) [15, 18-27], m-cresol [15, 27-32], toluene [18, 19, 33], chloroform ($CHCl_3$) [21, 34-37], benzyl alcohol [38], and in other solvents [15, 21, 22, 37, 39-41].

Miller et al.[18] found that PBLG-DMF samples went from a fluid state to a gel state upon entering the wide biphasic region by cooling. This observation suggests a change in morphology. Rheological studies done by Miller et al. on the PBLG-DMF system, a compatible system, and PBLG-toluene, a system where PBLG end-to-end aggregates, give similar results. The PBLG-toluene system and a PBLG-DMF-water system entered the wide biphasic region at room temperature and above.

Wee and Miller [25] constructed a temperature-composition phase diagram for the PBLG-DMF system in the temperature range of -20° to +140° C and a composition range of 0 to 40 weight percent polymer. Warren et al. [27] studied the molecular weight dependence of both the storage and loss moduli of PBLG in DMF and m-cresol in dilute solution.

In further work by Miller [15], the molecular dispersion of fairly polar solvents such as DMF and m-cresol show no evidence of association, while less polar solvents tend to associate even at high dilution. Miller contends that while the viscosity is highly concentration dependent for the isotropic phase, it drops sharply upon crossing into the narrow biphasic region. When the narrow biphasic region is traversed, the viscosity of the PBLG-DMF system rises again while no such effect is seen in the PBLG-m-cresol system.

Asada et al. [28] studied the rheological properties and structures of concentrated (10-40 weight %) solutions of PBLG in m-cresol at various shear rates. Similar studies have been conducted by Kiss and Porter [29] and more recently (1986) by Moldenaers and Mewis [30].

Ookubo et al. [31] attempted to interpret the results of studies on dilute solutions of PBLG in m-cresol by three mechanisms. The mechanisms are end-over-end rotation, flexural deformation, and side-chain motion. All of the mechanisms were successful in describing the viscoelastic relaxation of PBLG in m-cresol, however, the dependence on the contour length varied in each mechanism.

Miller et al. have also studied the PBLG-toluene system [18,19] finding that storage modulus is virtually independent of frequency, concentration, molecular weight, and temperature of formation [19]. Chakrabarti and Miller [33] examined PBLG-toluene aggregation as a function of concentration, temperature, molecular weight, molecular weight distribution, stereochemistry, and the presence of a hydrogen bonding competitor and discovered end-to-end aggregation is the predominant mode for PBLG in toluene.

Sasaki et al. [38] discovered two transition temperatures when cooling a PBLG-benzyl alcohol system from 70° C to room temperature. A different structure of the aggregates exists at each of the transiton temperatures. The authors assert that one transition is due to quenching and the other is due to slow cooling.

Additional studies have been done on PBLG structure [42-52], PBLG side-chain mobility [26, 39, 53], PBLG birefringence [54, 55], and PBLG aggregation [56, 57].

1.5 INTERPENETRATING POLYMER NETWORKS

IPN's have been studied in many forms. A problem continues to exist in the identification of the type of IPN being studied. In this section, no attempt has been made to classify the type of IPN being examined in a particular investigation. This has been consciously omitted due to the lack of detail presented in the cited references.

In many cases, the type of IPN is not specified; however, the synthesis techniques and morphology are discussed. While, in these cases, it may have been possible to determine a specific type of IPN studied, the value of such a determination would have little significance in view of the fact that no accepted standard nomenclature exists.

1.5-1 EARLY STUDIES ON IPN'S

Some of the earliest work on IPN's was done by Klempner, Frisch, and Frisch [58-59]. They looked at crosslinked poly(urethane-urea) (PUU) and linear poly(butadiene-acryonitrile) (PBA) [58] as aqueous emulsions which were mixed, together with crosslinking agents and stabilizers, cast as films, then cured to form the IPN. Later, they studied PBA with poly(styrene-butadiene) (PSB) and *polychloroprene* [59].

Other work on IPN's concludes that increasing the crosslink density of the initial polymer phase results in a noticeably finer cellular structure. This suggests that cell size is controlled by the swellability of the initial polymer phase [60]. Donatelli et al. [61] derived a semiempirical equation for the phase domain size of semi-1-IPN's with principal variables of the crosslink density of the initial polymer, the mass fraction of the second polymer, and the interfacial tension.

The two phase morphology tends to be controlled by the initial polymer, which generally forms a more continuous phase in IPN's, but is also modified by the degree of compatibility of the two polymers, the polymerization method, and the IPN composition [3].

In 1973, Allen et al. [62-65] studied a poly(urethane)(PU)-poly(methyl methacrylate)(PMMA) system. The system was prepared by interstital polymerization of the MMA monomer in a PU gel. The PU gel had been prepared in a state of dilution in the MMA monomer. The parameters varied were initiator concentration for MMA, the molar ratio of isocyanate to hydroxyl groups, time between gelation of PU and polymerization of MMA at various polymerization temperatures, the theoretical PU crosslink density, and the overall PU-PMMA composition. Some of the trends observed are:

> 1) the modulus decreases with increases in initiator concentration in the MMA, while impact strength was relatively constant.
>
> 2) shear modulus increases as the time between PU gelation and MMA polymerization increases, while impact strength remained constant.
>
> 3) increases in theoretical molecular weight between crosslinks (decreasing crosslinks) increases impact strength while lowering the modulus. A critical theoretical molecular weight between crosslinks appears to exist where both traits level off.
>
> 4) modulus decreases fairly rapidly from 0-10 % weight by weight PU from the PMMA homopolymer values. Above 10 % the decrease is more gradual.

Allen et al. also investigated the system's morphology [63], the effects of graft polymerization [64], and theoretical predictions of the modulus of interstitially polymerized composites [65].

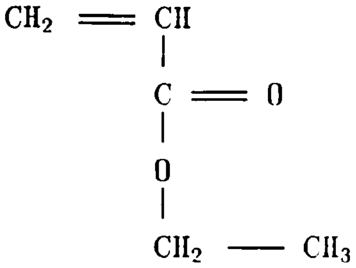
A similar study was done in the same time frame by Dickie et al. [66-68]. A two-stage emulsion polymerization technique was used to make a polyblend from MMA and butyl acrylate (BA). Only the BA was crosslinked; however, both semi-1-IPN's and semi-2-IPN's were formed. The morphology, optical properties. tensile modulus, thermal expansion coefficients [66], and Young's modulus [67] were examined. Also, a detailed investigation into the theoretical interpretation and equivalent mechanical models was included [68].

Later, Jordan et al. [69-71] synthesized polyblends of butadiene and acrylonitrile and copolymers of vinyl stearate and vinyl chloride. Glass transition and the storage modulus versus temperature curves of he blends and copolymers [69] and their variations caused by changing reaction temperature [70] were investigated. The results were analyzed in terms of compatibility of the polymers. Theoretical treatment was then given to the data obtained [71]. The authors suggested an explanation to the apparent contradiction that some polyblends are compatible by mechanical spectroscopy and incompatible by thermal analysis. Since the mechanical transition reflects the properties of a larger volume element of the microstructure than the glass (thermal) transition, the mechanical transition would be less sensitive to motion in each separate phase [70].

Locke and Paul [72] studied the effects when grafting was present in a poly(ethylene) (PE)-poly(styrene) (PS) system. They found both a higher yield strength and a longer elongation to break in the system with grafting. However, when crosslinking competes with grafting, the effects of increased grafting are diminished.

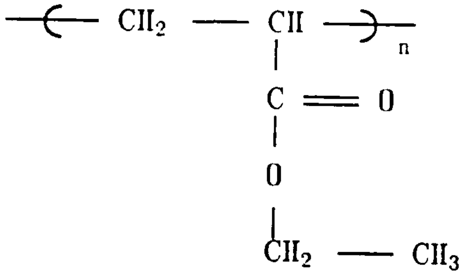
1.5-2 A RANDOM COIL POLYMER IN IPN'S: POLY(ETHYL ACRYLATE) - PEA

Ethyl acrylate (EA), shown in Figure 1.4, can be polymerized by free radical polymerization. The resulting random coil polymer is poly(ethyl acrylate) (PEA)(Figure 1.5). To control the reaction temperature, continuous addition of monomer at a rate which allows the heat of reaction to be dissipated by the heat transfer capacity of the reactor is often necessary [73].



$CH_2=CH-C(=O)-O-CH_2-CH_3$

Figure 1.4. Ethyl Acrylate (EA).



$-\!\left(CH_2-CH(-C(=O)-O-CH_2-CH_3)\right)_n\!-$

Figure 1.5. Poly(ethyl acrylate) (PEA).

In the late 1960's and early 1970's, PEA was studied in an IPN with poly(styrene-co-methyl-methacrylate) (PS-MMA) by Huelck et al. [74-75] and with poly (styrene) (PS) by Sperling and Friedman [76].

Huelck et al. found that incompatible materials exhibit two sharp glass transitions while semicompatible or compatible materials have one broad transition. Synthesis details in forming polymer blends tend to control the supermolecular morphology. The morphology, in turn, controls the physical and mechanical characteristics. Huelck et al. support the conclusion that the PEA-PMMA IPN's have extensive but incomplete mixing while the PEA-PS IPN's are incompatible. Later, Jordan et al. [69] found that, in addition to the differences in glass transition temperatures in compatible and incompatible polymer systems, a similar variation exists in the storage modulus versus temperature curves. Compatible systems tend to have families of modulus versus temperature curves that shift to lower temperatures as the softer component prevails. Incompatible systems exhibit a stepped nature in which two loss maxima, varying in intensity as composition changes, exist.

Sperling and Friedman found that in a PS-PEA system, the networks can be considered chemically independent but mechanically interlocked. Occasional random chain transfer to polymer does cause some block or graft copolymer formation. They discovered two distinct glass transitions with a relatively flat modulus plateau in between. Since the lower glass transition temperature increased from that of the homopolymer and the higher glass transition temperature decreased from that of the other homopolymer, this IPN affected the glass transition temperature in a manner similar to copolymers. This observation suggests that phase separation is incomplete.

1.6 A RIGID ROD POLYMER IN BLENDS AND COPOLYMERS: POLY(γ-BENZYL-L-GLUTAMATE) - PBLG

Early on, PBLG was often studied with an isomer, poly(γ-benzyl-D-glutamate) (PBDG). Mixtures of PBLG and PBDG are referred to as PBDLG. Various studies have been conducted using different PBDLG's.

Baba and Kagemoto [77] determined average values of the heat of dissociation of stacked side-chain benzyl groups in mixtures of PBLG and PBDG. Also, Tokita, et al. [78], studied the dynamic mechanical properties of various PBLG, PBDG mixtures.

Iizuka [79] studied poly(γ-ethyl-L-glutamate) (PELG) with PBDLG and noticed that under shear stresses, long rod-like molecular clusters form in the solution. Increases in shear rate produce a decrease in steady shear viscosity because of the orientation of molecular clusters or of aggregates.

Copolymers of BLG-butadiene, BLG-sytrene, and BLG-butadiene-BLG were studied by Gallot et al. [80] to determine their structure and conformation. Elias et al. [81], Aviram [45], and Kuroyanagi et al. [82], studied crosslinking of PBLG. Elias et al. found that PBLG crosslinks upon transesterifications of diols.

Also, PBDLG [83], PBLG and PS [84], PBLG and poly(β -benzyl aspartate) [84], PBLG and semi rigid poly(hexyl isocyanate) [85], and others [86, 87] have been explored.

1.7 THEORETICAL DEVELOPMENT

In this section, theories developed to explain the motion of random coil and rod-like particles in solution, the helix-random coil transition, and the modulus of composites are briefly discussed.

The theory pertaining to random coil and rod-like particles in solution relates to a random coil or rigid rod polymer in a diluent. The theoretical portion on the helix-random coil transition is important to understand as this thesis considers experiments done near the transition temperature. The third segment deals with the moduli of composites and parallels the rheological measurements conducted in this study.

1.7-1 MODELS OF RANDOM COILS IN VISCOUS FLOW

The earliest model of random coil macromolecules in solution was developed by Kuhn in 1932 [88]. This model was descibed by Kramers [89] as the "pearl necklace" model. It consists of a number of particles in which successive particles are connected by a weightless rod. The mass and frictional constant are the same for all these particles. The simplest form of the model assumes that the two rods which meet in the particle are completely free to rotate with respect to each other. Kuhn developed formula for viscosities based on his model [88,90]. Work done by Huggins [91], Kramers [89], and Kirkwood and Riseman [92] used the same basic model, but attempted to account for oversites in Kuhn's theory when developing their equations for viscosity of flexible macromolecules in a diluent.

Later, in the 1950's, Rouse [93] and Bueche [94] developed models. Rouse's model was predicated on three factors affecting elastic and flow properties. Those factors are the length of the polymer molecules, the flexibility of the molecular chains, and the interactions of the segments of a polymer molecule with other segments of the same and other polymer molecules. Rouse did not attempt to account for relaxation processes or the obstruction of the motions of a segment by other segments with which it happens to be in contact. Because of the latter exclusion, good agreement with experimental results can only be expected in dilute solutions. The model of a polymer molecule is a chain of freely jointed links, each of identical length with an identical number of submolecules. Rouse's model is less general than the Kirkwood-Riseman model because Rouse uses a less detailed description of the configuration of a molecule.

Bueche's model is a special chain having 3N links each having an identical average length. He also assumes the bond angle to be 90 degrees with steric hindrances such that the first link must be pointed in either the ± x direction, the second in the ± y direction, the third in the ± z direction, the fourth in the ± x direction, and so on. Bueche additionally assumes that any applied force acts in the x direction and therefore no consideration of applied forces in the y and z directions is given. Bueche's model fails to consider other than short time periods nor does it allow for varying friction factors.

Both Rouse and Bueche altered the Kirkwood-Riseman model by eliminating adjustable parameters from their theories.

In 1956, Zimm [95] made a model similar to Rouse and Bueche. Zimm's molecule model is a chain of N identical segments joining N + 1 identical beads with complete flexibility at each bead. He derived an exact solution, valid at all frequencies and strengths of applied force or flow fields, for a three dimensional chain problem with Brownian motion and hydrodynamic interaction. The calculations are possible because Zimm ignored internal viscosities and other forms of interaction which might introduce non-linearity into the coordinates.

1.7-2 MODELS OF RIGID ROD PARTICLES IN VISCOUS FLOW

As far back as 1951, Kirkwood and Auer [96] proposed a model for a rigid rod molecule in a diluent. They suggested a rigid array of 2n + 1 groups, each with a friction factor f, spaced at equal intervals b on a linear axis of length L. Each molecule is bathed in solvent. From this scenario, they mathematically developed the value of intrinsic viscosity based on L, b, and molecular weight.

In the late 1960's, Ullman [97] attempted to improve the Kirkwood-Auer model by considering the finite cross-section of the rod. He was able to remove intrinsic viscosity's dependence on an arbitrary bond length that Kirkwood and Auer found.

In 1978, Doi and Edwards [98-99] expanded Kirkwood and Auer's theory to deal with concentrated solutions. Doi and Edwards considered the difference in diffusion coefficients for a rod based on direction; motion along the axis of the rod having a greater diffusion coefficient than motion perpendicular to the rod axis.

1.7-3 MODELS OF HELIX - RANDOM COIL TRANSITION

In 1959, Zimm and Bragg [100] developed a theory for the phase transition between helix and random coil in polypeptide chains. They attempted to distinguish between the contributions of a bonded and of an unbonded segment to the partition function. Additionally, the theory considers the influence of the state of neighboring segments on these contributions. To accomplish this, Zimm and Bragg assume the state of a chain can be completely described by the state of the oxygen atoms alone or, in other words, that if bonding of a segment occurs, it is always to the third preceding segment. Finally, since this theory deals with the thermodynamics of the transition from random coil to helix, the authors do not describe quantum states or phase space of individual segments in detail.

The next year, Nagai [101] derived formal expressions for the mean square of the end-to-end distance and the electric moment of polypeptide molecules in the helix-coil transition region. In 1961, Nagai [102] used a less rigorous model to account for the effect of degree of polymerization, which he had neglected in his earlier model.

Also in 1961, Flory [103] outlined three first order transitions which are observed in polypeptide solutions. The transitons are:

> a) widely observed crystallization and melting of polymers; the crystalline phase comprising close packed molecular chains in their preferred rod-like (helical) conformations.
>
> b) dissolution and re-aggregation of the crystalline polymer to yield a dispersion of individual molecules without alternation of conformation and reversal of the process with reconstitution of fibrils.
>
> c) the familiar helix-coil transiton featured by synthetic polypeptides dispersed in dilute solutions.

Earlier, in 1956, Flory [104] used a model for long chain polymer molecules consisting of isodimensional segments which tend to arrange themselves in colinear succession. A fraction of the bonds is assumed to be bent out of the direction of the preceding segments.

Then, in 1965, Flory and Leonard [105] expanded Flory's model above to account for coexistence of a phase of high concentration in equilibrium with a dilute phase. This occurance suggests that the soluble-helical polypeptides, such as PBLG, no longer exist in solution as mixing is unfavorable.

Also, theories have been proposed by Rajan and Woo [106] and Kubo [23].

1.7-4 MODELS FOR MODULUS OF COMPOSITES

The simplest model used to consider the modulus of a composite or a blend was developed by MacKenzie [107] in 1950. The model has a bulk material that contains isolated spherical holes distributed at random throughout the volume of the material. The bulk material has homogeneous and isotropic elastic properties. Finally, the volume of holes is small compared to the total volume; however, the total volume contains a large number of holes.

In 1956, Kerner [108] described the shear modulus and the bulk modulus of a macroscopically homogeneous and isotropic composite in terms of the moduli and concentrations of its components. Kerner assumes the components to be in the form of grains. The grains are suspended in and bonded to some uniform suspending medium. Also, the grains are spherical and distributed randomly in space.

Later *in the 1950's, van der Poel [109] calculated the rigidity of a concentrated* solution of elastic spheres in an elastic medium. The theory accounts for the pure mechanical-geometrical effect of the presence of the particles only. Although the original theory was meant for dilute dispersions only, van der Poel found fair agreement with experimental data up to a 60 % volume concentration. The finding was supported in two systems. One system was mineral aggregate particles, such as sand, in soft and hard bitumen. The second was glass spheres in PMMA.

A major effort to develop a mechanical model of a composite system was made in 1963 by Takayanagi et al. [110]. A model for two components in parallel and a model for two components in series were first explained (Table 1.1). They then proposed two combinations of these parallel and series components to describe the system of composites (Table 1.2 - Model 1 and Model 2). The main difference in the two models is the relationship between the strain of the R element and the strain of the P element. In Model 1, the strain in the R element is always equal to the strain in the P element in parallel with it. In Model 2, the

Table 1.1
Takayanagi's Parallel and Series Models

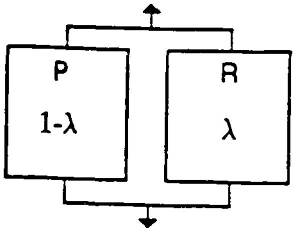
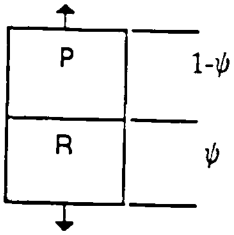
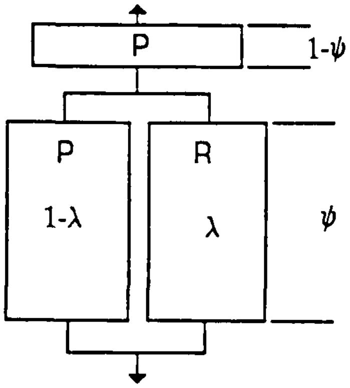
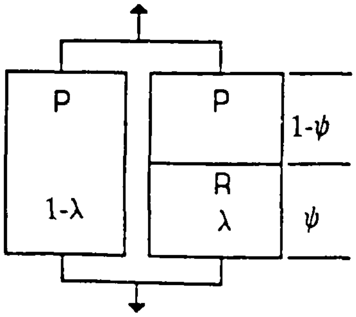
System	Diagram	Modulus
Parallel		$G^* = (1-\lambda) G_P^* + \lambda G_R^*$ (EQN 1.1)
Series		$G^* = \left(\frac{\psi}{G_R^*} + \frac{1-\psi}{G_P^*}\right)^{-1}$ (EQN 1.2)

Table 1.2
Takayanagi's Model 1 and Model 2 for a Composite Modulus

System	Diagram	Modulus
Model 1		$G^* = \left(\frac{\psi}{\lambda G_R^* + (1-\lambda) G_P^*} + \frac{1-\psi}{G_P^*}\right)^{-1}$ (EQN 1.3)
Model 2		$G^* = \lambda \left(\frac{\psi}{G_R^*} + \frac{1-\psi}{G_P^*}\right)^{-1} + (1-\lambda) G_P^*$ (EQN 1.4)

strain in the R element differs from the value of the strain in the P element in parallel with it. Later, they [111] computed two parameters, λ and ψ, representing the mixing state for a system of spherical particles. With ϕ_2 representing the volume fraction of the particles, equations 1.5 and 1.6 hold. Note that the product of λ and ψ is ϕ_2.

$$\lambda = (2 + 3\ \phi_2)/5 \qquad \text{(EQN 1.5)}$$

$$\psi = 5\ \phi_2/(2 + 3\ \phi_2) \qquad \text{(EQN 1.6)}$$

In 1964, Fujino [112] made models very similar to Takayanagi et al.'s using parallel and series mechanical relationships.

In the late 1960's and early 1970's, work by Neilsen and Lewis [113] lead to modification of Kerner's theory to account for the maximum packing factor of the filler [114-115]. Eventually, Neilsen and Lee [116] developed a correction to the modulus to account for skin effect in the rectangular cross section. They assumed the film thickness to be approximately equal to the radius of the filler particles.

1.7-5 COMPARISON WITH EXPERIMENTAL DATA

In 1964, Tschoegl and Ferry [117] examined solutions of PBLG in m-methoxyphenol and in dichloroacetic acid. Their findings suggested that the solutions behaved as an intermediate between predictions of Kirkwood and Auer for rigid rods and Zimm's theory for flexible random coils. At low frequencies, the hydrodynamic behavior is essentially rod-like. As frequency increases, deviations from the Kirkwood-Auer theory exist.

A similar study was done by Warren et al. [27] where the viscoelastic properties of solutions of PBLG in DMF and m-cresol were measured. They found essentially the same results, but concluded that a hybrid function of Zimm's flexible random coil theory and Ullman's rigid rod theory covered the entire frequency range.

Matsuo et al. [118] collected data on the viscoelastic properties of poly(acrylate) (PA)-PU IPN's and adequately described it by Model 2 presented by Takayanagi. They concluded that, since the model is capable of describing the IPN, the interaction between the two phases is very weak.

The work of Klempner et al. [58] cited previously also found that the Young's modulus seems to fit Takayanagi's Model 2.

Kraus et al. [119] studied the dynamic behavior of PS reinforced styrene-butadiene copolymer. They fit the data to Takayanagi's Model 2 and found the model reproduced all the essential features of the data. However, an exact fit of the storage and loss moduli was not obtained. Also noted was the fact that using the parameters for spherical inclusions did not produce a good fit with data.

The theories for elastic modulus of a composite are based on a rubbery matrix reinforced with istropic rigid particles. In most cases, this morphology is not present. Therefore, deviations from the calculated values should be expected. The model presented by van der Poel appears to give better results than the unmodified Kerner or Takayanagi models; however, it requires solving eight linear equations simultaneously [120].

1.8 THE FOCUS OF THIS THESIS: A RANDOM COIL - RIGID ROD POLYMER SYSTEM

This thesis examines a combination of polymers that is relatively unknown. Initially, the study of the network formed when the monomer solvent, ethyl acrylate, dissolves the rigid rod polymer, PBLG, and the system cools to form a gel is presented. Next, the gel formed above has the ethyl acrylate polymerized to form a network consisting of PEA, a random coil polymer, and PBLG, a rigid rod polymer. Finally, the ethyl acrylate is simultaneously polymerized and crosslinked throughout the PBLG gel state to form a semi-2-IPN.

Samples in each of the three catagories are investigated rheologically. The affects of swelling and leaching various samples is studied. Additionally, discussion of sample preparation considerations, to include changes in weight percent of rigid rod polymer, initiator, and crosslinking agent, is presented.

This thesis extends the idea of polymer solvent systems to include the polymer-monomer solvent system. Also, it extends IPN's to a new dimension as the monomer solvent becomes the random coil portion of a random coil-rigid rod semi-IPN.

CHAPTER TWO: EXPERIMENTAL

2.1 CHOICE OF THE PEA - PBLG SYSTEM

The initial choice of the system used in this research was based on two primary considerations. First, the ability of the vinyl monomer to dissolve PBLG at elevated temperature and form a visually uniform gel upon cooling to room temperature. The second primary concern was that the polymer formed from the vinyl monomer through polymerization after gel formation had to have a glass transition temperature below room temperature. Secondary concerns were cost, monomer volatility, and availability of the monomer. PBLG was mixed at about 4.8 weight percent PBLG with eight different acrylates or methacrylates (weight by weight). The eight solvents and the weight percent PBLG in the mixtures are shown in Table 3.1, page 45, where the results are discussed. All mixtures were heated until the PBLG went into solution or the solvent began boiling. When one of those points was reached, the mixtures or solutions were allowed to cool. Upon cooling to room temperature, acceptable systems could be identified by the formation of a gel with a visually uniform appearance.

The lack of gel formation under these conditions does not mean that under different conditions a gel could not form from a mixture of PBLG with any of these vinyl monomer solvents. Varying the weight percent of PBLG, the pressure, lowering the temperature even further, or changing the method of heating the mixtures may allow the formation of a gel. On the other hand, there is no guarantee that any of the mixtures which did not form gels under the given conditions will ever form a gel with PBLG.

This portion of the experimental work identified the monomer solvents which easily formed gels with PBLG at room temperature. Thus, ethyl acrylate (EA) was chosen as the solvent to use in this investigation.

The acrylate was purchased from Polysciences, Incorporated, lot number K595. All of the PBLG was bought from Sigma Chemical Company. The 120,000 molecular weight PBLG was lot number 107F-5053. The lot number for the 165,000 molecular weight PBLG was 96F-5011, while the 343,000 molecular weight PBLG was lot number 96F-5014.

2.2 FORMATION OF AN ETHYL ACRYLATE - PBLG GEL

The formation of an ethyl acrylate-PBLG gel was easily accomplished. Typically, an EA-PBLG sample was heated to about 80° C, stirred until the solution was visually homogeneous, poured into a teflon mold, and then brought to room temperature where a gel formed. The use of teflon molds was necessary to get samples as 25 mm diameter disks needed for the rheological measurements (see Figure 2.1). In making the 25 weight percent PBLG samples, it was necessary to dissolve the PBLG in N,N-dimethylformamide (DMF). After at least two days of stirring, the PBLG-DMF solution was poured into a teflon mold. Since a PBLG-DMF solution does not gel at room temperature, the samples were then refrigerated to form a PBLG-DMF gel. Once gelled, the sample was immersed in ethyl acrylate for at least one day with occasional agitation. This allowed the diffusion of the DMF out of the gel and diffusion of the ethyl acrylate into the gel.

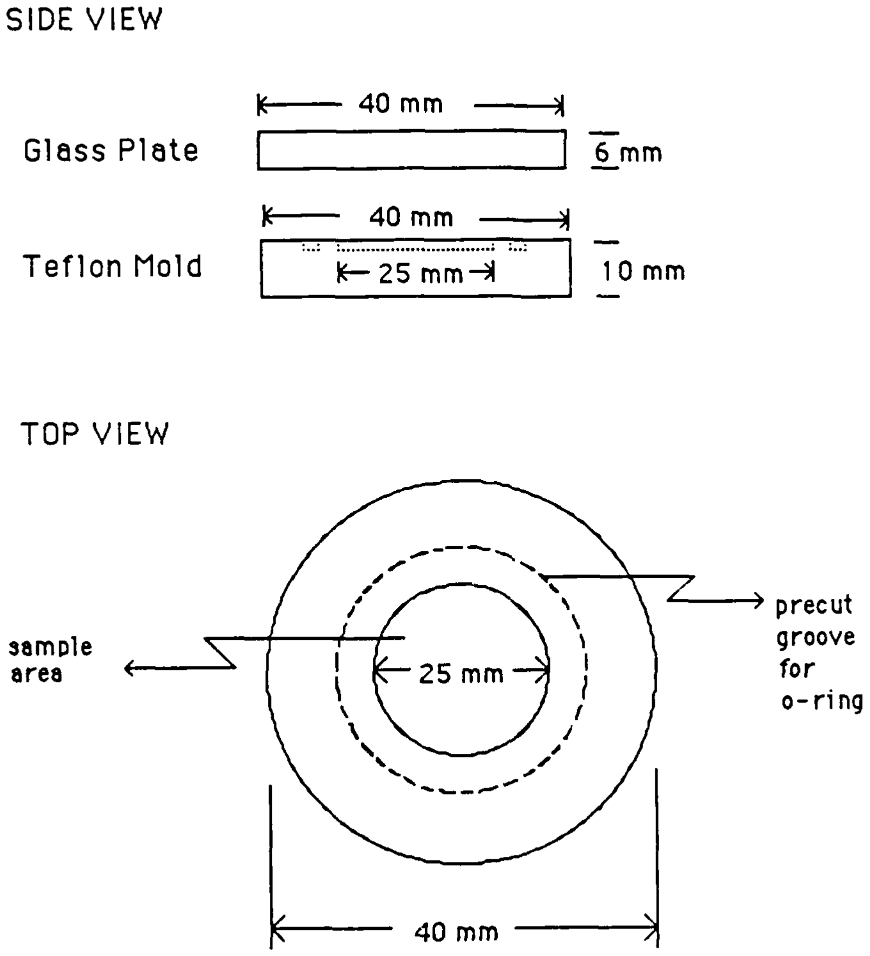


Figure 2.1. Teflon Mold for Preparation of Samples Used in Rheological Measurements.

These samples were tested directly after removal from the ethyl acrylate. The DMF was purchased from Fisher Scientific, lot number 871879.

There are many considerations that should be taken into account when trying to utilize the gel for experimental purposes. In the following sections, those considerations that needed special attention are addressed.

2.2-1 EVAPORATION OF THE SOLVENT

Ethyl acrylate evaporates readily at room temperature. For this reason, care must be taken to insure that evaporation is minimized prior to or during an experiment on a gel, or prior to polymerizing the solvent.

In the case of polymerizing the solvent from the gel, the heated solution was allowed to gel by cooling to room temperature after being poured into a 25 mm diameter teflon mold. The molds were either one or two millimeters deep. Upon reaching room temperature, a rubber o-ring was placed around the sample in a precut groove. The mold was then covered with a glass plate to minimize evaporation of EA. The glass plate was secured with a rubber band to provide tension on the o-ring and the glass plate. Note also that the lower the weight percent of PBLG present in the gel the longer it took for the gel to form. This may have allowed a slightly larger amount of EA to evaporate from the samples with lower PBLG concentration.

In the case of the rheological studies on the gels, the problem of EA evaporation during measurements was of concern. Samples were still made as 25 mm disks in the teflon molds. However, once removed from the mold the disk shaped gel went directly into the rheometer. The initial attempt to test the gel led to suspect results as the edges of the sample shrunk with the evaporation of EA. To contend with the evaporation problem, the gel sample was enclosed. The immediate environment became a volume of about 800 cubic centimeters. EA was placed around the sample and in a sponge within the volume to keep the environment saturated with ethyl acrylate vapors. This minimized the evaporation in the sample. By taking these precautions, no degradation of the sample was seen during the rheological study of the samples.

2.2-2 SOLUBILITY OF PBLG IN THE SOLVENT

While the initiators used in this research are covered in detail in section 2.3-1, it seems necessary to explain here their function so that their effect on PBLG solubility can be considered. When excited thermally, or photochemically for photoinitiators, an initiator forms free radicals which allow the vinyl monomer to polymerize. The heating of a mixture of EA and PBLG could thermally excite an initiator and bring about polymerization of the ethyl acrylate prior to the PBLG going into solution.

When the monomer solvent in the gels was not to be polymerized, it was not necessary to include an initiator in the sample when forming the gels. This made the preparation of gels far easier to do because the sample could be heated longer without fear of the initiator being thermally activated. Polymerization of the monomer prior to a gel being formed causes phase separation of the PEA and the PBLG. This results in a sticky white substance, which is similar to bubble gum in the manner in which it sticks to objects and shows elasticity.

Solubility was also affected by the weight percent of PBLG in the sample and the molecular weight of that PBLG. As the weight percent increased, it took longer to get the sample into solution. For PBLG of molecular weight 165,000, a five weight percent PBLG in EA mixture was about as high a weight percent as would go into solution in the presence of an initiator. With a 343,000 molecular weight PBLG, a four weight percent PBLG mixture could not be gotten completely into solution even in the absence of an initiator.

The samples of PEA-PBLG made with three percent or higher weight percent PBLG were all made with PBLG of molecular weight 165,000 or less. At one and two weight percent, both the 165,000 molecular weight and 343,000 molecular weight PBLG were used. Attempts to obtain a five weight percent 343,000 PBLG PEA-PBLG sample led to the boiling of the EA as the temperature needed to get the PBLG into solution was higher. This was accompanied by a rapid increase in the viscosity of the sample.

2.3 SOLVENT POLYMERIZATION IN THE PBLG - SOLVENT GEL

Once a way of forming the gel samples had been found, an extension of that technique allowing polymerization of the ethyl acrylate needed to be developed (see Figure 2.2). To polymerize the vinyl monomer, an initiator would be identified which did not interfere with the forming of the ethyl acrylate-PBLG gel. The PEA-PBLG film was formed by polymerizing the EA once an EA-PBLG gel had been made. Normally, polymerization of EA in a solution of EA and PBLG, leads to phase separation of the polymers as discussed above. By polymerizing the EA in the gel state with PBLG, further phase separation is avoided.

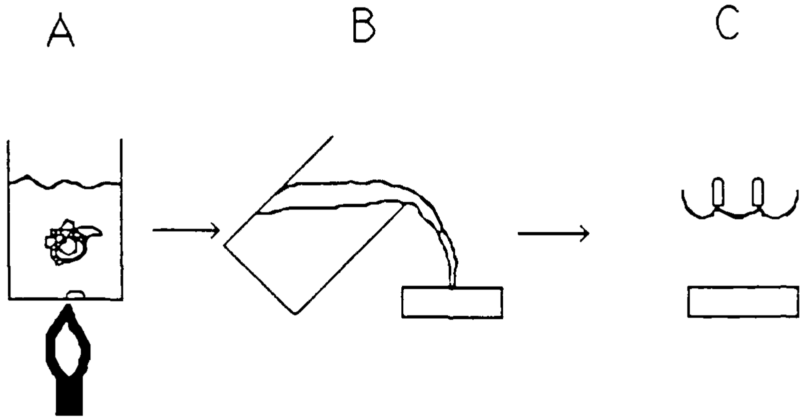


Figure 2.2. Steps in the Processing of PEA-PBLG Films and Interpenetrating Polymer Networks.

A: Ethyl acrylate-PBLG mixture is heated and stirred until a solution is formed.

B: Solution is poured into a teflon mold, allowed to cool to room temperature, and a gel is formed.

C: Gel is subjected to ultraviolet radiation. If the gel contains initiator, the ethyl acrylate will polymerize. If the gel contains both initiator and crosslinker, the ethyl acrylate will polymerize and be crosslinked.

All of the gels formed were immediately put into the oven or photochemical reactor, depending on the initiator being used, to begin the polymerization and avoid evaporation of EA. To control EA evaporation, an open beaker of EA was put into the oven or reactor to try to saturate the environment within. This did not appear to affect the polymerization. The fact that the molds were covered with a glass plate forming a seal with the o-ring or top of the mold makes the possibility of evaporation small. The practice was discontinued after just a few reactions.

Again, the 25 weight percent PBLG samples were formed by diffusing EA into a PBLG-DMF gel; however, now the samples were removed from an ethyl acrylate-initiator solution after a day and put directly into the reactor. Both the o-ring and glass plate cover were still used.

It should be noted that samples of PEA without any PBLG were also made. These pure PEA samples served as a control group for the PEA-PBLG films being tested. The major difference in the technique of forming a PEA film versus forming a PEA-PBLG film was due to the differences in behavior before polymerization of the solvent. With the EA, the teflon molds were still used. However, the use of o-rings only facilitated the EA to leave the mold. Contact between the EA and the glass cover would bring the EA over the mold's edge by capillary action. This action would cause contact with the rubber o-ring and the sample would fill the void between the top of the mold and the glass plate. Thus, in the 25 mm diameter mold about half of the EA would rise above the top of the mold. To alleviate this problem, the o-ring was not used when polymerizing samples of liquid EA. The samples done in this manner stuck to the glass plate when removed from the reactor after polymerization. The sample was separated from the glass plate with a razor blade. After an initial edge of a sample was free from the plate, the

PEA samples could be removed from the glass plate without destroying or permanently deforming the sample.

2.3-1 THERMAL VERSUS PHOTOCHEMICAL INITIATION FOR PEA FORMATION

The first attempts to make PEA-PBLG films were made using benzoyl peroxide as the initiator. Benzoyl peroxide is a thermal initiator, meaning that free radicals are formed at elevated temperatures. The benzoyl peroxide was from Matheson Coleman and Bell, lot number BX470 2838. Attempting to reheat a gel into solution and then adding benzoyl peroxide was not successful. The benzoyl peroxide would not dissolve in the solution as the increased temperature of the solution caused the benzoyl peroxide to burn upon contact. The next step was adding benzoyl peroxide to the mixture prior to heating and forming the gel. It was determined by trial and error that 0.25 weight percent benzoyl peroxide in the mixture would allow heating the mixture to form a solution, and subsequent gel formation, without causing the EA to polymerize.

Using a thermal initiator gave need to heating the sample in an oven to cause polymerization to occur. There were several complications that arose. First, at about 40° C the reaction could take up to four or five days to go to completion. This was, obviously, very time consuming and sometimes lead to ethyl acrylate evaporation. Higher temperatures, in the neighborhood of 60-70 °C, were near the gel-sol temperature for the PBLG-solvent gel. Although gel was still visible, it was also apparent that a liquid state was forming. Normally, at these elevated temperatures, the reaction took less time (18-24 hours). However, the fatal drawback was that phase separation between the PEA and PBLG frequently occurred.

Another, previously mentioned, complication also affected using a thermal initiator. Evaporation of the EA was enhanced by the increases in temperature needed to increase the number of free radicals generated by the initiator. This added to the difficulty in obtaining a usable sample from this technique.

In an attempt to overcome the complications of using a thermal initiator, a photochemical initiator, 2,2-azobisisobutyronitrile (AIBN), was tried. By using a comparable amount of AIBN instead of benzoyl peroxide, 0.25 weight percent, heating of the mixture to form a gel was not a problem. AIBN is also a thermal initiator. It is similar to benzoyl peroxide in its response to thermal decomposition to form free radicals [121]; however, it is not necessary to heat the sample to cause polymerization. Exposure to ultraviolet light will also produce the free radicals necessary for polymerization. The AIBN was from Polysciences, Inc., lot number 23482.

The reactor was a Srinivasan-Griffen photochemical reactor from The Southern New England Reactor Company. This model was named Rayonet and was Model RPR-100. The Rayonet was outfitted with tubes radiating at a wavelength of 3500 nanometers. The Rayonet was fan cooled. The fan's efficiency was hampered by the placement of aluminum foil over the top of the Rayonet. The purpose of the foil was to keep the ultraviolet rays from harming human eyes. To compensate for the increase in temperature from covering the Rayonet, it was necessary to place most samples in a cooling cylinder. The cylinder had cold water running through its outer shell and keep samples at or below room temperature. Samples in the bottom of the cooling cylinder were cold to the touch even after completion of polymerization. Those samples supported in the top portion of the cooling cylinder were at room temperature when removed. Samples outside the cooling cylinder were warm when removed from the reactor. The cooling cylinder kept the thermal effects of the photochemical reactor from dominating the reaction kinetics.

2.3-2 REACTION TIME WINDOWS

The reaction time was varied. Three time windows were used. They were four to six hours, 16 to 20 hours, and over 40 hours spent in the Rayonet with the ultraviolet light on. By using time windows, the relative reaction time can be compared. Actual reaction times would be meaningless for a number of reasons.

First, the variations in film depth caused by using molds of one or two millimeters in depth meant variations in sample volume. Second, the temperature variations due to the location of the sample within the Rayonet led to reaction temperature variations. Third, the difficulty in measuring those different temperatures made the errors difficult to quantify. Finally, the difficulty in controlling the amount of sample going into the mold meant even molds of the same size did not necessarily contain the same volume of sample. This was due to the fact that the sample would gel in a pipet during transfer as the heat rapidly dissipated from the glass pipet. Thus, time windows are thought to be well within the experimental error introduced by the factors mentioned .

2.3-3 CONFIRMATION OF PEA CHARACTERISTICS

PEA was purchased from Polysciences, Incorporated, lot number 42309, and was shipped as a ten percent solution in toluene. To precipitate the PEA, cyclohexanol was added to the PEA-toluene solution. The PEA was removed and washed twice with cyclohexanol. The washed PEA was then placed in a vacuum oven at approximately 80° C for 18 hours.

A PEA sample made from photochemical initiation was dissolved in methanol. The solution was then treated as above with cyclohexanol and the precipitated PEA vacuum dried. Similarly, a PEA-PBLG film was put in methanol. Methanol is a non-solvent for PBLG. The film was battered by the stirring rod and lost all continuity of its shape. The resulting mixture was centrifuged to separate the solution of PEA and methanol from the particulate matter. Once separated, the solution was also treated with cyclohexanol and the precipitated PEA vacuum dried.

Confirmation of the structure of the PEA samples was done by nuclear magnetic resonance (NMR) spectroscopy. Two weight percent PEA was dissolved in deuterated methanol and a proton spectrum run on each sample. The spectra were compared to varify that all the PEA samples were the same. The molecular weight distribution, relative to polystyrene standards, was obtained by conducting gel permeation chromatography. The samples were 0.5 weight percent in 1-methyl-2-pyrrolidinone (NMP).

2.4 FORMATION OF PEA - PBLG IPN

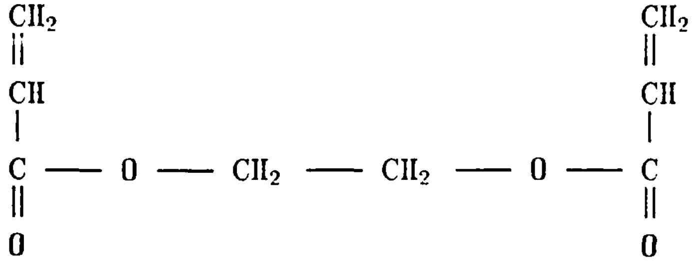
The techniques used in forming the PEA-PBLG film from a gel state are basically the same as those used to form the PEA-PBLG IPN's from a gel state. The only difference is the addition of a polyfunctional vinyl comonomer. Similar problems with evaporation and formation of crosslinked PEA samples as a control group existed. The initiator used was AIBN. The same Rayonet operating at wavelength 3500 nanometers was also used.

As with the PEA-PBLG film, the 25 weight percent PBLG samples were formed from the PBLG-DMF gels. The solution covering the gel contained the AIBN, crosslinker, and EA. Again, samples went directly from the diffusing solution to the reactor.

Polymerization of the vinyl monomer in the gel state were uneventful. Problems, however, arose in the absence of PBLG. The remainder of this section will deal with the crosslinking agent used and the problem of stresses formed in the preparation of crosslinked PEA samples.

2.4-1 THE CROSSLINKING AGENT: ETHYLENE DIACRYLATE

Ethylene diacrylate (EDA) was used as the crosslinking agent because of its similarity to the EA monomer. The EDA molecule has the form shown below. The EDA was purchased from Polysciences, Inc., lot number 3-1003. It has a functionality of four owing to the two carbon-carbon double bonds.



$$CH_2{=}CH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_2{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH{=}CH_2$$

Figure 2.3. Ethylene Diacrylate (EDA).

2.4-2 AVOIDING STRESS BUILD UP IN CROSSLINKED PEA

The technique used to polymerize EA worked well at one weight percent EDA in the total mixture. However, at five and ten weight percent EDA the sample would curl upon removal from the glass plate. This leads to the conclusion that during polymerization the sample may not crosslink and polymerize uniformly throughout the sample. Wetting of the glass plate may also lead to uneven stresses. To avoid contact between the liquid sample and the glass plate, a deep well teflon mold was used. The teflon mold was still 25 mm in diameter, but now it was eight millimeters deep. The amount of sample put into the mold was still only one to two millimeters deep. The extra space above the sample in the mold allowed for use of the rubber o-ring without contact with the liquid sample. This was not successful as it appeared that the ultraviolet rays did not reach the sample in the deep well. After four days in the Rayonet, polymerization of samples in the deep well molds had not begun.

2.4-3 SWELLING AND LEACHING OF CROSSLINKED SAMPLES

Crosslinked samples do not dissolve in solvents for the non-crosslinked polymer. To insure that crosslinking was occurring in the samples polymerized with ethylene diacrylate present, samples were soaked in methanol. Methanol is a good solvent for PEA. To measure swelling the soaking lasted at least four hours with gentle stirring. This was accomplished by using a 190 millimeter diameter by 100 millimeter deep Pyrex dish. The sample was on one side of the dish while the stir bar slowly rotated on the opposite side. The sample was gently pinned to the bottom of the dish with a glass tube. Measurements of sample diameter and dry weight were taken before and after soaking. Vacuum drying of the samples for 16 hours was completed after soaking and before the dry weight measurements were taken.

The time required for the uncrosslinked PEA and unpolymerized EA monomer to diffuse from the IPN was far longer than that needed for the film to swell to its maximum size. Very little increase in size was observed after the first two hours of soaking. So, while the set up of the leaching experiments was identical, the amount of time spent in the solvent was over 48 hours. The equation governing diffusion out of a slab [122] can be approximated at sufficiently long times as

$$\frac{\hat{c}-c_f}{c_i-c_f} = \frac{8}{\pi^2} \exp \frac{(-t\,\pi^2 D)}{h^2} \qquad \text{(EQN 2.1)}$$

where $\hat{c}$ is the concentration of interest, c_i is the initial concentration, c_f is the final concentration, t is the time in seconds, D is the diffusion constant in cm ^{2}/sec, and h is the slab width in cm. This equation was used to predict the best and worst case times for diffusion of half the uncrosslinked PEA and unpolymerized EA to diffuse from the film. With the left hand side of equation 2.1 equal to 0.5 and assuming D to be between 10^{-7} and 10^{-8} cm^2/sec, the best case would be h equal to 0.05 cm and D equal to 10^{-7} cm^2/sec. This gives a result of 1223.8 seconds, or 20 minutes and 24 seconds. The worst case would be h equal to 0.1 cm and D equal to 10^{-8} cm^2/sec; giving a result of 48951.2 seconds, or 13 hours and 36 minutes. This depends, of course, on the accuracy of the estimated values for D. By almost tripling this worst case figure, the 40 hours spent leaching the samples should give an excellent indication of over eighty-five percent of the total amount leachable.

2.5 RHEOLOGY

Rheological measurements give the response of a material to an applied stress. The rheological experiments were done on a Rheometrics System 4. The dynamic mode with parallel plate fixtures was used. All samples tested were 25 mm in diameter and varied from 0.75 to 2.5 mm in thickness. The experiments were run as frequency sweeps from 0.1 to 100 radians per second. The percent strain utilized ranged from 0.3 % to 5.0 % strain. All runs were done at room temperature, approximately 26° C. The storage modulus, G', and the loss modulus, G'', were recorded over the frequency and strain ranges.

The rest of this section gives the background and theory of the rheology measurements taken for this thesis. Emphasis is placed on the more conceptual physical meaning as opposed to the mathematical derivation of the theory.

2.5-1 RHEOLOGICAL BACKGROUND

Various rheological studies have been done on a number of PBLG systems. None of them really compare to the type of data taken in this work. Most are PBLG in dilute [27,117], semidilute [28, 123-125], or concentrated [79] solutions. Some are of PBLG in a liquid crystlline phase [29, 79, 126] or films [127]. Rao et al. [128] also did a study comparing PBLG in solvents which broke down the α-helix versus PBLG in solvents where the α-helix structure remained.

Both PEA and PBLG have been studied as a copolymer [129-137]. The majority of the literature on random coil and PBLG copolymers is on the synthesis of block copolymers [129-136] with random coil polymers other than PEA. Synthesis of a block copolymer from EA and the N-carboxyanhydride of methyl D-glutamate was studied by Yamashita [137]. No study of PBLG and PEA dealing with synthesis techniques or rheology was found.

There was only Chen et al.'s rheological study [138] of a PBLG-polybutadiene-PBLG tri-block copolymer. Most others dealt with whether PBLG was in the α-helical conformation [134-135, 139-140]. Others dealt with PBLG-PS and PBLG-PMMA systems [133, 141-142] and their relation to plasma proteins [133, 142] or as concentrated solutions in dimethylformamide [141].

Chen et al.'s study looked at the dependence of the dynamic storage modulus and loss modulus on temperature. They showed that Takayanagi's Model 1 and Equation 1.3 yielded excellent results when the values of λ and ψ were optimized. The systems were PBDLG-polybutadiene-PBDLG and PBLG-polybutadiene-PBLG. The systems had 81.1 mole percent PBDLG and 81.6 mole percent PBLG respectively. Other mole percents were studied, but comparisons with Takayanagi's Model 1 were not given.

More recently, studies on the rheological properties of PBLG gels have been done [143-144]. Murthy and Muthukumar [143] did studies of PBLG-benzyl alcohol gels. They found that both the storage and loss moduli increased as frequency increased. Also, a maximum storage and loss moduli was found as a function of the weight percent of PBLG in the sample.

McKay [144] did studies of PBLG in gels with DMF, toluene, and benzyl alcohol. He found that the storage modulus increased with increasing weight percent PBLG in PBLG-toluene gels up to two weight percent PBLG. McKay also found that the storage modulus changed very little as a function of strain in PBLG-toluene gels. However, with PBLG-benzyl alcohol gels, the storage modulus decreased about an order of magnitude as strain was increased from one to six percent.

2.5-2 RHEOLOGICAL THEORY

The complex shear modulus, G^*, of a substance is described as the sum of the contributions of the storage modulus, G', and the loss modulus, G''. The equation form is

$$G^* = G' + iG''. \qquad \text{(EQN 2.2)}$$

The storage modulus [145] is defined as the stress in phase with the strain in a sinusoidal deformation divided by the strain. It measures the energy stored and recovered per cycle. Normally, it is plotted versus the frequency in radians per second with logarithmic scales.

The loss modulus [145] is defined as the stress 90 degrees out of phase with the strain divided by the strain. It measures the energy dissipated or lost as heat per cycle. It also is plotted versus the frequency in radians per second with logarithmic scales.

Both the stress and strain will oscillate sinusoidally at the same frequency; however, the stress is usually shifted out of phase by a constant phase angle δ with respect to the strain wave. If γ_o and σ_o are the maximum strain and maximum stress, respectively, then the strain and stress can be represented as

$$\gamma = \gamma_o \sin(\omega t) \qquad \text{(EQN 2.3)}$$

and

$$\sigma = \sigma_o \sin(\omega t + \delta) \qquad \text{(EQN 2.4)}$$

where ω is the frequency in radians per second and t is the time the stress is applied. This allows the storage and loss moduli to be mathematically expressed as

$$G' = (\sigma_o/\gamma_o) \cos \delta \qquad \text{(EQN 2.5)}$$

and

$$G'' = (\sigma_o/\gamma_o) \sin \delta. \qquad \text{(EQN 2.6)}$$

The ratio of G''/G' is known as $\tan \delta$ as the sin function divided by the cos function is the tangent function.

CHAPTER 3: RESULTS AND DISCUSSION

3.1 FORMATION OF PBLG - VINYL MONOMER GELS

Many vinyl monomers were initially tried in an effort to form gels by cooling a PBLG-vinyl monomer solution to room temperature. Including ethyl acrylate, eight different vinyl monomers were used. The other seven were n-propyl acrylate, iso-butyl acrylate, tert-butyl methacrylate, sec-butyl methacrylate, n-hexyl acrylate, n-octyl methacrylate, and n-octyl acrylate. Table 3.1 shows the results of those attempts to form a gel with PBLG and the given vinyl monomer. It is not surprising to find lack of gel formation in systems in which the PBLG did not dissolve significantly at 100° C.

Table 3.1
Ability of Various Vinyl Monomers to Form Gels with Given Weight Percent PBLG at Room Temperature

Chemical	Wt % PBLG	PBLG Dissolves	Gels on Cooling
ethyl acrylate	4.41	YES	YES
n-propyl acrylate	4.78	YES	YES
iso-butyl acrylate	4.78	Partially	NO
tert-butyl methacrylate	4.77	Partially	NO
sec-butyl methacrylate	4.81	NO	NO
n-hexyl acrylate	4.81	NO	NO
n-octyl methacrylate	4.78	NO	NO
n-octyl acrylate	4.74	NO	NO

3.2 ETHYL ACRYLATE - PBLG GELS: RHEOLOGY

The major difficulties in studying gels centered around keeping the gel intact when transferring the disk from the teflon mold to the rheometer. Rheological properties of the EA-PBLG gels were measured and effects of variations in frequency, strain, and weight percent PBLG were determined.

3.2-1 FREQUENCY DEPENDENCE OF EA - PBLG GELS' DYNAMIC MODULI

Frequency was varied from 0.1 to 100 radians per second. The results are shown in Figures 3.1 and 3.2, pages 61 and 62, for plotted data and in the Appendix for tabulated data. At one weight percent PBLG, G′ increased slightly over a thousand fold increase in frequency. Under the same conditions, G″ decreased slightly over the range of frequencies, and was always lower than G′ except at high strain and PBLG concentration. With four and 25 weight percent PBLG, both G′ and G″ increased slightly over the frequency range.

3.2-2 STRAIN DEPENDENCE OF EA - PBLG GELS' DYNAMIC MODULI

Strains of 0.3 %, 1.0 %, and 5.0 % were applied to the samples. The data was shown in Figures 3.1 and 3.2 and replotted in Figures 3.3 (storage modulus) and 3.4 (loss modulus) at selected frequencies. The data show that G′ decreased with increasing strain while G″ increased with increasing strain. At 25 weight percent PBLG the loss modulus showed an overall decrease, but had a maximum. G′ recovered as the strain was decreased back to 0.3 %

strain, however only to 50 to 80 percent of the initial value. Complete tabulated data can be found in the Appendix.

3.2-3 PBLG CONCENTRATION DEPENDENCE OF EA- PBLG GELS' DYNAMIC MODULI

Gels of one, four, and 25 weight percent PBLG were investigated. The increase in PBLG concentration led to increases in both G′ and G″. At lower percent strain, the effects were more dramatic than at 5.0 % strain. In most cases, the increase was well over an order of magnitude when increasing from one to 25 weight percent. At 0.3 % strain it was common to see a change of over an order of magnitude, while at 5.0 % strain G′ may have changed less than an order of magnitude. The data is exhibited in Tables 3.2 (G′) and 3.3 (G″) below as well as in Figures 3.1 through 3.4.

3.2-4 TRENDS IN EA - PBLG GELS' DYNAMIC MODULI

The trends found in the behavior of ethyl acrylate-PBLG gels are summarized below. The storage modulus increases with increasing frequency and weight percent PBLG while decreasing with increasing strain. The most dramatic response is when PBLG concentration is varied. The variations analyzed in both frequency and strain do not usually change the storage modulus over an order of magnitude, ie, the storage modulus showed less than the c^1 PBLG concentration dependence.

The loss modulus was not nearly as easy to quantify. The trends were less reliable. This is likely due to G″ values being less reliable than G′ values, as the stress-strain phase angle is typically close to zero. The loss modulus generally showed a minimum over the frequency range investigated. The exception was at low PBLG concentration where G″ was relatively constant or decreasing over the entire frequency range. Variations in strain caused fluctuations in G″. For 25 weight percent PBLG, G″ tended to decrease with increasing strain. With lower weight percent samples, G″ tended to increase with increasing strain. Finally, the effect of higher weight percent PBLG was to increase the loss modulus. In the 25 weight percent PBLG gel, G′ strain softened to the point where it fell below the loss modulus. At lower PBLG concentration, G′ is typically two to ten times higher than G″.

Table 3.2.
Storage Moduli (G′)[(dynes/cm^2) x 10^4] for EA - PBLG Gels.

Frequency (rad/s)		0.1	1.0	10.0	100.0
% Strain	Wt % PBLG				
0.3	1	4.8	7.8	8.8	9.9
	4	23.0	29.8	32.6	36.6
	25	139.8	174.4	176.9	195.0
1.0	1	5.4	6.7	7.7	8.6
	4	22.4	25.0	27.5	31.3
	25	87.6	73.6	76.1	105.9
5.0	1	3.9	4.4	4.8	5.7
	4	7.9	7.8	8.4	9.7
	25	7.2	7.6	11.2	24.

Table 3.3.
Loss Moduli (G'')[(dynes/cm^2) X 10^4] for EA - PBLG Gels.

Frequency (rad/s)		0.1	1.0	10.0	100.0
% Strain	Wt % PBLG				
0.3	1	2.7	1.3	0.75	0.88
	4	4.0	2.8	3.5	3.3
	25	67.6	30.9	33.7	34.6
1.0	1	2.0	1.2	0.88	0.86
	4	3.8	4.4	4.7	5.0
	25	57.9	53.7	64.9	86.3
5.0	1	1.8	1.6	1.7	1.6
	4	6.2	6.7	7.7	8.8
	25	17.6	19.2	25.9	43.5

3.3 PEA - PBLG FILMS: RHEOLOGY

PEA-PBLG films with zero, one, two, three, four, five, and 25 weight percent PBLG were investigated. The dependence on frequency, strain, and PBLG concentration were determined. Typical data are shown in Figures 3.5-3.7.

3.3-1 FREQUENCY DEPENDENCE OF PEA - PBLG FILMS' DYNAMIC MODULI

The storage modulus tended to increase very slightly with increasing frequency, having typically a $\omega^{0.1}$ or less frequency dependence . Referring to Figure 3.5, one observes that at 0.3 % strain from zero to five weight percent PBLG, G' increased over the frequency range. From Figure 3.6, it appears that the same trend holds at 1.0 % strain, however the increase is more modest. At 5.0 % strain (Figure 3.7), all the values of G' are very similar from zero to five weight percent PBLG. It appears that the higher the strain the less effect frequency has on the storage modulus.

The loss modulus also increases over the frequency range investigated. The 0.3 and 1.0 % strain data again show slight increases. The 5.0 % strain exhibits even less of an effect on G″ as frequency increases. The final point is that the frequency has only a small effect on the loss modulus of films with PBLG. More dramatic increases in G″ are observed with the pure PEA films over the frequency range.

3.3-2 STRAIN DEPENDENCE OF PEA - PBLG FILMS' DYNAMIC MODULI

Figures 3.8 and 3.9 display the responses of G′ and G″, respectively, as strain was varied. Films with one, three, and five weight percent PBLG were charted. G′ exhibits minor decreases as percent strain increases. G″ appeared far more constant over the range of percent strains.

Figure 3.10 shows the effects of strain variations on the storage and loss moduli for 25 weight percent PBLG films. At 25 weight percent, G′ and G″ decreased from 0.3 to 5.0 % strain with an approximate dependence of $\gamma^{-2.0}$. This same decrease in the moduli was observed with EA-25 weight % PBLG gels, though not as dramatic.

In Figures 3.11 and 3.12, the effects of taking the rheological measurements at increasing strain is compared to values obtained when decreasing the strain. Increasing strain went from 0.3 to 1.0 to 5.0 percent strain, decreasing strain was in the reverse order. Notice, in nearly every case, the values for a sample type at the given strain are very close to one another. However, two trends exist. For G′ higher values tend to be obtained when increasing strain, while for G″ lesser values are obtained when increasing strain than when decreasing strain. Even so, it is not a significant amount in relationship to the overall variance in data taken for a given sample type. The overlap of values at 5.0 % strain was considerable and made a plot of that data of little value. The data for the two, four, and five weight percent PBLG when increasing and decreasing strain are given in the Appendix.

3.3-3 PBLG CONCENTRATION DEPENDENCE OF PEA - PBLG FILMS' DYNAMIC MODULI

In contrast to the ethyl acrylate-PBLG gels, no distinct pattern of increases or decreases in the storage modulus exists. At 0.3 % strain, G′ appears to reach a maximum as weight percent PBLG is increased. The storage moduli of all the films with PBLG (one to five weight percent) are, in essence, equal at 1.0 % strain. At 5.0 % strain, most of the data supports that G′ has leveled out and is relatively constant from one to five weight percent PBLG. When comparing one, five, and 25 weight percent PBLG data, as done in Figures 3.13 through 3.15 and Table 3.4, there is an increase in the storage modulus as the PBLG concentration increases. However, by 5.0 % strain, the previously consistent pattern of increasing G′ is no longer present.

The loss modulus does not show a distinct pattern either. While G″ has a maximum at 0.3 and 1.0 % strain, it also levels out at 5.0 % strain. The comparison of one, five and 25 weight percent PBLG data in Table 3.5 (also Figures 3.13-3.15) shows that G″ increases until a 5.0 % strain is applied. Then the increases in G″ with increased PBLG concentration is not present.

The PEA storage modulus is virtually the same as those of the films with PBLG; however, G″ is considerably smaller than the values for PEA-PBLG films.

Table 3.4
Storage Moduli (G′)[(dynes/cm^2) x 10^4] for PEA - PBLG Films.

Frequency (rad/s)		0.1	1.0	10.0	100.0
% Strain	Wt % PBLG				
	1	78.2	94.0	111.5	145.9
0.3	5	148.9	169.1	189.0	223.6
	25	296.2	440.1	532.5	731.1
	1	70.8	82.9	99.4	135.7
1.0	5	125.0	139.5	157.6	181.3
	25	190.2	216.0	223.9	211.4
	1	49.4	58.3	69.7	86.9
5.0	5	66.0	67.5	70.4	16.7
	25	27.3	22.9	13.7	7.1

Table 3.5
Loss Moduli (G″)[(dynes/cm^2) x 10^4] for PEA - PBLG Films.

Frequency (rad/s)		0.1	1.0	10.0	100.0
% Strain	Wt % PBLG				
	1	13.0	11.9	20.2	51.5
0.3	5	34.3	35.1	39.3	60.3
	25	143.6	141.3	181.1	285.1
	1	14.5	15.2	22.0	51.0
1.0	5	25.7	26.2	32.4	52.0
	25	128.1	146.0	169.9	188.8
	1	15.6	16.6	22.0	45.0
5.0	5	27.7	28.1	29.0	30.5
	25	56.9	54.0	39.1	35.0

3.3-4 TRENDS IN PEA - PBLG FILMS' DYNAMIC MODULI

The storage and loss moduli increase with increases in frequency over the frequency range investigated. Conversely, G′ decreases as the percent strain is increased, while G″ remains relatively constant from 0.3 to 5.0 % strain. The effects of varying the weight percent PBLG from one to five in PEA-PBLG films is negligible, but at 0.3 and 1.0 % strains a clear increase in G′ and G″ is observed from one to 25 weight percent PBLG. A significant decrease in G′ and G″ for 25 weight percent PBLG films occurs at 5.0 % strain.

3.4 PEA - PBLG INTERPENETRATING POLYMER NETWORKS: RHEOLOGY

The IPN's were primarily made at one weight percent PBLG with varying EDA concentration (one to ten weight percent). Some difficulties in preparing samples with ten weight percent EDA were encountered. Often ten weight percent EDA samples could be put in the Rayonet for over 72 hours and still no polymerization would be evident. Thus, when 25 weight percent PBLG samples were to be made and crosslinked for comparison, the chosen weight percent EDA was only five weight percent. The results are plotted in Figures 3.16-3.21 and discussed below.

3.4-1 FREQUENCY DEPENDENCE OF PEA - PBLG INTERPENETRATING POLYMER NETWORKS' DYNAMIC MODULI

The storage modulus tends to increase slightly over the frequency range investigated. When the weight percent of both the crosslinker, EDA, and PBLG are high, G′ may decrease. The interaction between EDA and PBLG may lessen G′, in addition to the effects of high strain. With one weight percent PBLG and one weight percent EDA, G′ increases. But with one weight percent PBLG and five or ten weight percent EDA, G′ increases at 0.3 and 1.0 % strain while decreasing at 5.0 % strain. A 25 weight percent PBLG and five weight percent EDA sample has

EDA sample has a G′ increase at 0.3 % strain, but a decrease at higher percent strain. Comparison of Figures 3.16 - 3.18 exhibit these traits.

The loss modulus increases in every case except two. Those again correlate to high PBLG (25 weight percent) and EDA (five weight percent) concentrations at strains of 1.0 and 5.0 percent. Figures 3.19-3.21 confirm these characteristics of the loss modulus as a function of frequency.

3.4-2 STRAIN DEPENDENCE OF PEA - PBLG INTERPENETRATING POLYMER NETWORKS' DYNAMIC MODULI

Increasing the percent strain consistently reduced the storage modulus in the IPN's. Figure 3.22 shows that, for IPN's with various weight percents of EDA, G′ does in fact decrease. In contrast, as shown in Figure 3.23, G′ increases with increasing strain in PEA films.

A dramatic change in the response of G′ to strain is seen as weight percent PBLG is increased. At one weight percent PBLG, the decrease in G′ is gradual and small, while at 25 weight percent PBLG G′ dives two orders of magnetude from 0.3 to 5.0 % strain. Figures 3.22 and 3.23 illustrate the rate of change for G′.

For the loss modulus, increasing percent strain also tended to reduce its value. However, this trend was not as consistent nor as dramatic as it was for G′. Figures 3.24 and 3.25 illustrate the response of G″ to strain.

3.4-3 PBLG CONCENTRATION DEPENDENCE OF PEA - PBLG INTERPENETRATING POLYMER NETWORKS' DYNAMIC MODULI

The storage modulus increased about two fold for a 25 fold increase in PBLG at 0.3 % strain. As strain was increased to 1.0 %, a 25 fold increase in PBLG led to a three to five fold decrease in G′. When strain was 5.0 %, the decrease in G′ was almost ten fold over the entire frequency range for a 25 fold increase in PBLG. This is shown in Figures 3.16-3.18.

The loss modulus shows increases of two to three fold at 0.3 % strain and of no increase to three fold at 1.0 % strain for a 25 fold increase in PBLG. A one to three fold decrease in G″ for a 25 fold increase in PBLG is seen at 5.0 % strain. Again, this supports that the PBLG structure may be breaking at high strain. These results are illustrated in Figures 3.19-3.21.

3.4-4 EDA CONCENTRATION DEPENDENCE OF PEA - PBLG INTERPENETRATING POLYMER NETWORKS' DYNAMIC MODULI

Both the storage and loss moduli increase from one to five weight percent EDA and then decrease from five to ten weight percent EDA. Figures 3.22 and 3.24 show the dependence on crosslinker concentration for G′ and G″ respectively. Each weight percent of EDA is represented by a different type of line. Notice also that with variations in crosslinker concentration the storage modulus is more sensitive at 5.0 % strain while the loss modulus is more sensitive at 0.3 % strain.

The fact that a maximum value for both G′ and G″ is found from one to ten weight percent EDA is not expected. The increases in available crosslinker should increase both G′ and G″. This increase is observed for G″ from 0.3 to 1.0 %

strain. The decreases at 5.0 % strain may be due to the erosion of the PBLG matrix discussed earlier. However, this discrepancy may have been caused, or at least assisted, by the fact that the crosslinker was not washed of its inhibitor. While it was necessary to leave the inhibitor in the ethyl acrylate when heating the solvent to avoid polymerization, the crosslinker's inhibitor concentration may have been larger than that of the vinyl solvent. The increase in inhibitor may have prevented the free radicals from being available to propagate as quickly as expected. This could lead to a reduction in actual crosslink density even though more crosslinker was present. This possibility has not been explored as part of this work.

3.4-5 TRENDS OF PEA - PBLG INTERPENETRATING POLYMER NETWORKS' DYNAMIC MODULI

IPN's consistently have increasing G' as frequency increases. G'' has the same tendency, yet is not as consistent. Strain increases tend to decrease both moduli of IPN's, while the effects of weight percent PBLG on G' and G'' of IPN's appears to be strain dependent. At low strain, moduli increase with increasing weight percent PBLG; at high strain, the opposite is true. Finally, increases in weight percent crosslinker appear to have G' reach a maximum, while G'' increases unless the strain is large. This is based on the values obtained for the three different concentrations of EDA studied here.

3.5 PEA CHARACTERISTICS

Proton nuclear magnetic resonance spectra (NMR) were run on commercial PEA, PEA made in the laboratory, and PEA made in the laboratory from the EA-PBLG gel. The latter two polymers were prepared using photoinitiation. The mechanism of polymerization of the commercial sample is unknown. The spectra of commercial and laboratory PEA are in Figures 3.26 and 3.27, respectively. The spectrum of laboratory PEA formed from an EA-PBLG gel is shown in Figure 3.28. The resonances have been marked corresponding to the hydrogen atoms which they represent. The similarity of the spectra indicate that little or no chain transfer is present in the methanol soluble portion of the photochemical initiated PEA.

The molecular weight distribution of the PEA was examined by gel premeation chromatography. Seventeen polystyrene standards were used for calibration. The polystyrene calibration data, standards' molecular weights and corresponding elution volumes in milliliters, is given in Table 3.6. The PEA from Polysciences, Incorporated is shown in Figure 3.29. This sample appears to have a bimodal distribution with a larger percent of low molecular weight PEA. This may be due to a different polymerization method. From Figures 3.30 and 3.31, it is apparent that in contrast to commercial PEA both laboratory-made samples have similarly hugh molecular weights relative to polystyrene. Both also display polydispersity.

Table 3.6.
Polystyrene Calibration Data

MW	El Vol	MW	El Vol	MW	El Vol
2.7 M	10.500	390 K	11.900	35 K	14.183
2.3 M	10.667	300 K	11.933	17.5 K	14.667
1.8 M	10.717	233 K	12.317	9 K	15.467
0.9 M	11.133	100 K	13.217	4 K	16.100
0.6 M	11.267	50 K	13.767	1.8 K	16.617
				0.8 K	17.667

MW is molecular weight in daltons. El Vol is elution volume in milliliters.

3.6 SWELLING AND LEACHING IN PEA - PBLG INTERPENETRATING POLYMER NETWORKS

The swelling and leaching of PEA-PBLG IPN's was of interest as it pertained to crosslinked PEA samples and linear PEA-PBLG samples, previously referred to as films. The data were taken after a four hour soaking in methanol and again after a subsequent 48 hour exposure to methanol. The data are compiled in Table 3.7.

Some factors possibly affecting the results need to be considered. First, the measurement of the diameter of the PEA-PBLG film was not very precise. This is because the films would curl around the edges. Attempts to flatten the sample would only fracture what had become a fragile film. Second, the measurement of the thickness of the PEA-PBLG IPN's was less accurate than their diameter measurements. This is the result of samples not always being equally thick throughout. However, the diameter measurements should not be affected by this as in most cases a 25 millimeter sample was used. The effects of inconsistent sample thickness is estimated to be much less than that of sample curling. Third, for one and five weight percent EDA IPN's, the scale being used to weigh samples required an adjustment to level the scale so that the scale's zero could be set. This occurred between the four hour data reading and the 48 hour data reading. This may account for the apparent increase in weight for the one weight percent EDA sample from the four hour data to the 48 hour data when leached in methanol.

Table 3.7 clearly shows that crosslinking the PEA allows for swelling of the samples in methanol. As weight percent EDA is increased, swelling decreases. Additionally, the presence of PBLG in the sample firms up the matrix and decreases swelling. The greater the amount of PBLG present the less the swelling. However, without the crosslinker present, swelling is drastically reduced.

The length of time the sample was soaked in solvent had a nonlinear effect on the swelling. While crosslinked samples might swell to 25 percent greater diameter in four hours, twelve times that length of time might only lead to a 27 percent increase in size for crosslinked samples. Linear PEA-PBLG films saw increases of about ten percent of the total initial diameter from the four hour to the 48 hour data.

Swelling was not isotropic. Swelling in the plane of the diameter appeared to be crosslinker concentration dependent. However, axial swelling was nearly equal for the one and five weight percent EDA samples tested. This may partially be due to the way the samples were formed. As polymerization occurred, the sample was restricted by the edges of the teflon mold. This may have added stresses to the edges of the sample not suffered by the top and bottom of the disk. Swelling in the axial direction was nearly twice as great as that in plane.

Leaching for the crosslinked PEA and crosslinked PEA-PBLG were very similar at both the four and 48 hour measurements. In every crosslinked case, the amount of leachable material was less than three percent over a 48 hour soaking. From four to 48 hours exhibited increases in the amount leached, but never as much as in the first four hour session.

The PEA-PBLG films lost significantly more sample over the course of the 48 hour session. The amount at least doubled and even quadrupled depending on the sample. Also, the overall loss varied from 5.2 percent of the original sample for the five weight percent PBLG film to 23 percent for the one weight percent PBLG film. Thus, the pore size of the linear PEA-PBLG samples must be significantly larger than those in the crosslinked samples. It appears that the presence of PBLG has little effect on the amount of leachable material in a crosslinked sample.

Table 3.7
Swelling and Leaching of Crosslinked PEA, PEA-PBLG Films, and PEA-PBLG IPN's.

Sample		Time in Solvent					
		Four Hours			Forty-Eight Hours		
% EDA	% PBLG	Swell	thick	Leach	Swell	thick	Leach
1.0	0.0	36	----	0.38	37	----	0.49
5.0	0.0	25	----	0.80	27	----	0.96
10.0	0.0	22	----	2.1	24	----	2.2
0.0	1.0	11	----	8.6	18	----	23
0.0	3.0	4.1	----	2.5	15	----	10
0.0	5.0	5.8	----	1.3	14	----	5.2
1.0	1.0	27	43	0.30	28	50	0.16
5.0	1.0	19	45	0.69	19	44	1.1
10.0	1.0	12	----	2.6	13	----	2.6

All values are percent gain original diameter for swelling. All values are percent loss original weight for leaching. Swelling of the thickness measurements are given in the thick column while diameter measurements are in the swell column.

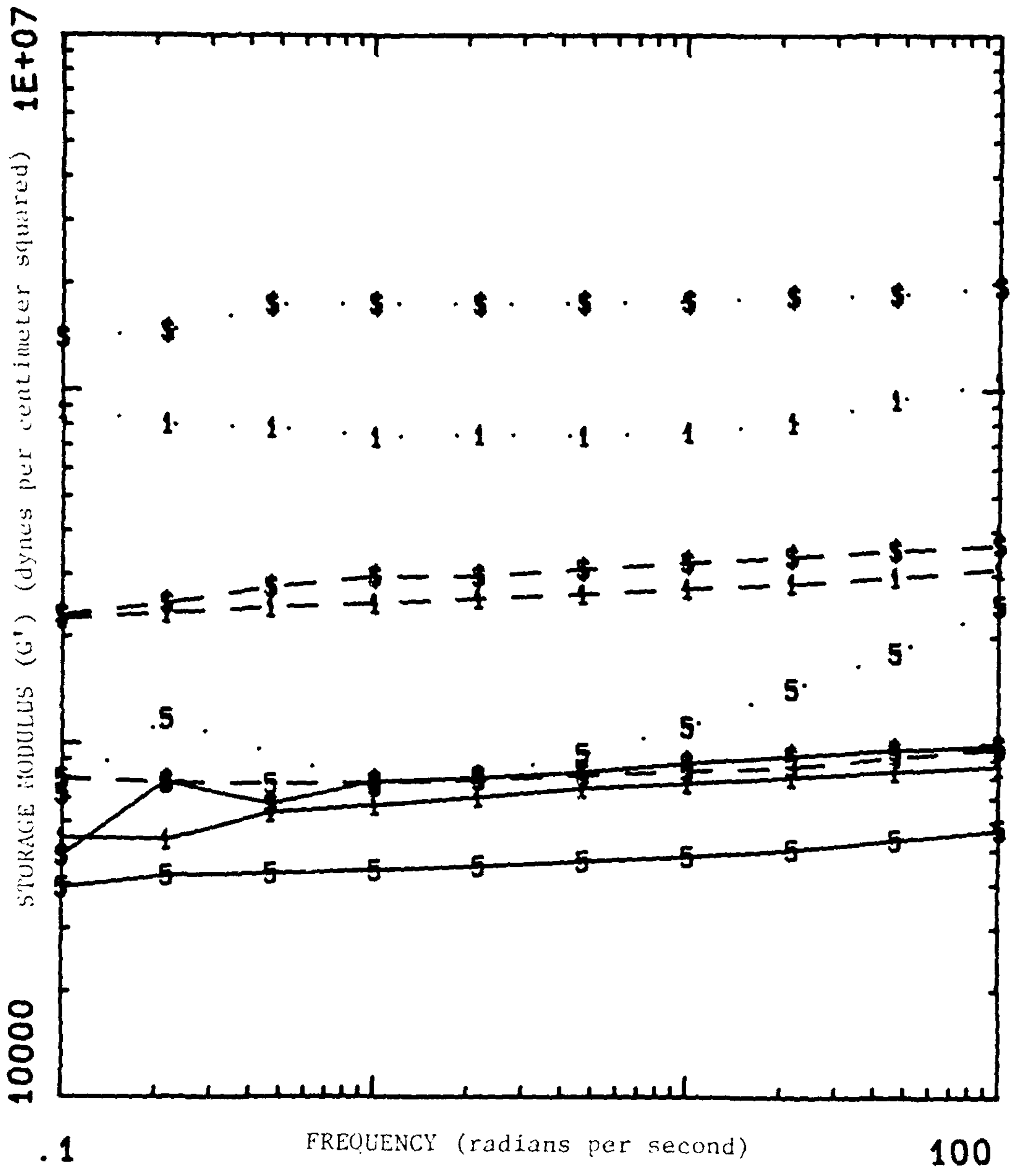


Figure 3.1. Storage Modulus v.s. Frequency for Ethyl Acrylate-PBLG Gels.
% Strain: 0.3 ($), 1.0 (1), 5.0 (5)
Wt. % PBLG: 1 (——), 4 (- -), 25 (....)

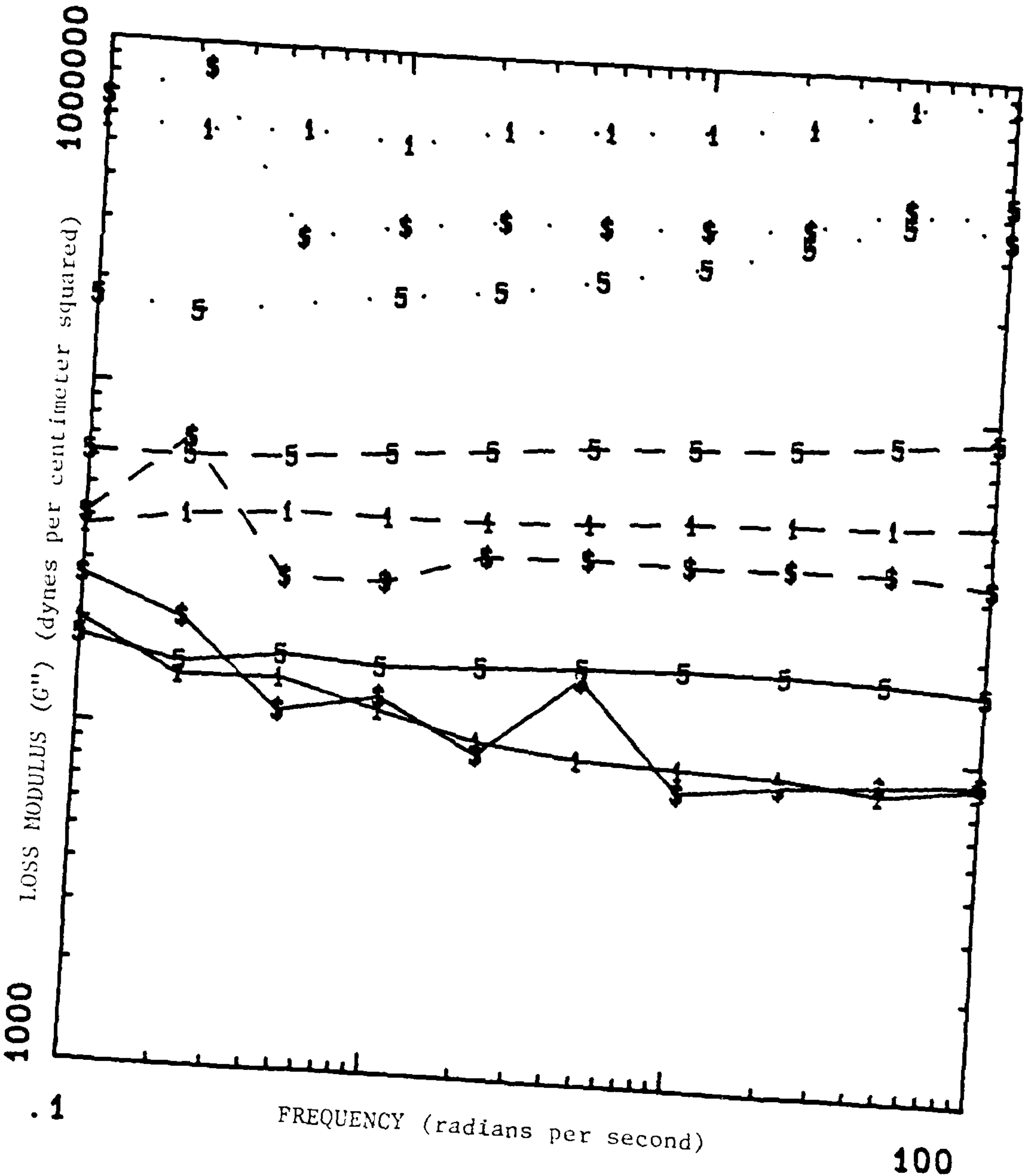


Figure 3.2. Loss Modulus vs. Frequency for Ethyl Acrylate-PBLG Gels.
% Strain: 0.3 ($), 1.0 (1), 5.0 (5)
Wt. % PBLG: 1 (——), 4 (- -), 25 (....)

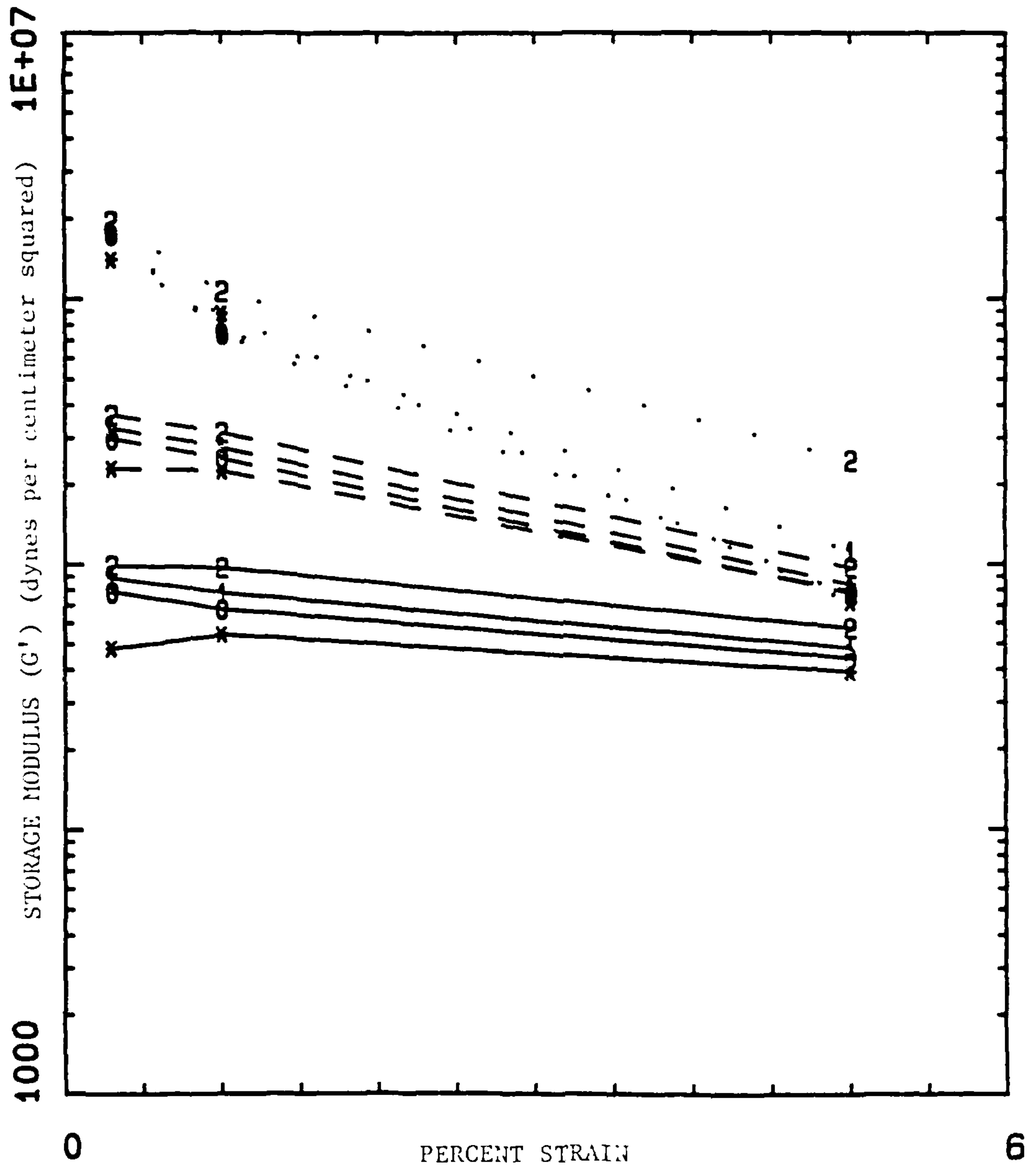


Figure 3.3. Storage Modulus vs. Percent Strain for Ethyl Acrylate-PBLG Gels.
Frequency (rad/sec): 0.1 (*), 1.0 (0), 10.0 (1), 100.0 (2)
Wt. % PBLG: 1 (——), 4 (- -), 25 (....)

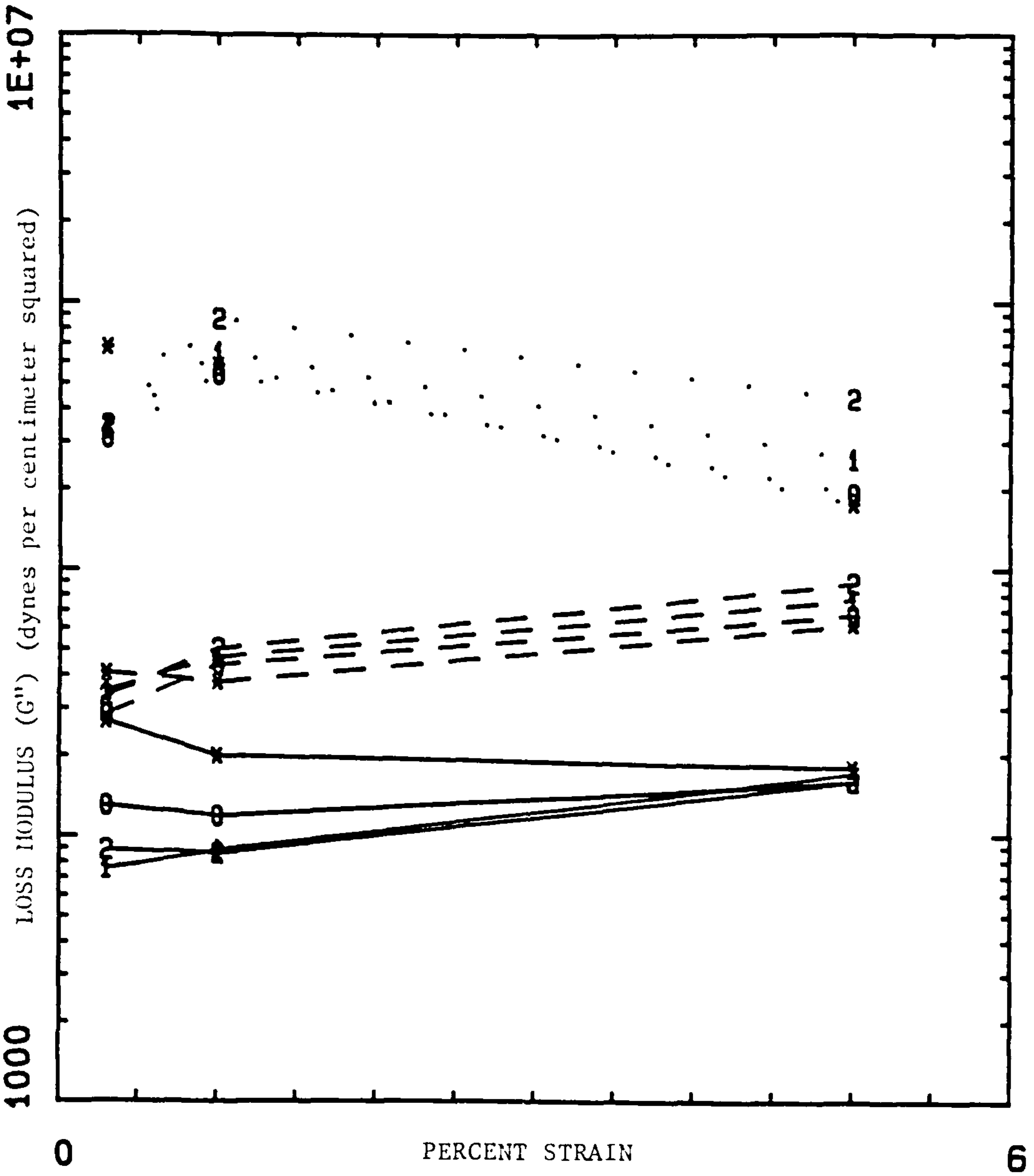


Figure 3.4. Loss Modulus vs. Percent Strain
for Ethyl Acrylate-PBLG Gels.
Frequency (rad/sec): 0.1 (*), 1.0 (0), 10.0 (1),
100.0 (2)
Wt. % PBLG: 1 (——), 4 (- -), 25 (....)

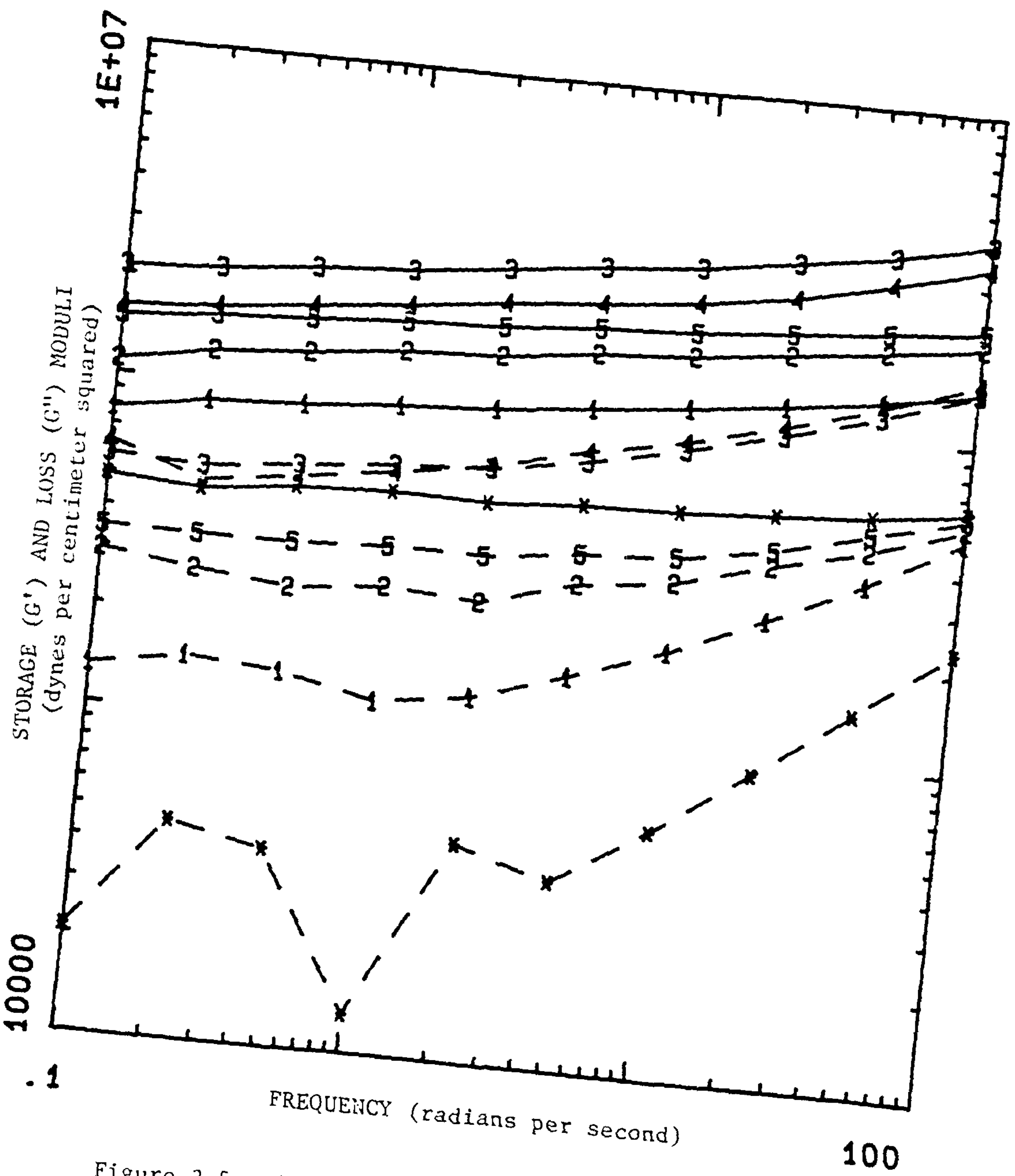


Figure 3.5. Storage and Loss Moduli vs. Frequency for PEA-PBLG Films at 0.3 Percent Strain.
Wt. % PBLG: 0 (*), 1 (1), 2 (2), 3 (3), 4 (4), 5 (5)
Modulus: G' (———), G" (- - -)

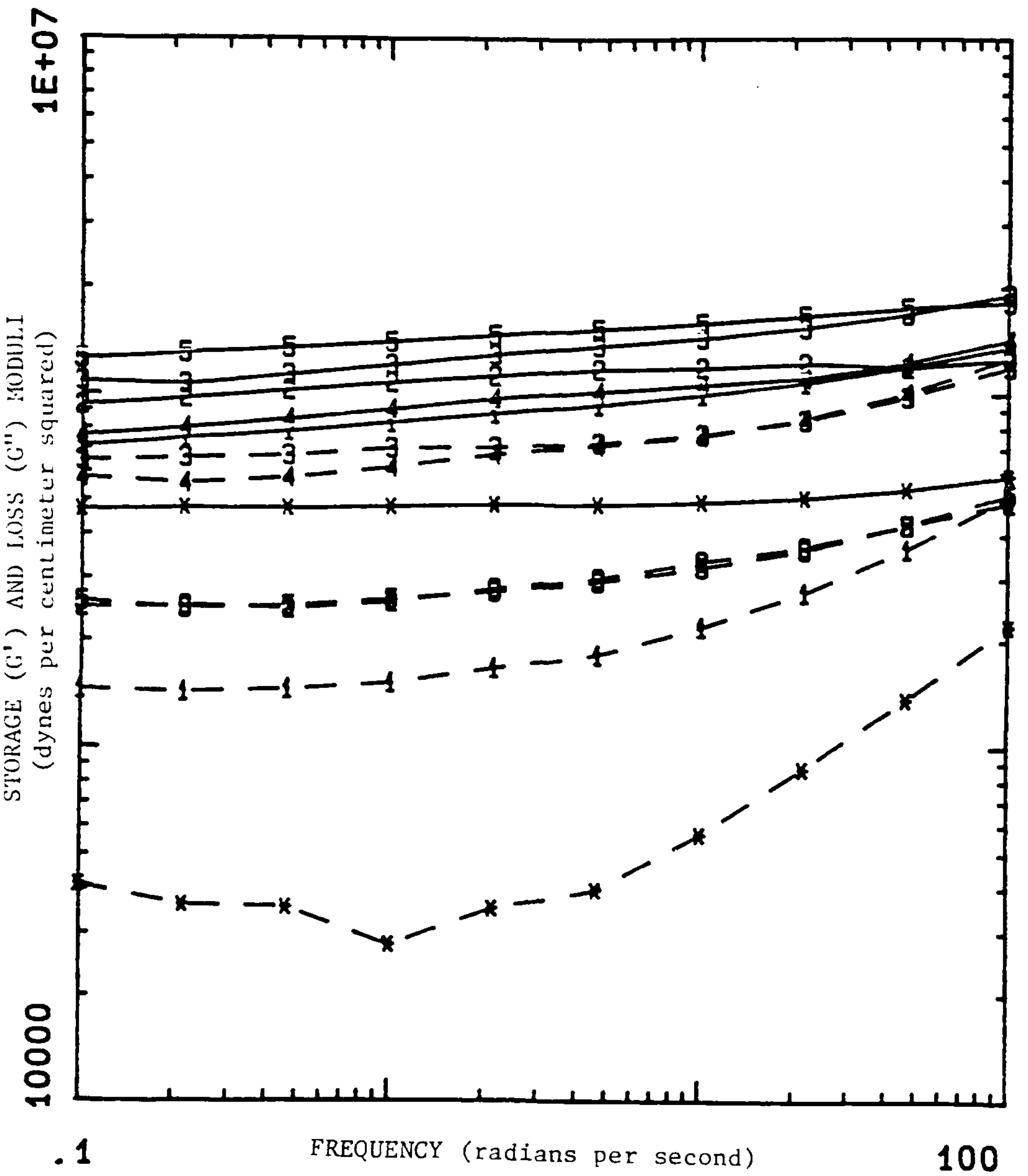


Figure 3.6. Storage and Loss Moduli vs. Frequency for PEA-PBLG Films at 1.0 Percent Strain.
Wt. % PBLG: 0 (*), 1 (1), 2 (2), 3 (3), 4 (4), 5 (5)
Modulus: G' (———), G" (- - -)

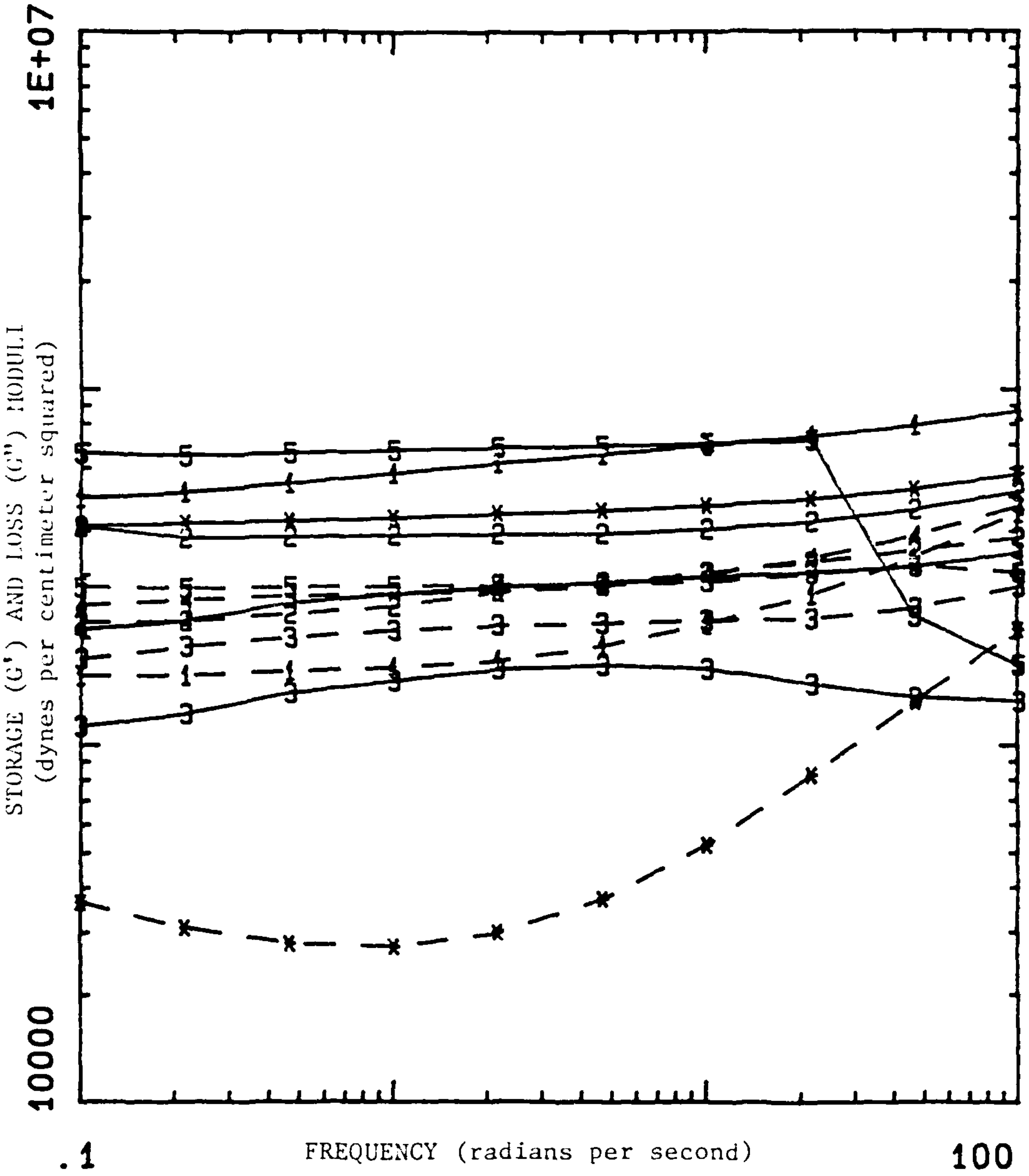


Figure 3.7. Storage and Loss Moduli vs. Frequency for PEA-PBLG Films at 5.0 Percent Strain.
Wt. % PBLG: 0 (*), 1 (1), 2 (2), 3 (3), 4 (4), 5 (5)
Modulus: G' (———), G" (- - -)

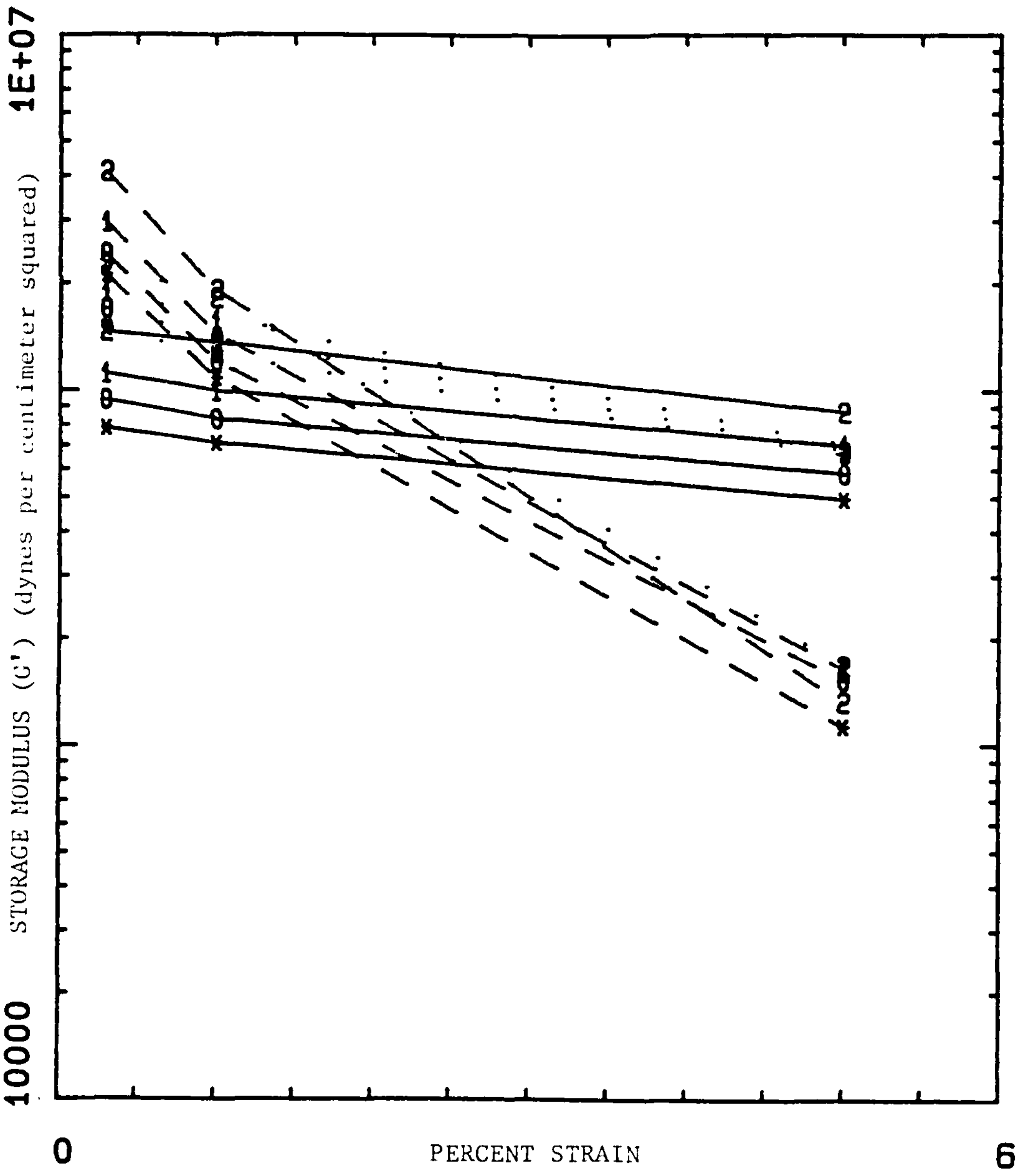


Figure 3.8. Storage Modulus vs. Percent Strain for PEA-PBLG Films.
Frequency (rad/sec): 0.1 (*), 1.0 (0), 10.0 (1), 100.0 (2)
Wt. % PBLG: 1 (——), 3 (- -), 5 (....)

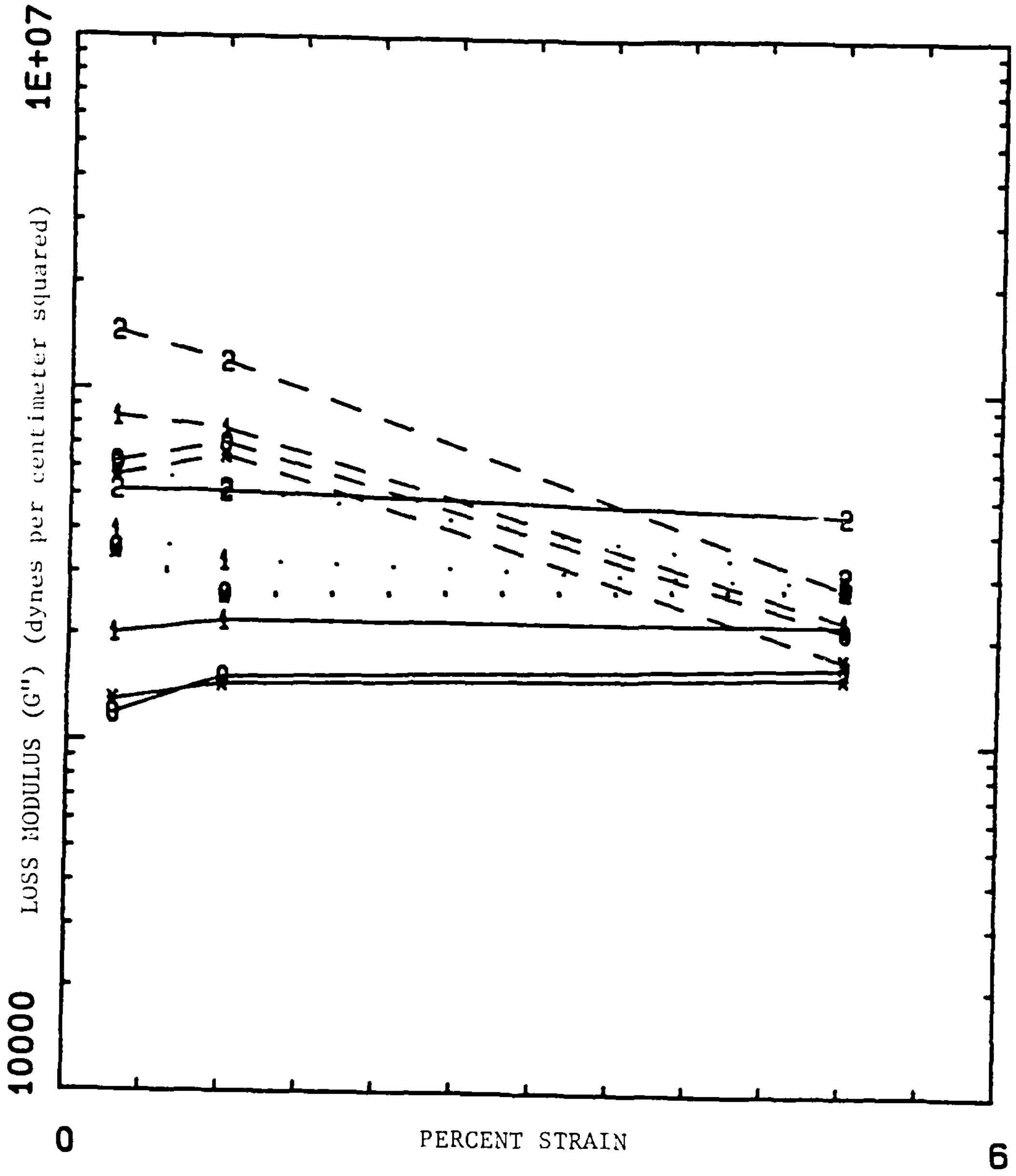


Figure 3.9. Loss Modulus vs. Percent Strain for PEA-PBLG Films.
Frequency (rad/sec): 0.1 (*), 1.0 (0), 10.0 (1), 100.0 (2)
Wt. % PBLG: 1 (——), 3 (- -), 5 (....)

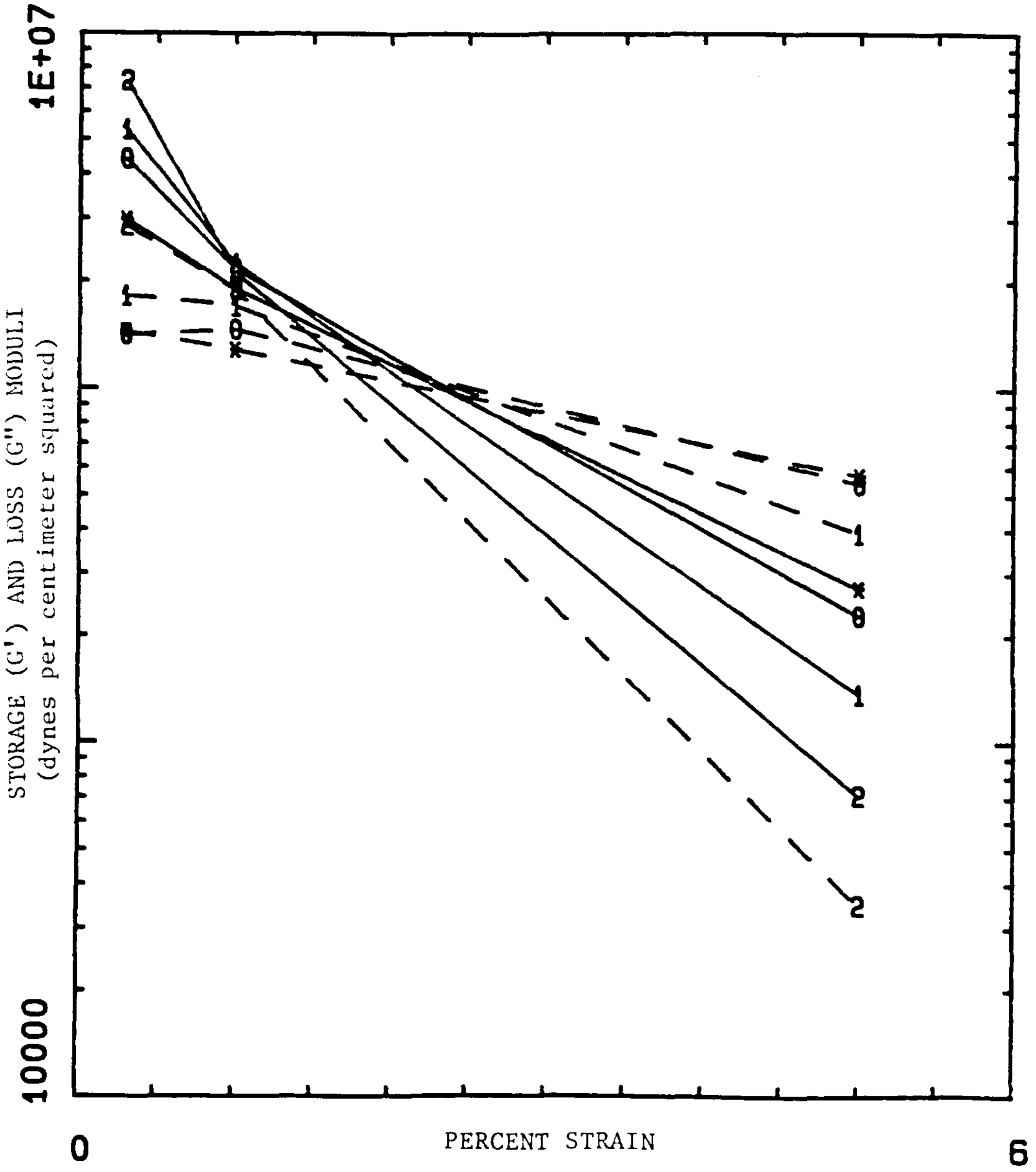


Figure 3.10. Storage and Loss Moduli vs. Percent Strain for 25 Weight Percent PBLG PEA-PBLG Films.
Frequency (rad/sec): 0.1 (*), 1.0 (0), 10.0 (1), 100.0 (2)
Modulus: G' (———), G" (- - -)

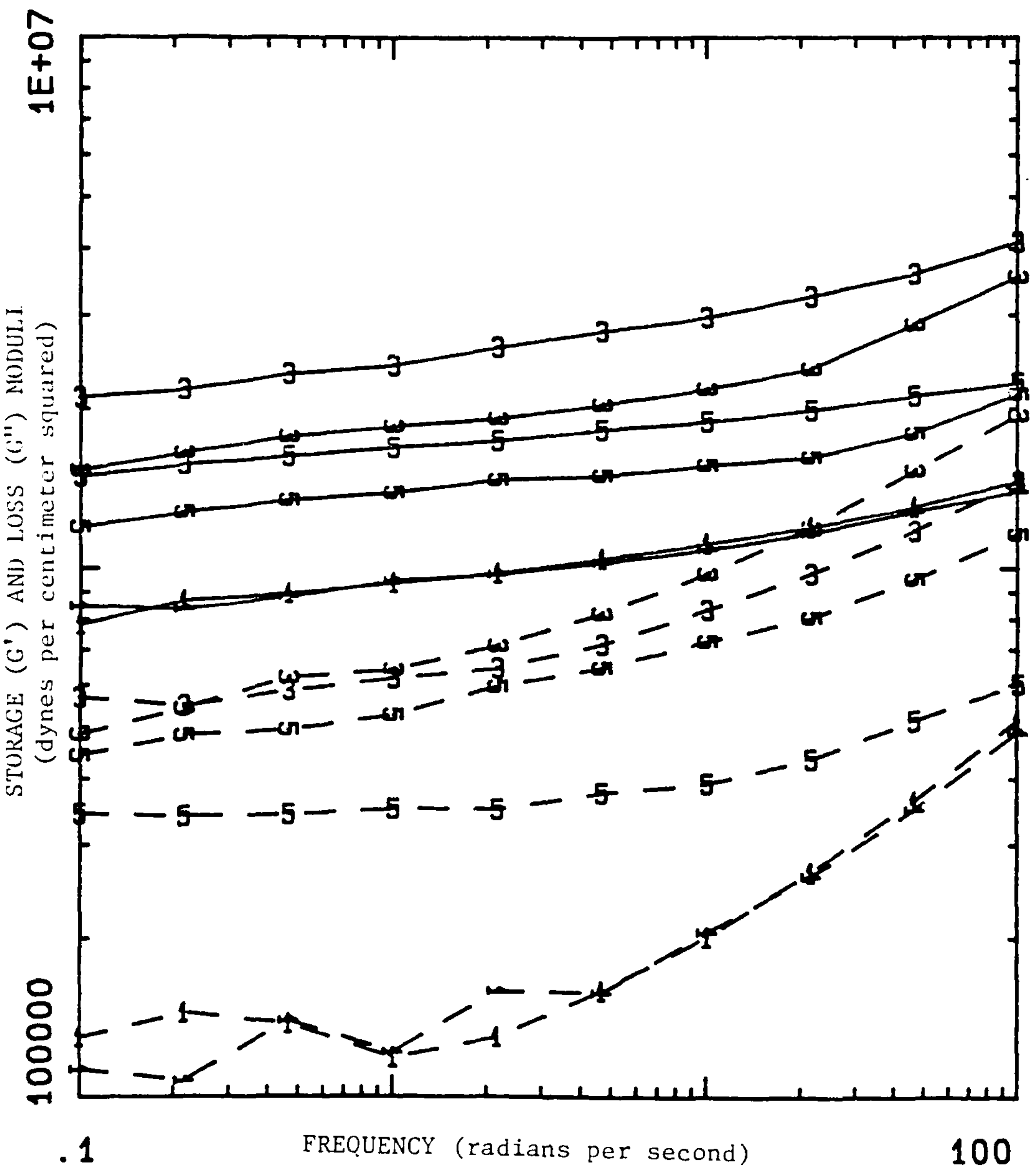


Figure 3.11. Storage and Loss Moduli vs. Frequency for PEA-PBLG Films at 0.3 Percent Strain.
Wt. % PBLG: 1 (1), 3 (3), 5 (5)
Modulus: G' (———), G" (- - -)
number right side up: starting strain
number sideways: finishing strain

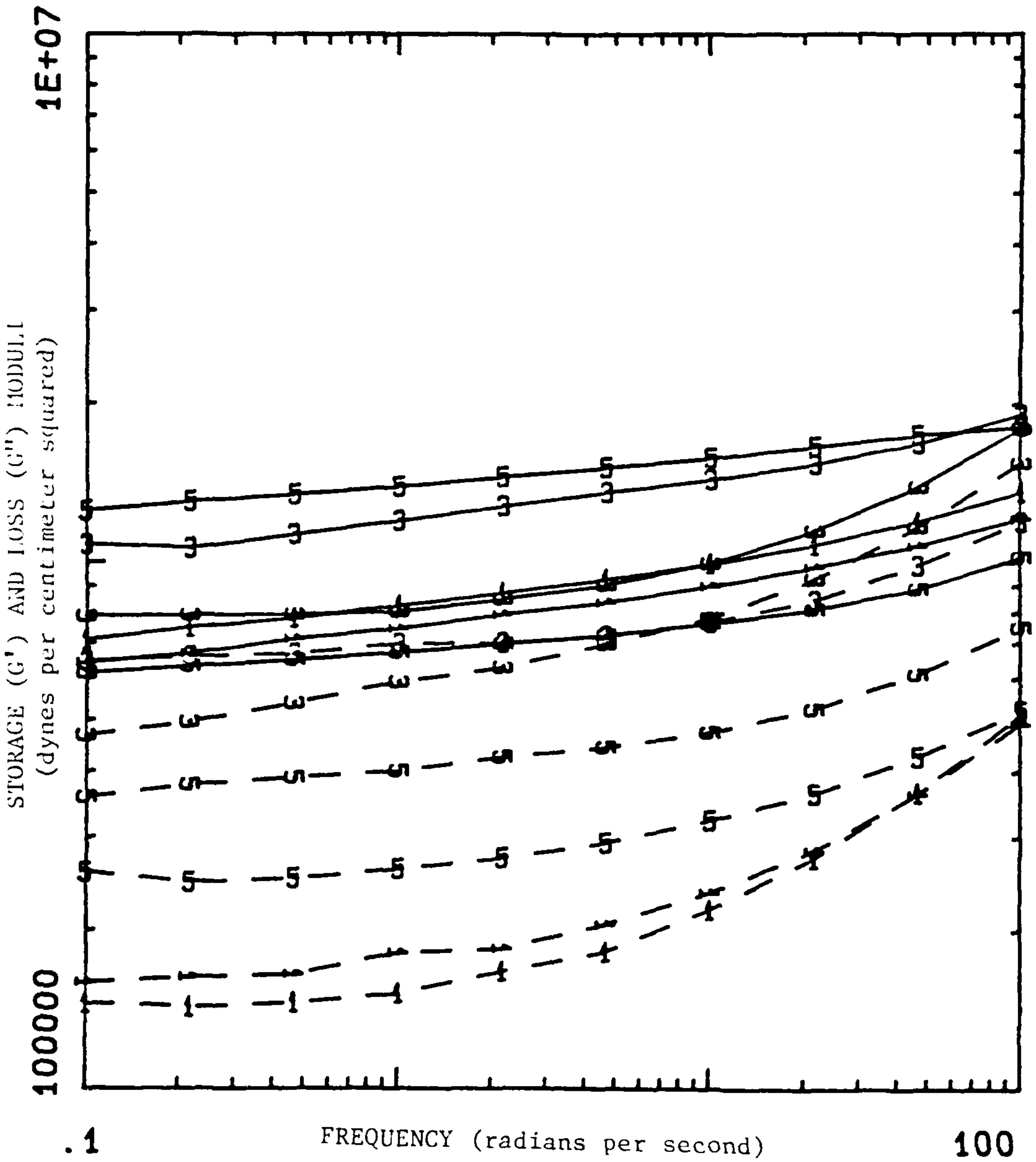


Figure 3.12. Storage and Loss Moduli vs. Frequency for PEA-PBLG Films at 1.0 Percent Strain.
Wt. % PBLG: 1 (1), 3 (3), 5 (5)
Modulus: G' (———), G" (- - -)
number right side up: increasing strain
number sideways: decreasing strain

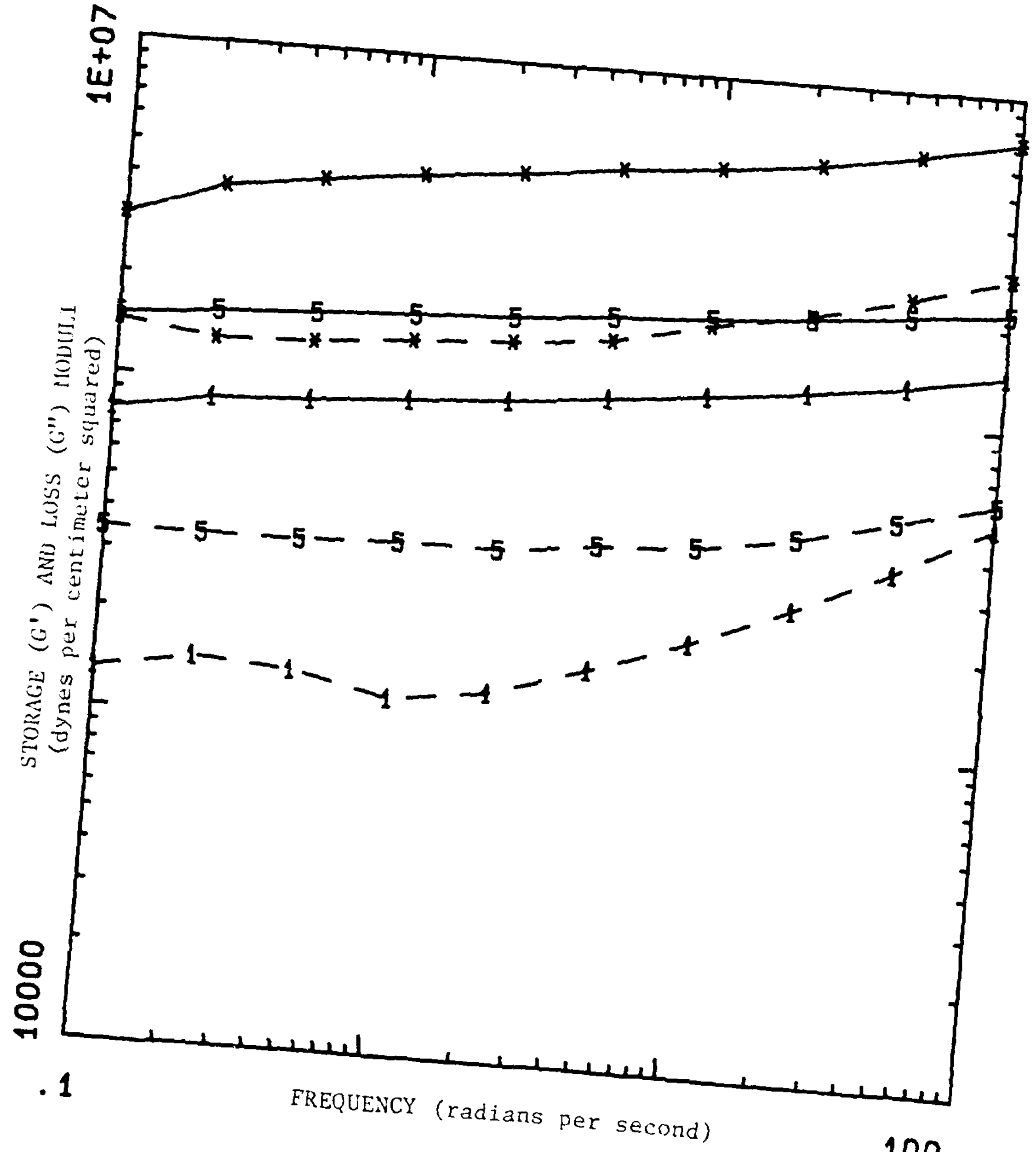


Figure 3.13. Storage and Loss Moduli vs. Frequency for PEA-PBLG Films at 0.3 Percent Strain.
Wt. % PBLG: 1 (1), 5 (5), 25 (*)
Modulus: G' (———), G" (- - -)

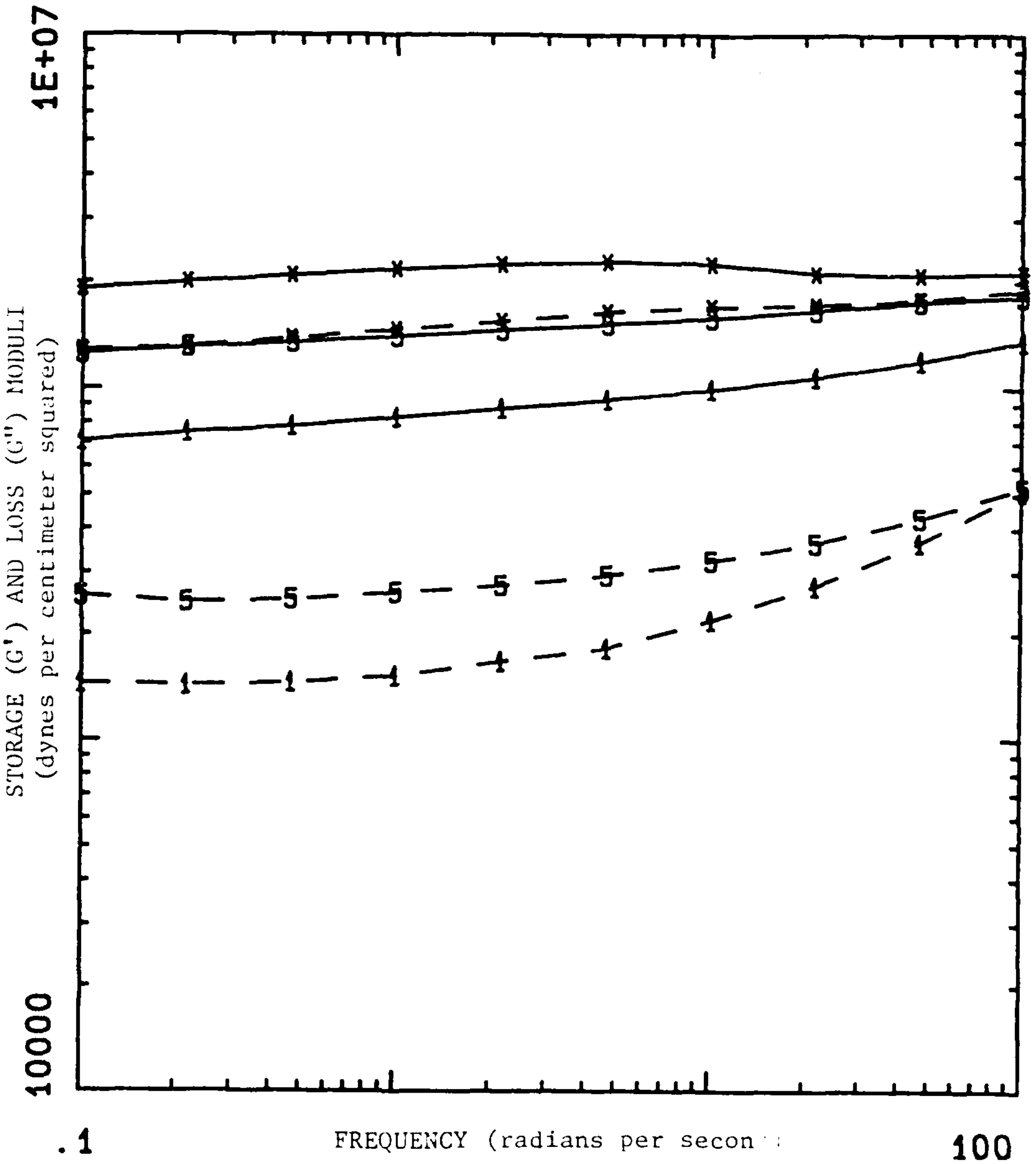


Figure 3.14. Storage and Loss Moduli vs. Frequency
for PEA-PBLG Films at 1.0 Percent Strain.
Wt. % PBLG: 1 (1), 5 (5), 25 (*)
Modulus: G' (———), G" (- - -)

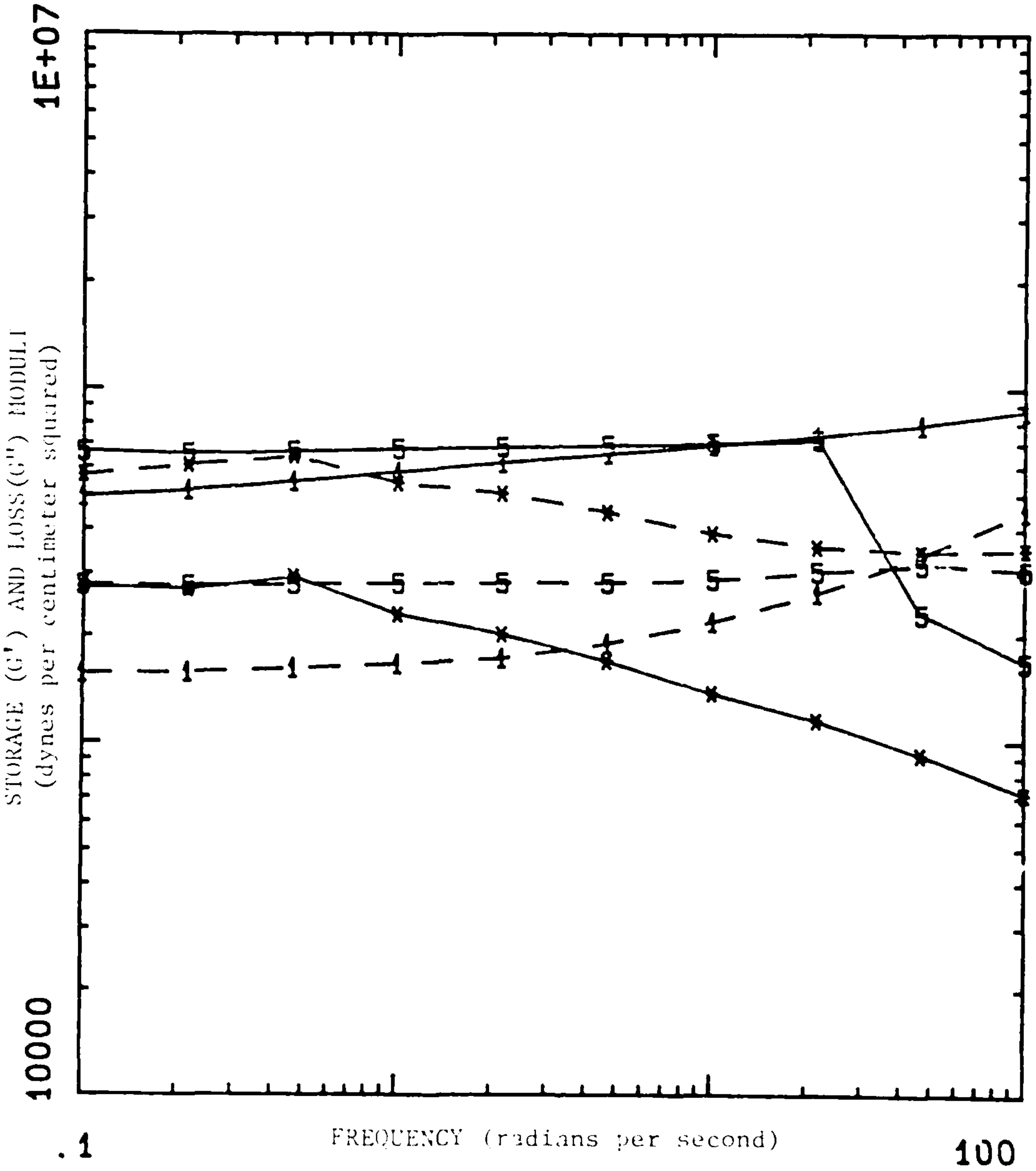


Figure 3.15. Storage and Loss Moduli vs. Frequency
for PEA-PBLG Films at 5.0 Percent Strain.
Wt. % PBLG: 1 (1), 5 (5), 25 (*)
Modulus: G' (———), G" (- - -)

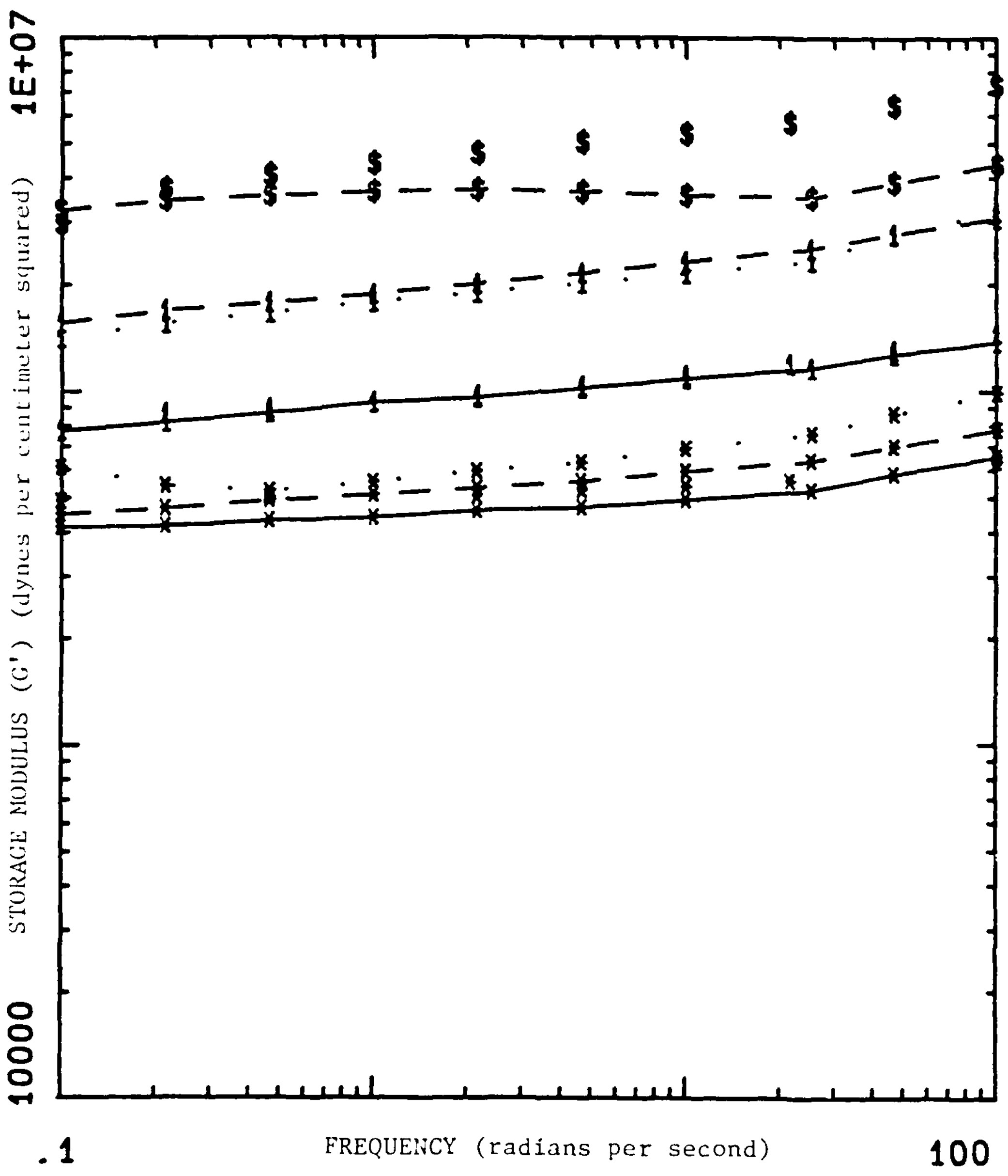


Figure 3.16. Storage Modulus vs. Frequency for PEA-PBLG IPN's at 0.3 Percent Strain.
Wt. % PBLG: 0 (*), 1 (1), 25 ($)
Wt. % EDA: 0 ( ), 1 (———), 5 (- - -), 10 (.....)

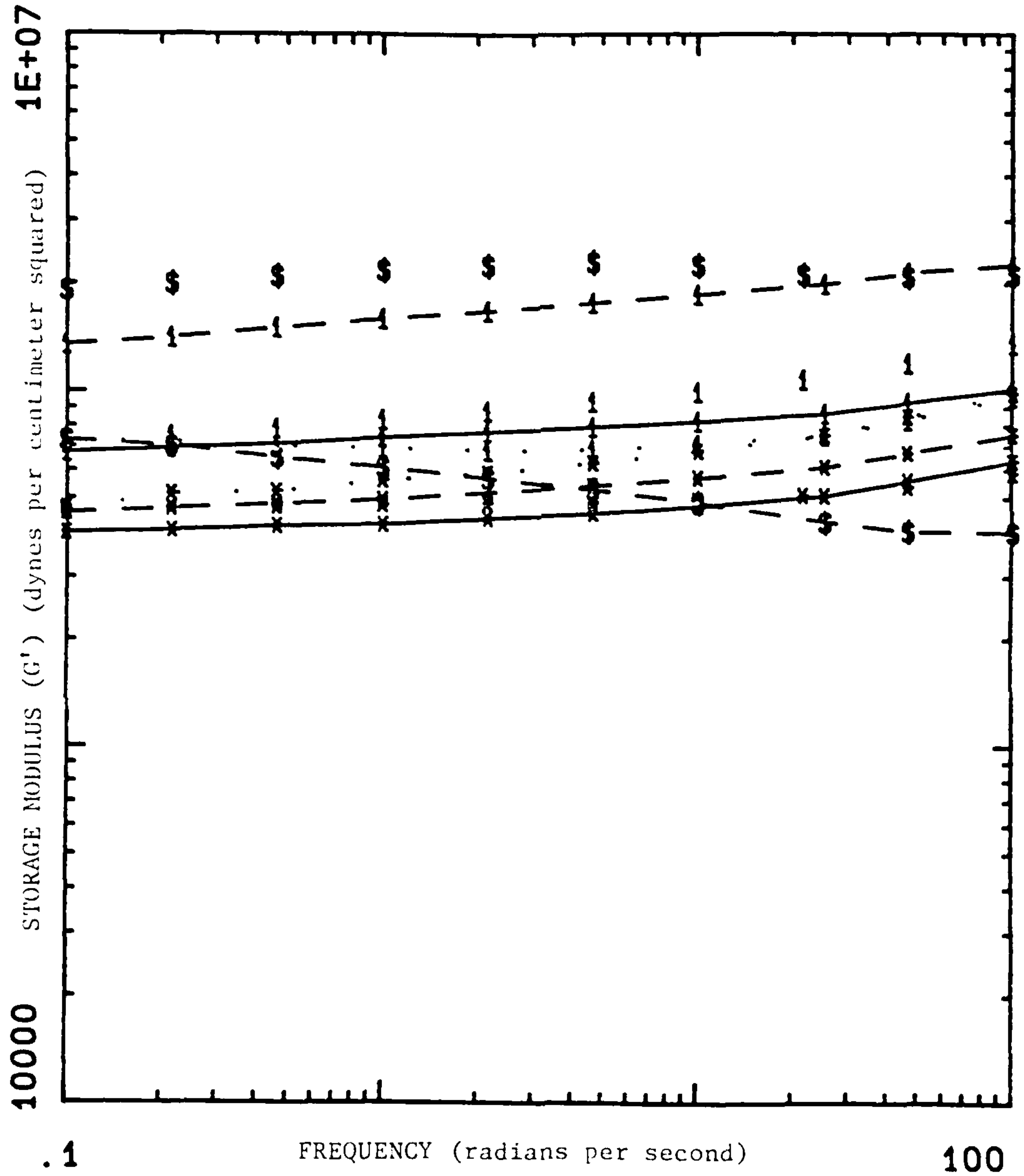


Figure 3.17. Storage Modulus vs. Frequency for PEA-PBLG IPN's at 1.0 Percent Strain.
Wt. % PBLG: 0 (*), 1 (1), 25 ($)
Wt. % EDA: 0 ( ), 1 (———), 5 (- - -), 10 (.....)

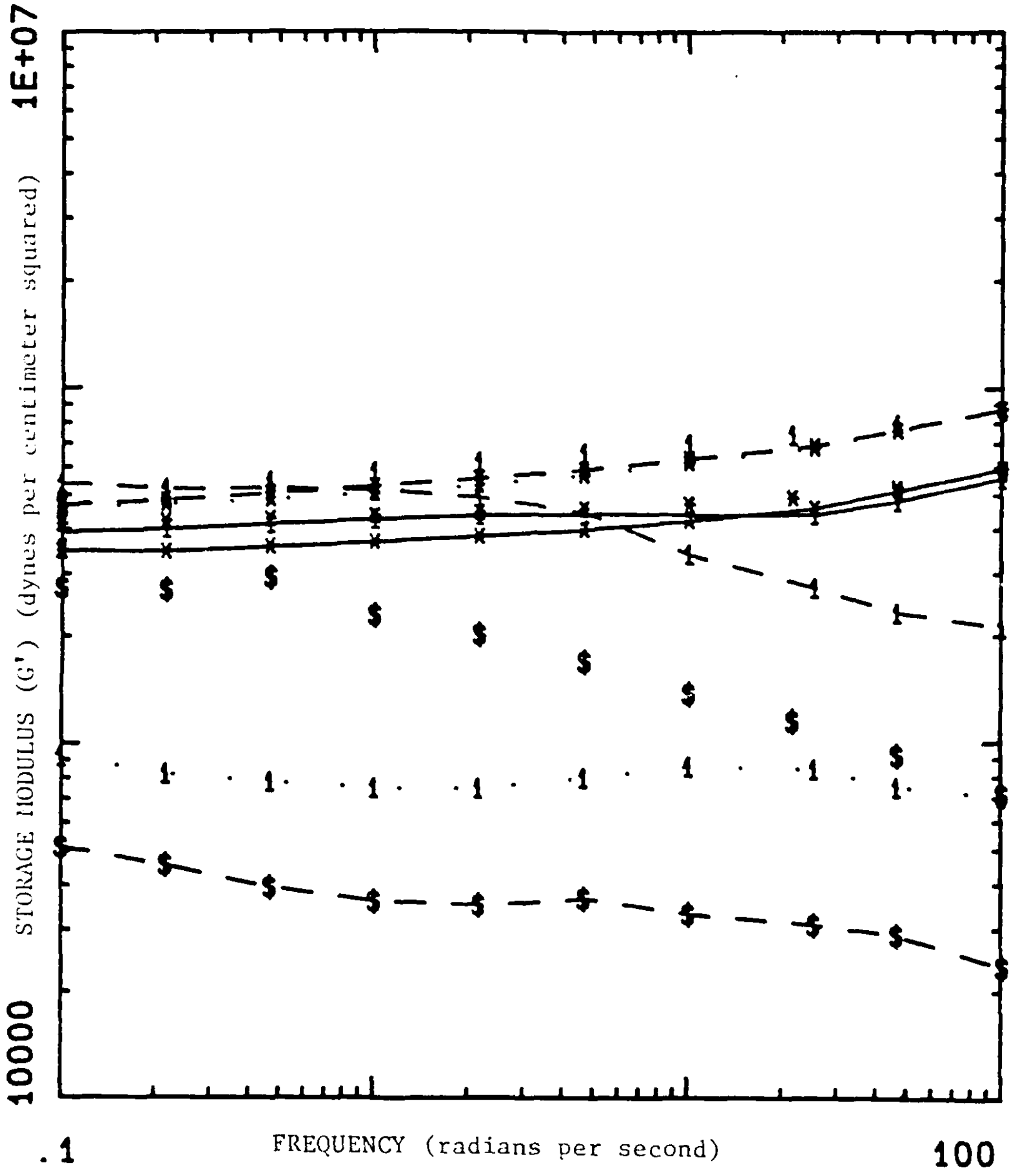


Figure 3.18. Storage Modulus vs. Frequency for PEA-PBLG IPN's at 5.0 Percent Strain.
Wt. % PBLG: 0 (*), 1 (1), 25 ($)
Wt. % EDA: 0 ( ), 1 (———), 5 (- - -), 10 (.....)

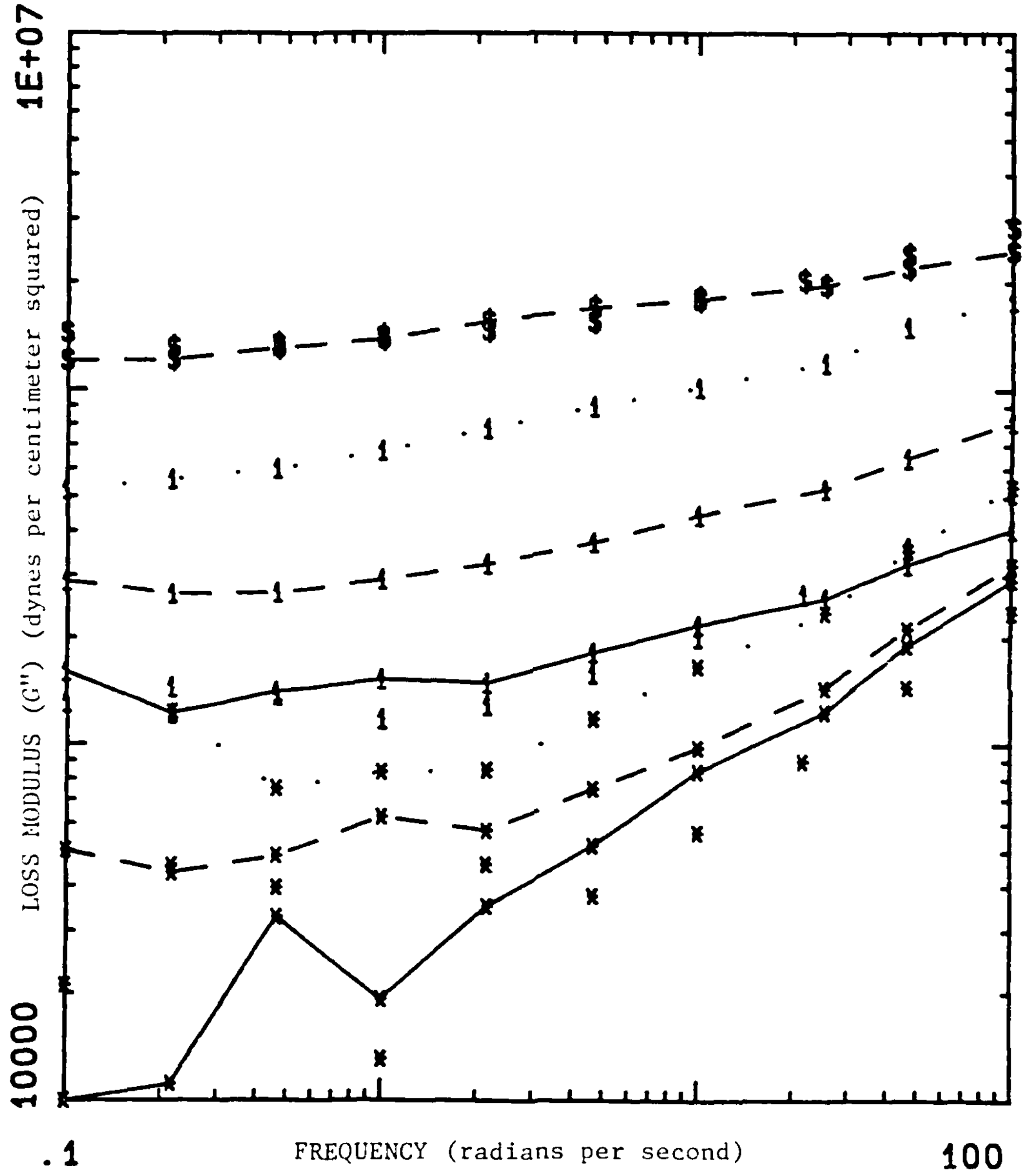


Figure 3.19. Loss Modulus vs. Frequency for PEA-PBLG IPN's at 0.3 Percent Strain.
Wt. % PBLG: 0 (*), 1 (1), 25 ($)
Wt. % EDA: 0 ( ), 1 (———),
5 (- - -), 10 (.....)

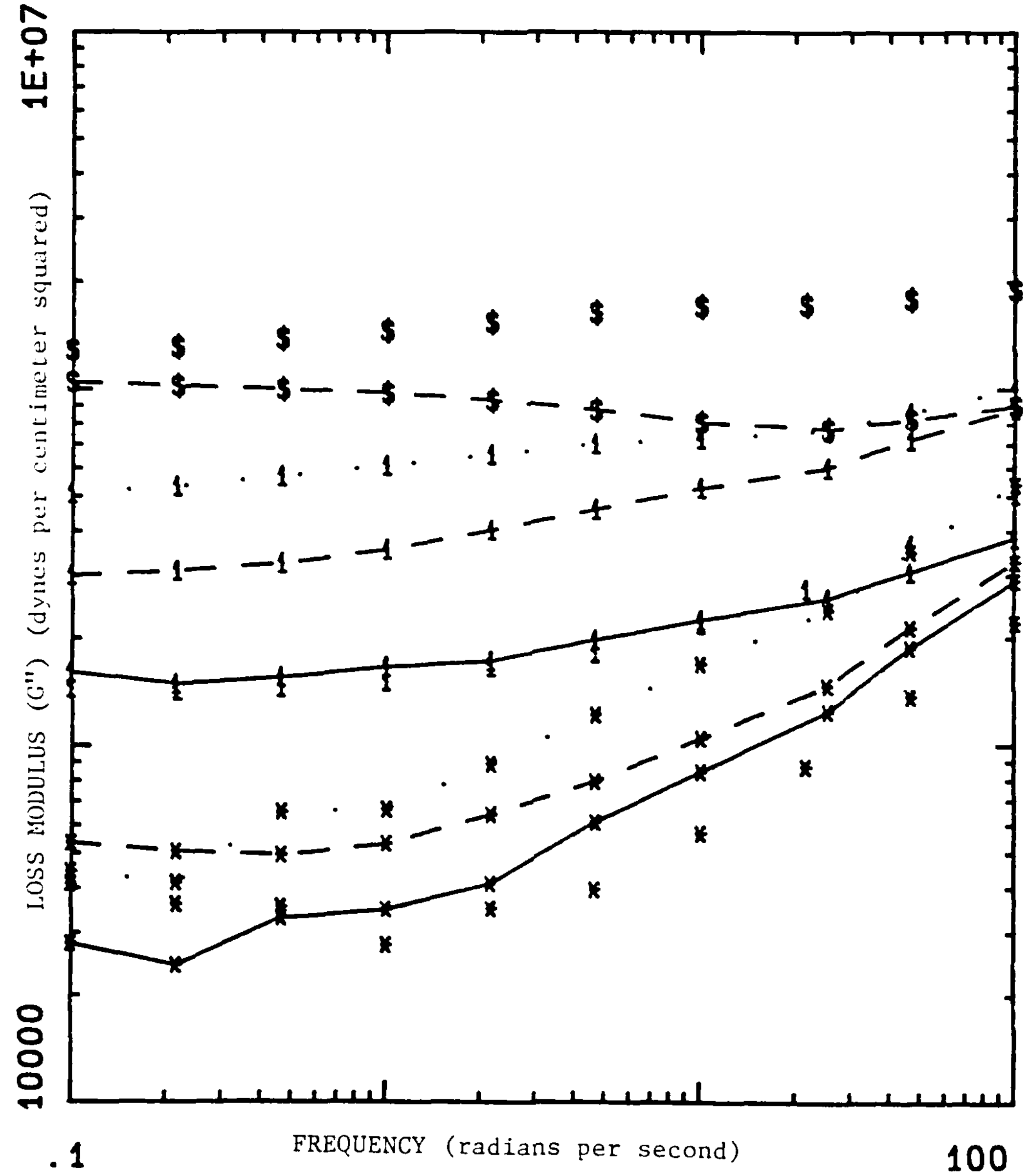


Figure 3.20. Loss Modulus vs. Frequency for PEA-PBLG IPN's at 1.0 Percent Strain.
Wt. % PBLG: 0 (*), 1 (1), 25 ($)
Wt. % EDA: 0 ( ), 1 (——), 5 (- - -), 10 (.....)

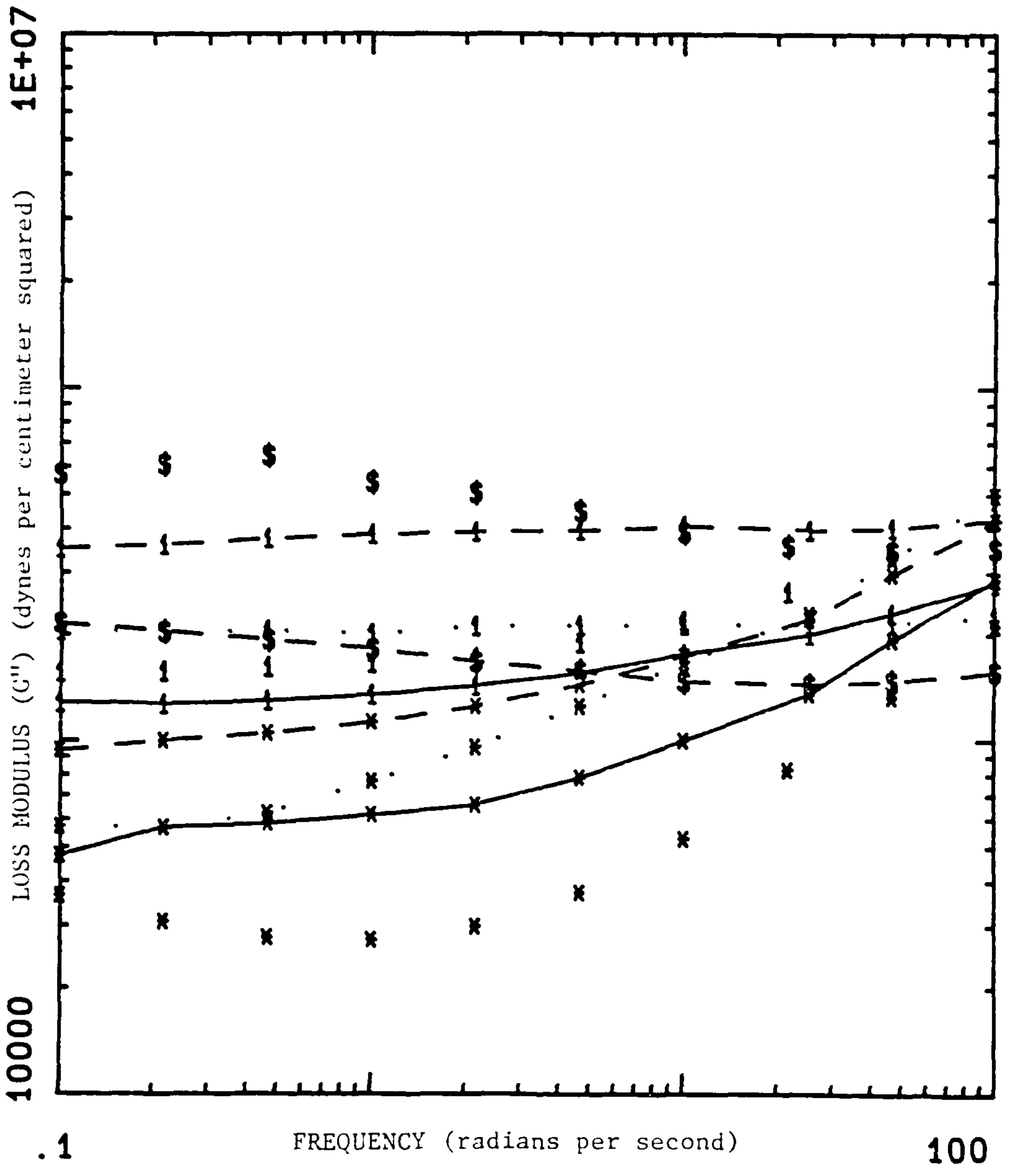


Figure 3.21. Loss Modulus vs. Frequency for PEA-PBLG IPN's at 5.0 Percent Strain.
Wt. % PBLG: 0 (*), 1 (1), 25 ($)
Wt. % EDA: 0 ( ), 1 (———),
5 (- - -), 10 (.....)

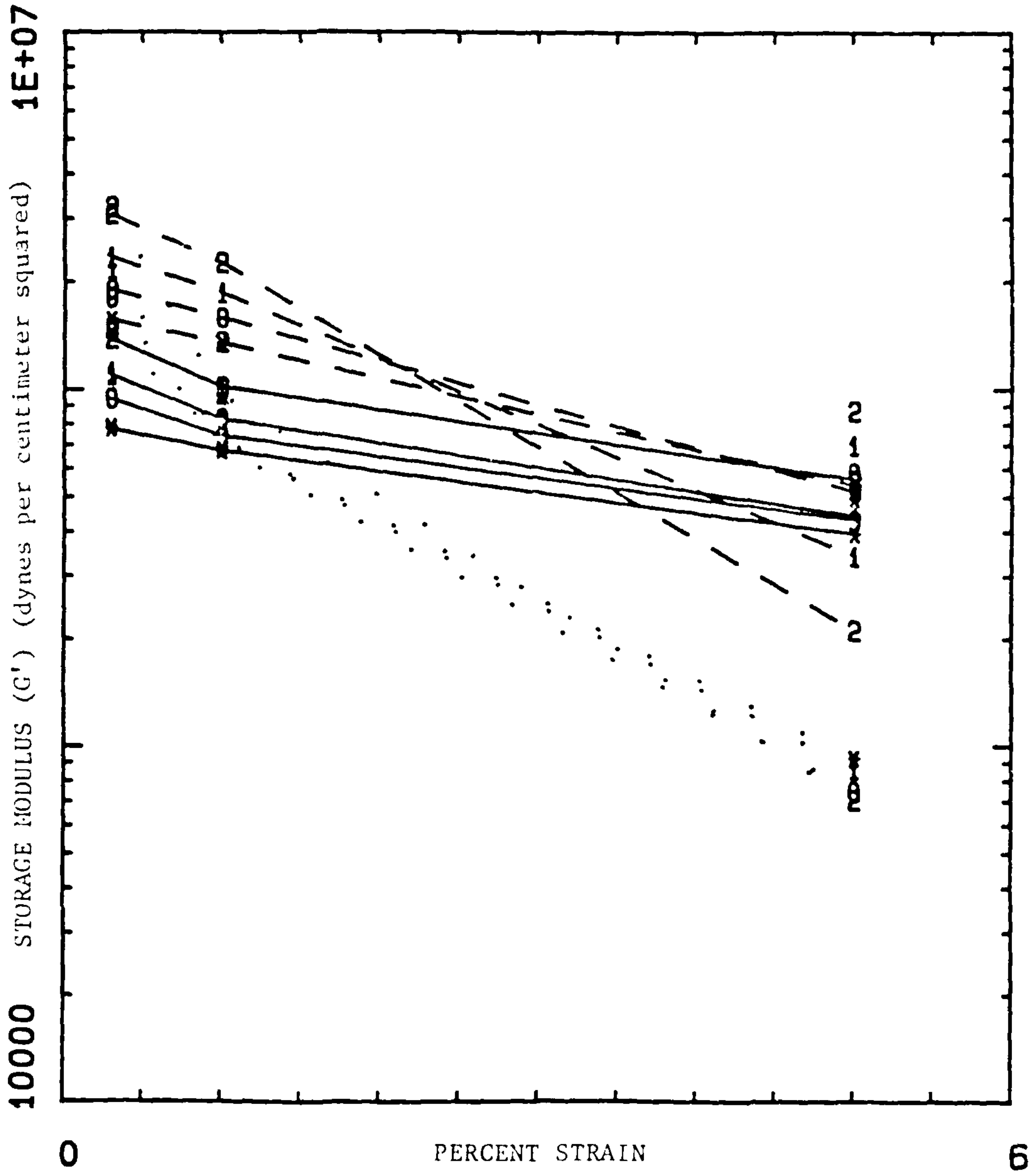


Figure 3.22. Storage Modulus vs. Percent Strain for PEA-PBLG IPN's with One Weight Percent PBLG.
Frequency (rad/sec): 0.1 (*), 1.0 (0),
10.0 (1), 100.0 (2)
Wt. % EDA: 0 (   ), 1 (———), 5 (- - -),
10 (.....)

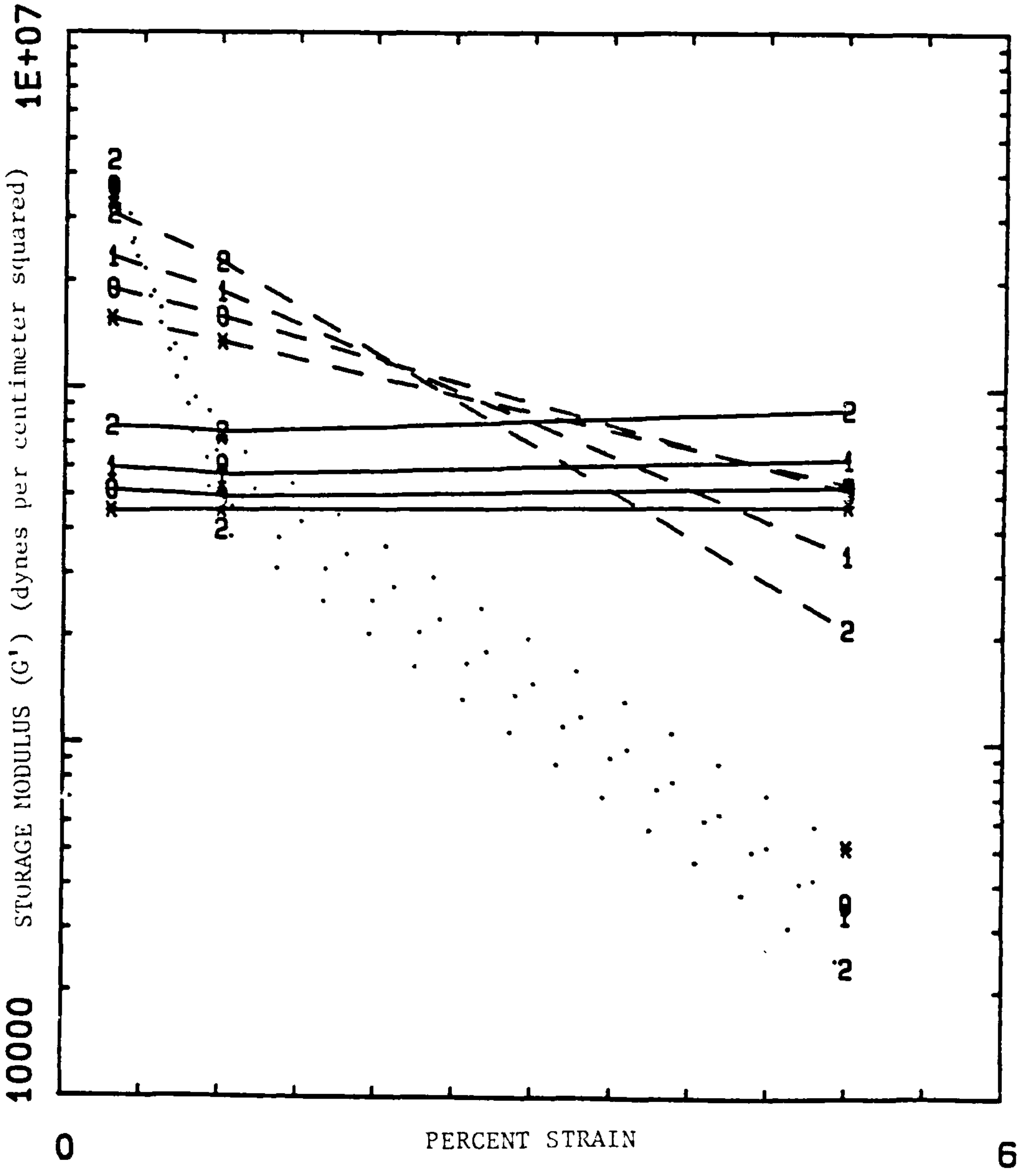


Figure 3.23. Storage Modulus vs. Percent Strain for PEA-PBLG IPN's with Five Weight Percent EDA. Frequency (rad/sec): 0.1 (*), 1.0 (0), 10.0 (1), 100.0 (2) Wt. % PBLG: 0 (———), 1 (- - -), 25 (.....)

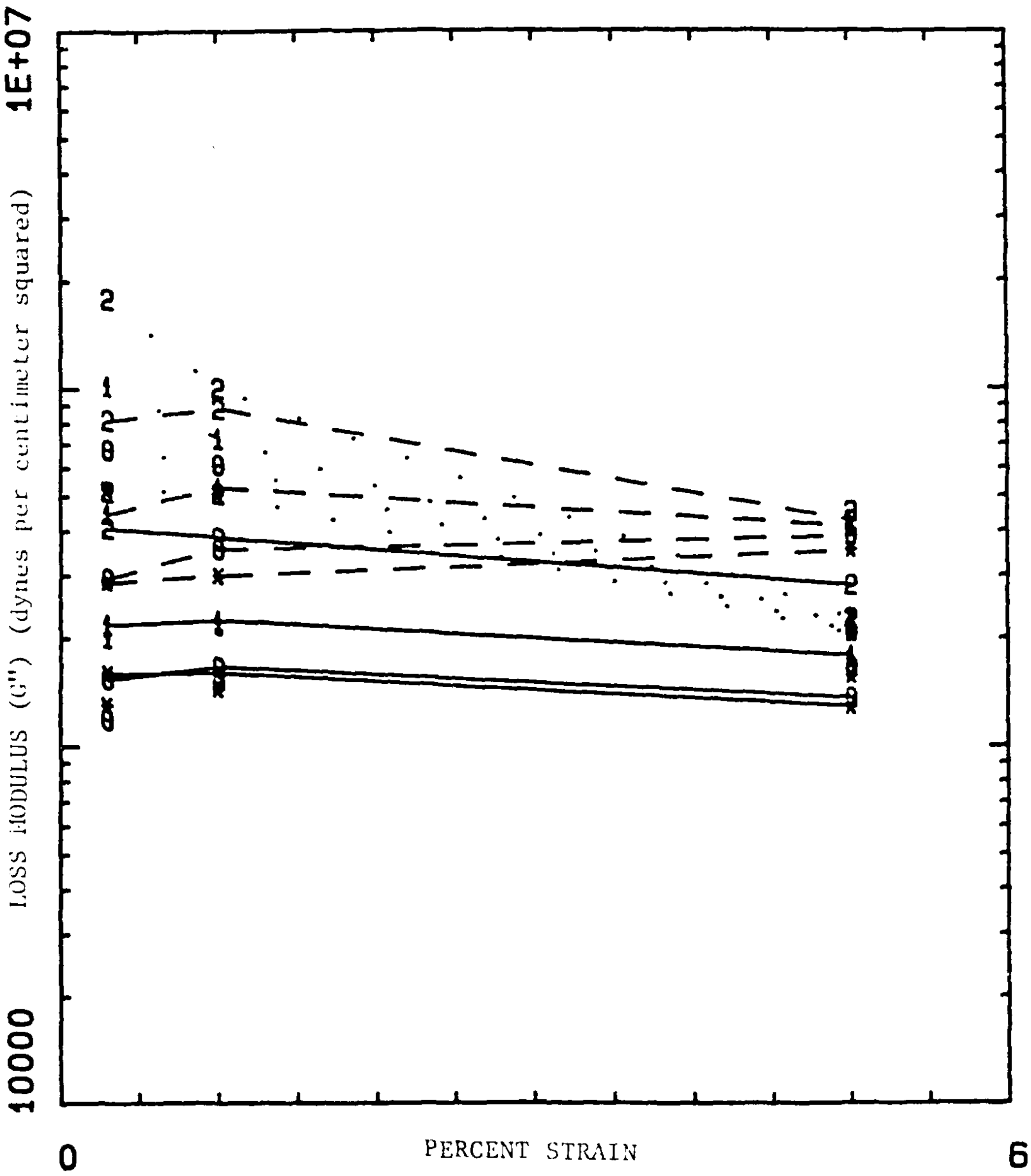


Figure 3.24. Loss Modulus vs. Percent Strain for PEA-PBLG IPN's with One Weight Percent PBLG.
Frequency (rad/sec): 0.1 (*), 1.0 (0),
10.0 (1), 100.0 (2)
Wt. % EDA: 0 ( ), 1 (———), 5 (- - -),
10 (.....)

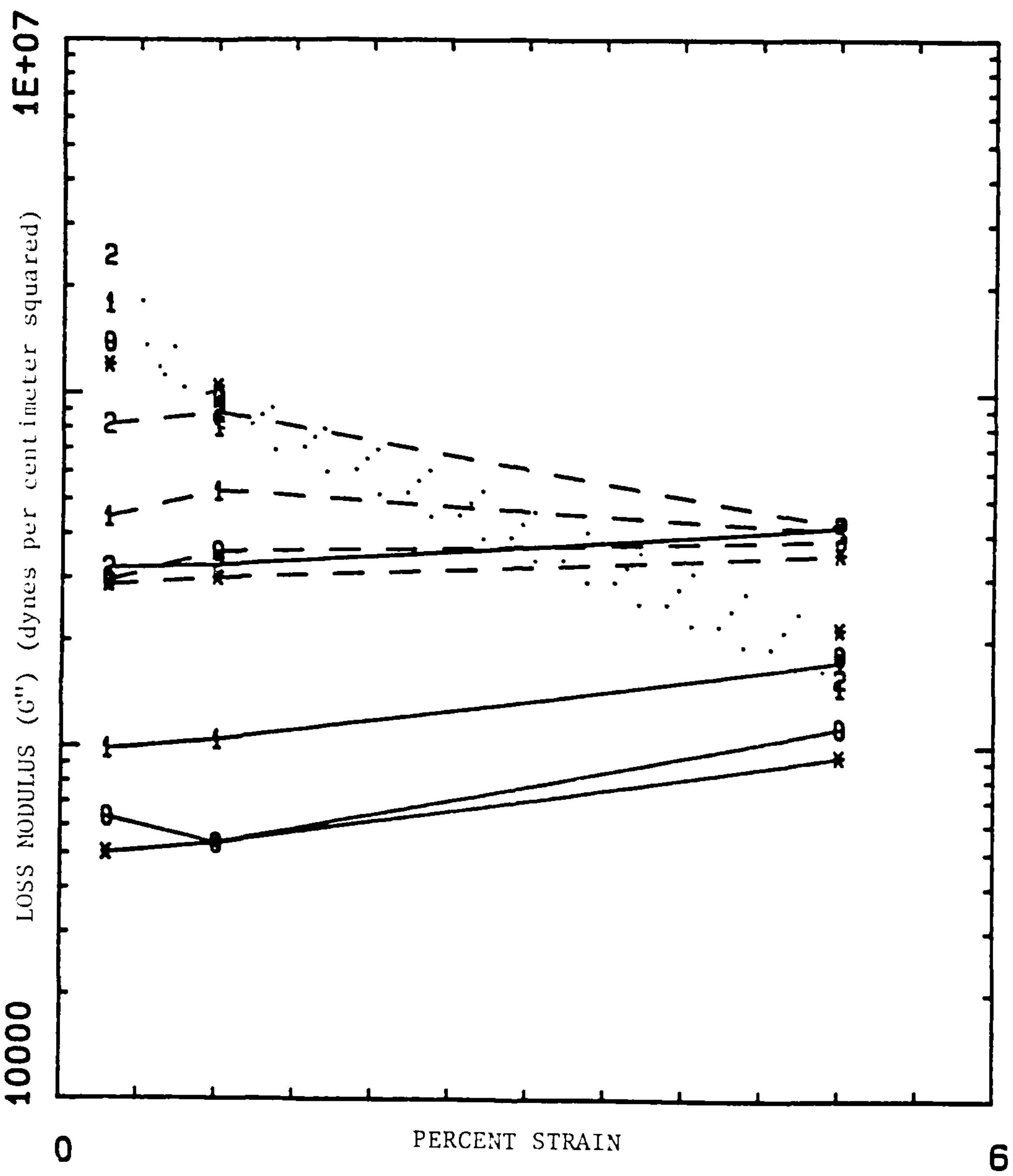


Figure 3.25. Loss Modulus vs. Percent Strain for PEA-PBLG IPN's with Five Weight Percent EDA.
Frequency (rad/sec): 0.1 (*), 1.0 (0),
10.0 (1), 100.0 (2)
Wt. % PBLG: 0 (———), 1 (- - -), 25 (.....)

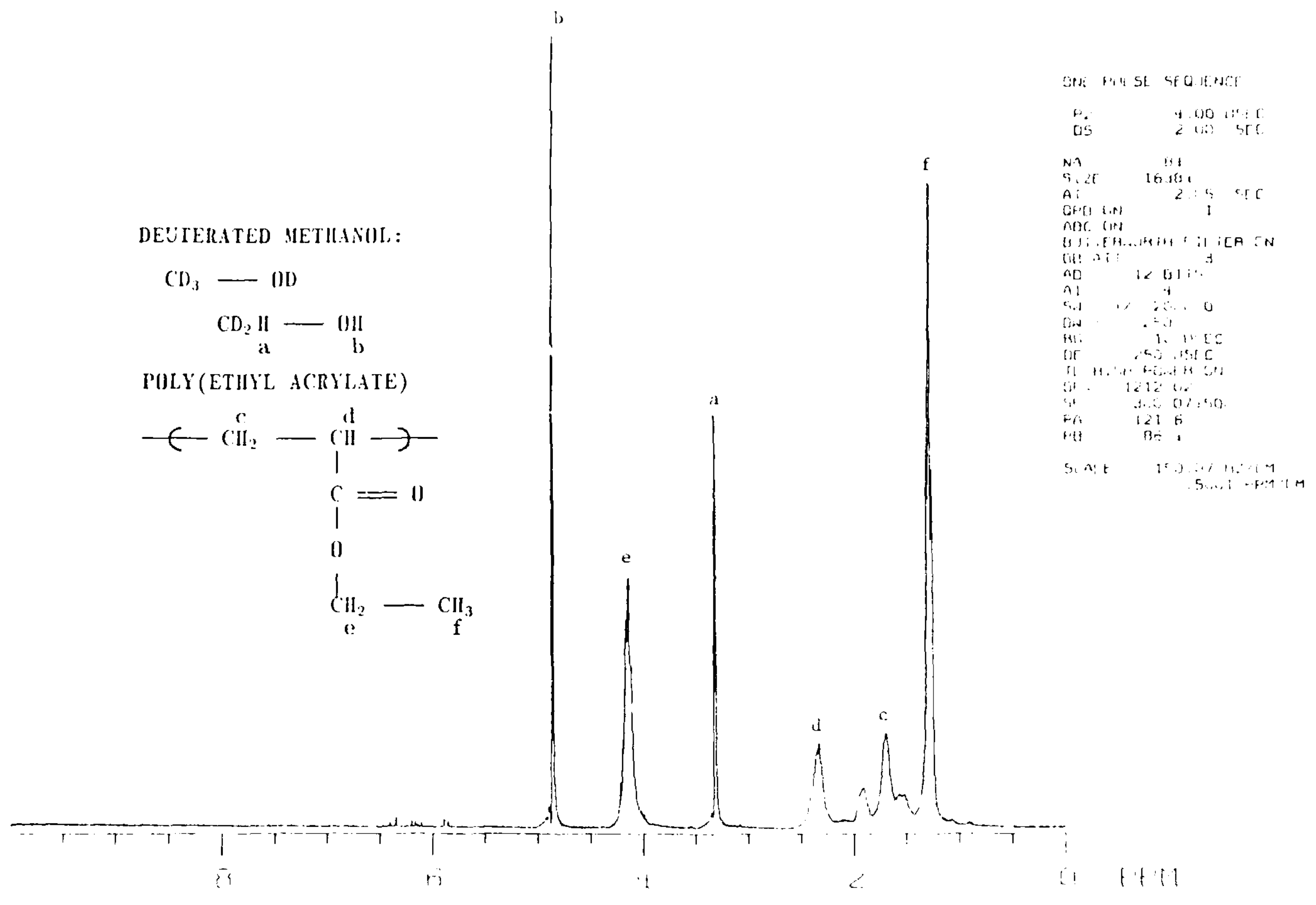


Figure 3.26. NMR Spectrum of Commercial PEA.

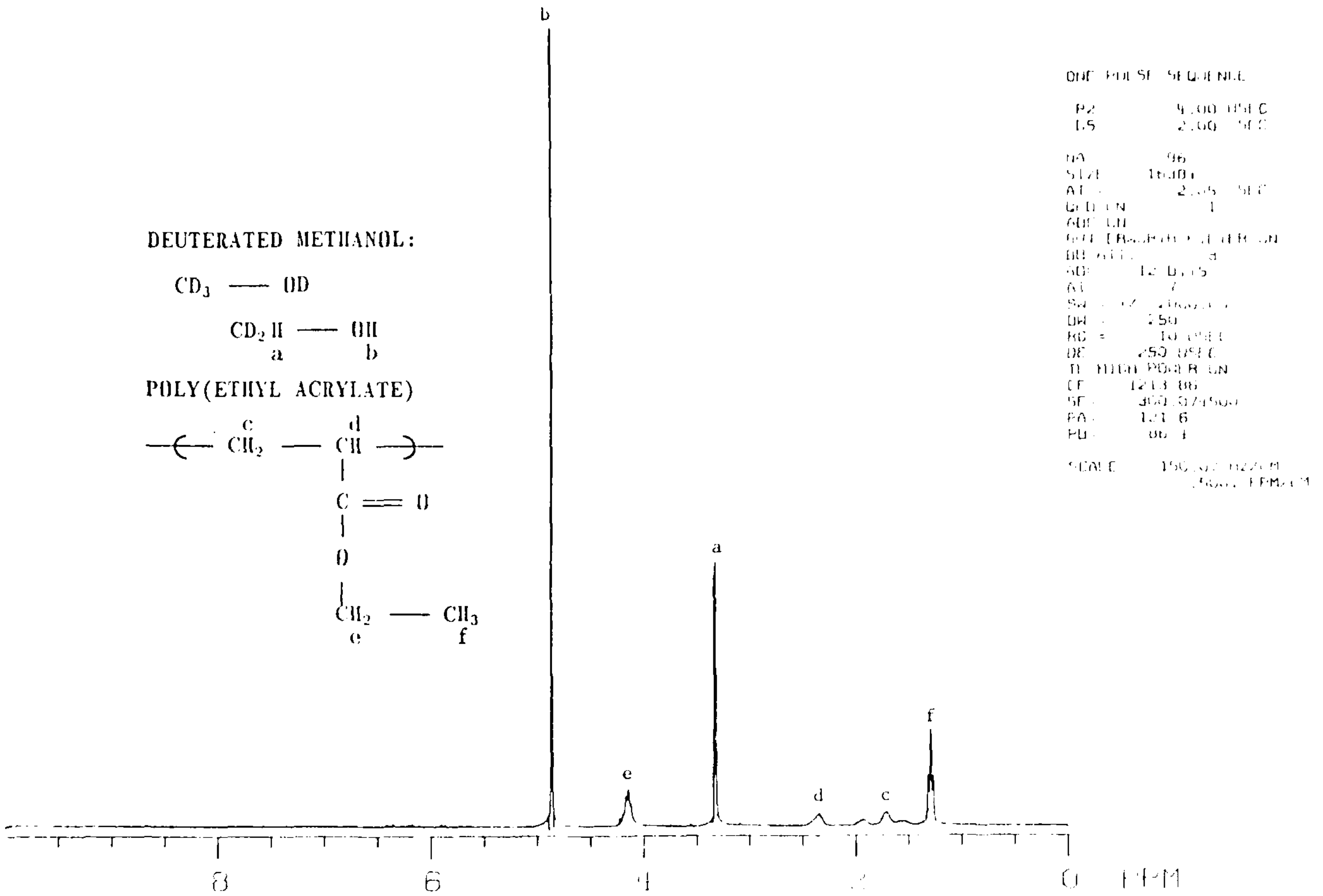


Figure 3.27. NMR Spectrum of Laboratory PEA.

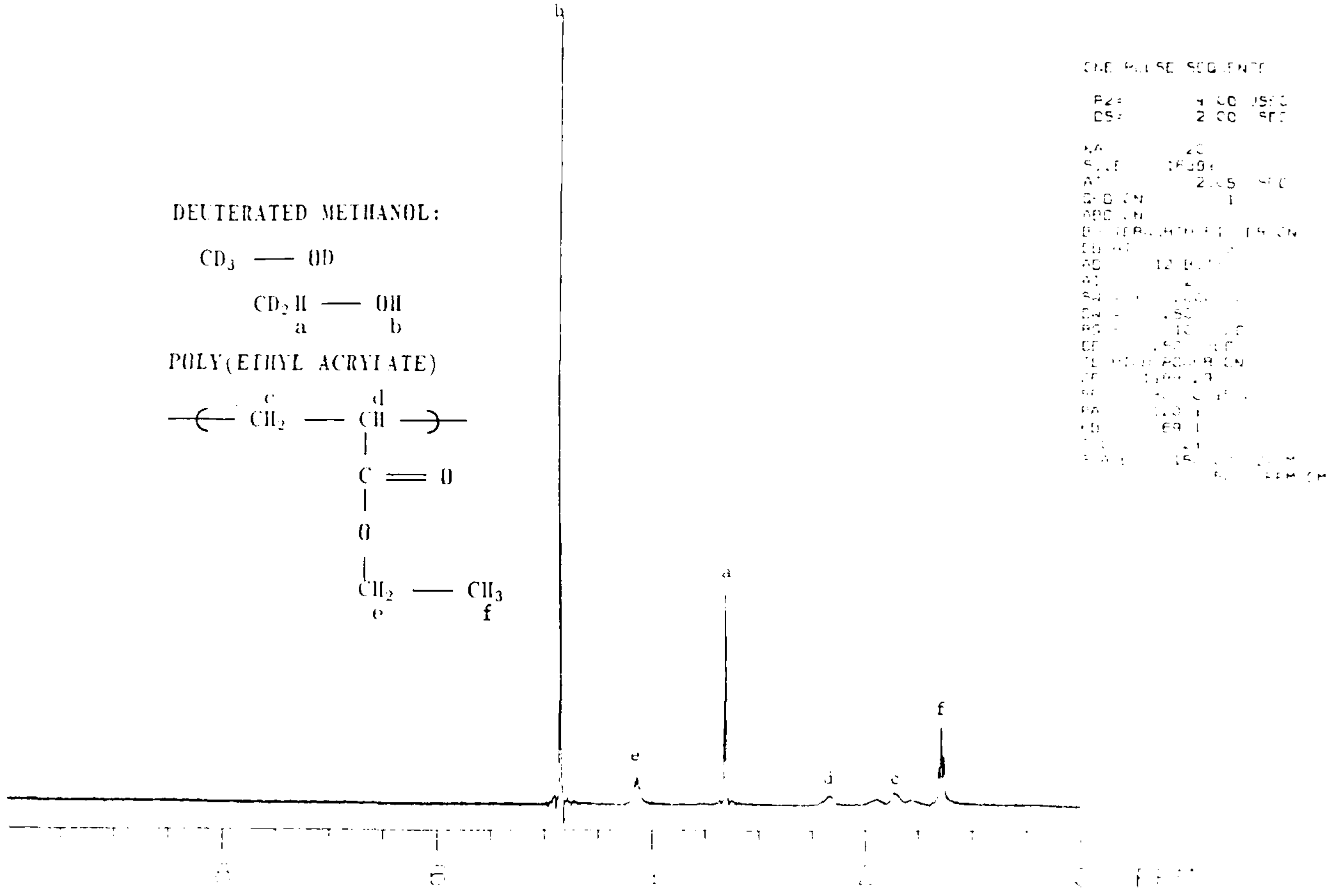


Figure 3.28. NMR Spectrum of Laboratory PEA Made in the Presence of PBLG.

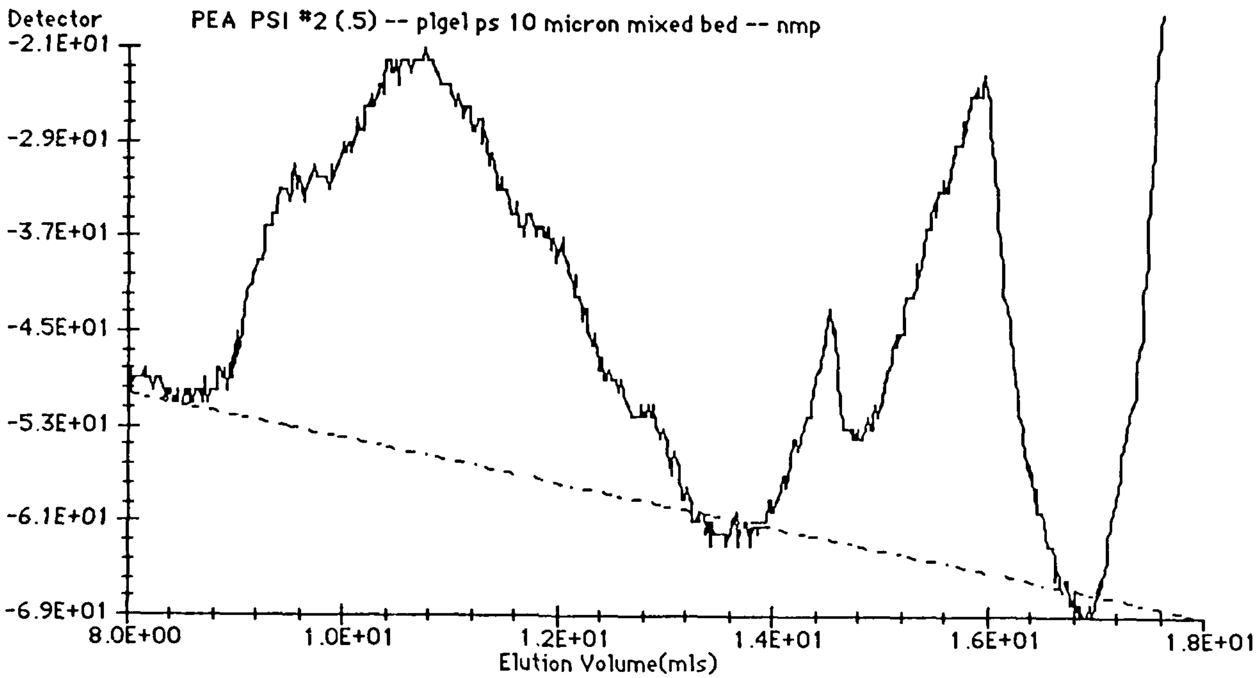


Figure 3.29. Signal vs. Elution Volume for Commercial PEA.

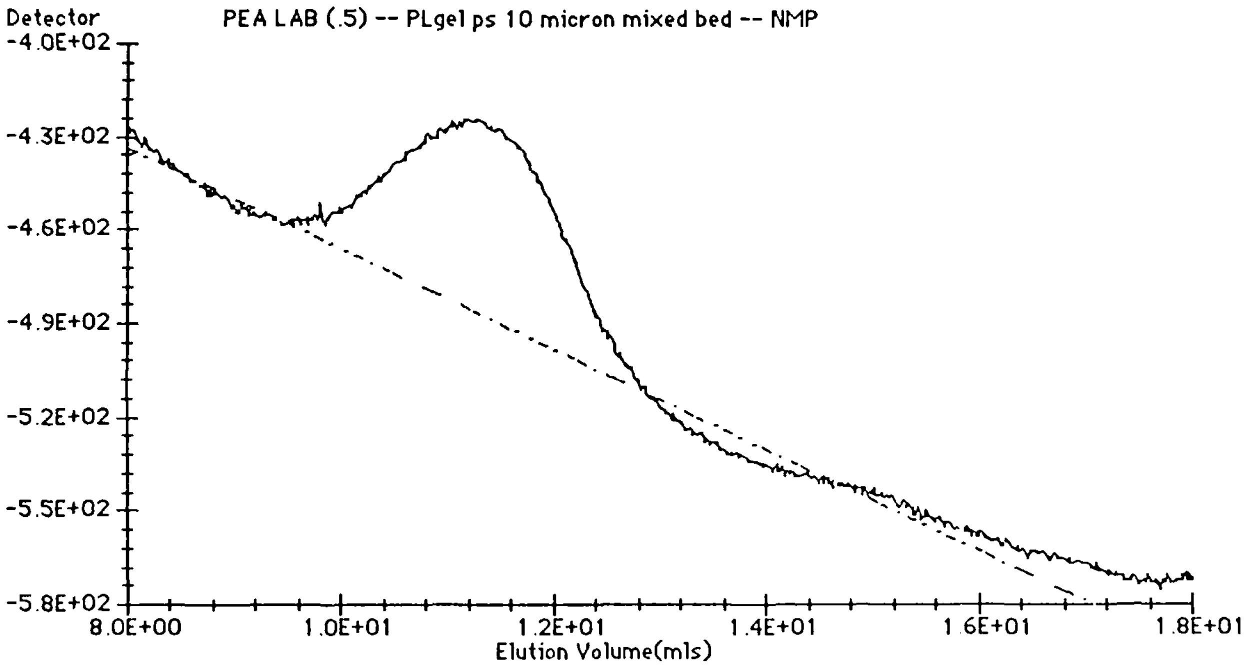


Figure 3.30. Signal vs. Elution Volume for Laboratory PEA.

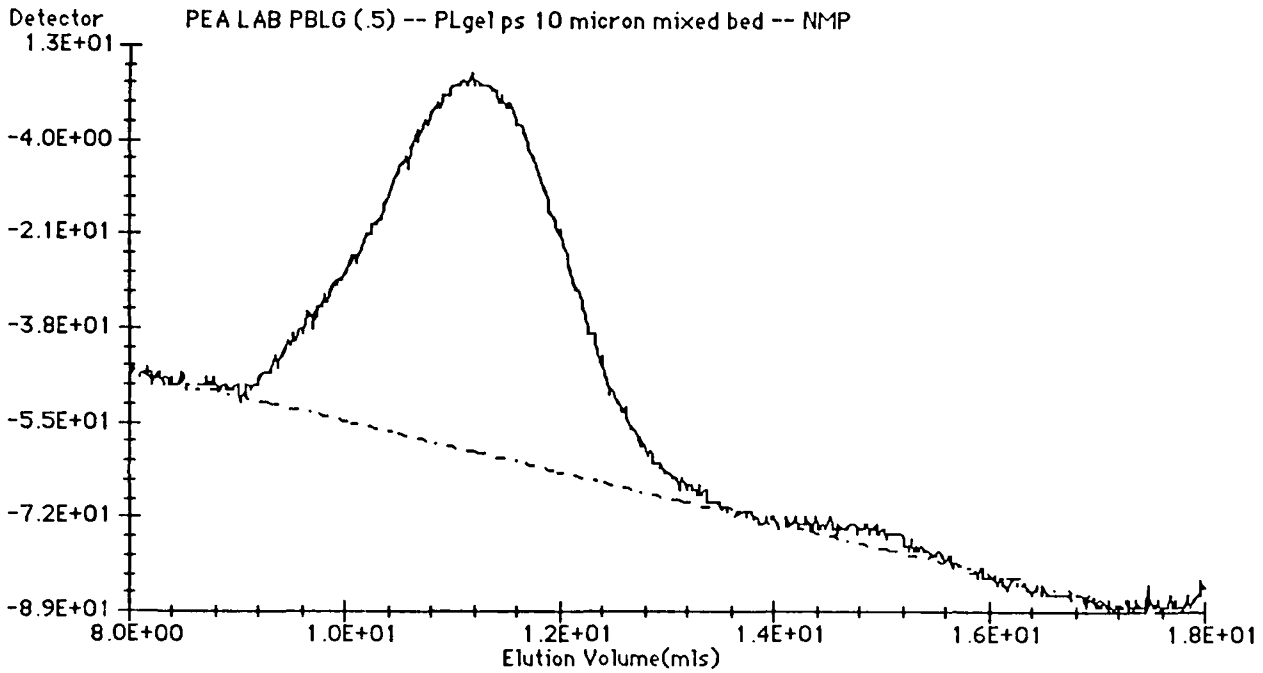


Figure 3.31. Signal vs. Elution Volume for Laboratory PEA Made in the Presence of PBLG.

CHAPTER FOUR: CONCLUSIONS

The ability to form a polymer network from a rigid rod polymer-monomer solvent gel has been shown. The use of a photoinitiator to initiate the polymerization of the monomer allows better control of the process than the use of a strictly thermal initiator. The use of a photoinitiator leads to a hugh molecular weight PEA portion of the sample without inducing further phase separation.

In the study of the dynamic properties of the three different catagories of samples, identification of the contribution from the separate constituents of the sample to the storage and loss moduli was made. The rheological studies indicate that G′ is controlled by the PBLG concentration in the EA-PBLG gels. For the PEA-PBLG films, the samples at or below three weight percent PBLG appeared to have G′ primarily controlled by PBLG concentration. The 25 weight percent PBLG sample followed suit below 5.0 % strain; however, at 5.0 % strain it exhibited a sharp decline in storage modulus. This might be due to a break down of the rigid rod structure of the PBLG at that strain. However, the recovery of the storage modulus upon returning to low strains was from 50 to over 90 % of its original value for the 25 weight percent PBLG film. Thus, the film appears to suffer little permanent structural damage. The four and five weight percent PBLG films tended to be slightly lower than from the three weight percent film, however the entire range of values for G′ from one to five weight percent PBLG was small. Thus, although the decline in G′ may be due to a minor break down in the PBLG structure at these PBLG concentrations, any effects are small and less than the experimental error in the rheological measurements.

The IPN's storage moduli were controlled by the PBLG concentration at 0.3 % strain. At higher strain, the effects of five or ten weight percent EDA could be observed. A drop in storage modulus was observed. This also may be attributed to the breaking of the sample structure at high strain; however, here it may be the crosslinked PEA portion of the sample being broken at 1.0 % strain as 1.0 % strain did not appear to decrease G′ as drastically in the gels or films. Breakage of both the crosslinked PEA and PBLG may occur at 5.0 % strain. G′ shows a drastic decrease with increasing strain when the PBLG concentration is increased 25 fold and the EDA is at 5 weight percent. G′ drops almost an order of magnitude for a three fold increase in strain and ten fold for a five fold percent strain increase. This sample's rigidity makes it possible that the higher strain causes substantial damage to the network structure.

The loss modulus' response in EA-PBLG gels and films was dominated by the PBLG concentration also. Small increases in G″ with a thousand fold increase frequency are present, while increasing strain brings slight decreases in the loss modulus. However, a four to six fold increase in PBLG concentration yields an increase from three to ten fold in the loss modulus for both gels and films.

The IPN's loss moduli show a modest two fold increase when crosslinker is increased from one to five weight percent, but the increase from five to ten weight percent yields a drop of three to four fold in G″. A 25 fold increase in PBLG concentration with constant crosslinker concentration brings a three fold increase at 0.3 % strain, virtually no change at 1.0 % strain, and a two fold decrease at 5.0 % strain. The strain dependence of the 25 weight percent PBLG-five weight percent EDA sample showed a ten fold decrease over sixteen fold increase in strain. This was less than G′.

The NMR spectra support the conclusion that little or no grafting between the PEA and PBLG was present in the portion that was methanol soluble during the polymerization of the ethyl acrylate. Additional studies as to the amount of grafting of PEA on to PBLG should be conducted. A possible scheme to attain more information on the presence of grafting between the PEA and PBLG would be to take the portion of the PEA-PBLG sample which did not dissolve in methanol and dissolve it in a good solvent for PBLG. By comparing that spectrum with a spectrum of pure PBLG in the same solvent, an idea of the amount of PEA grafting to the PBLG could be obtained.

The GPC spectra show that a large molecular weight PEA sample forms when a photochemical initiator is used. Though the method of initiation is unknown for the commercial sample, the molecular weight is much lower. This suggests that photochemical initiation produces a small number of free radicals which terminate slowly in comparison to their propagation rate.

Also, a calculation of the radius of gyration, r_g, can be made from the best available data for both PEA and PS. Using the molecular weight of a monomer segment, M^* (104 for PS and 100 for PEA), their characteristic ratios, C (10 for PS, about 9 for PEA), and a arbitrary molecular weight, M (2 million), a comparison can be made. Assuming both of the backbone segments to be a carbon-carbon bond long, l (1.5 angstroms), and the number of bonds, n, to be twice the number of monomeric units then using the relationships below (EQN's 4.1-4.3), the radii of gyration are 380 and 367 angstroms for PS and PEA, respectively. This means that the actual PEA molecular weights are most likely slightly less than those from the GPC chromatograph. The solvent goodness for each of the polymers may change the relative values.

$n = 2(M/M^*)$ EQN 4.1

$r^2 = C\, n\, l^2$ EQN 4.2

$r_g^2 = r^2/6$ EQN 4.3

The swelling data show that while crosslinking the PEA leads to significant swelling, the PEA-PBLG network is capable of swelling also. The PBLG structure alone, however, will not maintain the integrity of PEA-PBLG films shape. Additionally, the amount of crosslinker present in the sample inversely relates to the amount of swelling the sample does in methanol.

Leaching rate of the IPN's reaches a maximum much sooner than an uncrosslinked sample. Also, the amount of leachable material for an IPN is far less than for the linear PEA-PBLG samples. This indicates that the crosslinked PEA forms a much tighter network than the linear PEA-PBLG films. Correspondingly, the pore size of the linear PEA-PBLG films is much larger than that of the crosslinked PEA-PBLG IPN's. By assuming the 48 hour data to be 100 percent of the leachable material, the four hour data and EQN 2.1 can be used to estimate a diffusion coefficient. With a sample thickness of two millimeters, h equals 0.1 centimeters, and D ($\times 10^{-8}$) equals 1.8, 5.4, and 8.3 for the five weight percent EDA IPN, the one weight percent PBLG film, and the three and five weight percent PBLG films, respectively. These appear reasonable when compared to the proposed values.

The combining of rigid rod and random coil polymers continues to be a field where there is much progress to be made. This study only highlights the fact that interpenetrating networks of polymers can be vastly different based on the sequence of steps and conditions used in the formation of the network.

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APPENDIX

Table A.1
List of Samples for Which Rheological Data is Included in Table A.2

ETHYL ACRYLATE-PBLG GELS

SAMPLE	% AIBN*	% PBLG*	% EDA*	RXN T	MM WD	MW PBLG
1,I	0.00	0.99	0.00	N/A	2	343
2,I-D	0.00	1.00	0.00	N/A	1	343
3,I	0.00	3.96	0.00	N/A	1	120
4,I	0.00	3.94	0.00	N/A	2	343
5,I	0.00	24.99	0.00	N/A	2	120

LINEAR PEA-PBLG FILMS

SAMPLE	% AIBN*	% PBLG*	% EDA*	RXN T	MM WD	MW PBLG
6,I	0.26	0.0	0.0	B	1	N/A
7,I	0.26	1.03	0.0	C	2	165
8,D	0.26	1.03	0.0	A	1	165
9,I	0.27	0.99	0.0	B	2	343
10,I	0.23	1.93	0.0	B	1	343
11,D	0.23	2.08	0.0	A	1	165
12,I	0.24	2.04	0.0	B	2	343
13,I	0.28	2.91	0.0	A	1	165
14,I-D	0.26	2.98	0.00	C	2	120
15,I-D	0.24	3.99	0.00	B	2	120
16,I-D	0.24	3.99	0.00	C	2	120
17,I	0.24	4.71	0.0	A	2	165
18,I-D	0.28	5.01	0.00	C	2	120
19,I-D	0.25	24.98	0.00	B	2	120

CROSSLINKED PEA-PBLG IPN'S

SAMPLE	% AIBN*	% PBLG*	% EDA*	RXN T	MM WD	MW PBLG
20,I	0.26	0.0	0.98	B	1	N/A
21,I	0.28	0.0	4.99	B	1	N/A
22,I	0.23	0.0	5.04	A	1	N/A
23,I-D	0.23	0.00	9.89	C	1	N/A
24,I	0.22	1.03	1.04	B	2	343
25,I	0.25	1.00	1.00	A	1	343
26,I	0.23	0.98	5.13	B	2	343
27,I	0.15	1.11	5.26	B	2	343
28,I	0.20	0.98	10.30	C	1	343
29,I-D	0.24	1.00	9.91	B	2	343
30,I-D	0.25	24.98	5.06	B	2	120

* ALL % ARE WEIGHT PERCENT OF TOTAL MIXTURE

I represents taking data at 0.3, then 1.0, then 5.0 % strain.

D represents taking data at 5.0, then 1.0, then 0.3 % strain.

RXN T represents reaction time window:
A: 4 to 6 hours
B: 16 to 20 hours
C: over 40 hours

Table A.2
Rheological Data for Selected Gel, Film, and IPN Samples.
(Sample Description from Table A.1)

Storage Moduli for Ethyl Acrylate - PBLG Gels at Various Weight Percent PBLG and Strains.
(All Moduli Values in Dynes per Centimeter Squared)

SAMPLE FREQ (rad/s)	1I	2I	2D	3I	4I	5I
0.3 PERCENT STRAIN						
.1000	4.801E4	4.968E4	2.020E4	2.297E5	2.210E5	1.398E6
.2155	7.795E4	5.957E4	1.180E4	2.490E5	2.153E5	1.460E6
.4642	6.741E4	4.692E4	2.554E4	2.775E5	2.579E5	1.735E6
1.000	7.839E4	5.857E4	4.208E4	2.977E5	2.704E5	1.744E6
2.155	8.041E4	5.951E4	3.965E4	2.980E5	2.866E5	1.738E6
4.642	8.359E4	6.357E4	4.220E4	3.125E5	2.996E5	1.757E6
10.00	8.834E4	6.561E4	4.307E4	3.263E5	3.218E5	1.769E6
21.54	9.249E4	6.923E4	4.497E4	3.391E5	3.388E5	1.829E6
46.41	9.607E4	7.091E4	4.639E4	3.524E5	3.585E5	1.850E6
100.0	9.876E4	7.519E4	4.911E4	3.656E5	3.766E5	1.950E6
1.0 PERCENT STRAIN						
.1000	5.393E4	3.154E4	2.336E4	2.242E5	2.039E5	8.756E5
.2155	5.328E4	3.713E4	2.931E4	2.334E5	2.043E5	8.000E5
.4642	6.388E4	4.360E4	3.118E4	2.432E5	2.135E5	7.803E5
1.000	6.717E4	5.014E4	3.443E4	2.495E5	2.247E5	7.361E5
2.155	7.088E4	5.135E4	3.711E4	2.575E5	2.347E5	7.484E5
4.642	7.520E4	5.336E4	3.875E4	2.656E5	2.495E5	7.420E5
10.00	7.747E4	5.419E4	4.044E4	2.748E5	2.625E5	7.605E5
21.54	8.057E4	5.578E4	4.211E4	2.841E5	2.772E5	8.104E5
46.41	8.347E4	5.775E4	4.369E4	2.960E5	2.933E5	9.402E5
100.0	8.648E4	6.071E4	4.625E4	3.132E5	3.119E5	1.059E6
5.0 PERCENT STRAIN						
.1000	3.912E4	1.826E4	1.841E4	7.906E4	1.128E5	7.163E4
.2155	4.236E4	2.092E4	2.020E4	7.735E4	1.063E5	1.170E5
.4642	4.298E4	2.115E4	1.984E4	7.695E4	1.068E5	0.000E0
1.000	4.398E4	2.201E4	1.935E4	7.774E4	1.085E5	7.578E4
2.155	4.521E4	2.058E4	1.776E4	7.929E4	1.137E5	8.067E4
4.642	4.673E4	1.919E4	1.620E4	8.180E4	1.208E5	9.388E4
10.00	4.801E4	1.690E4	1.460E4	8.375E4	1.290E5	1.115E5
21.54	5.018E4	1.551E4	1.398E4	8.587E4	1.376E5	1.428E5
46.41	5.327E4	1.617E4	1.531E4	9.132E4	1.461E5	1.802E5
100.0	5.702E4	2.051E4	1.961E4	9.693E4	1.527E5	2.457E5

Loss Moduli for Ethyl Acrylate - PBLG Gels at Various Weight Percent PBLG and Strains.
(All Moduli Values in Dynes per Centimeter Squared)

SAMPLE FREQ (rad/s)	1I	2I	2D	3I	4I	5I
0.3 PERCENT STRAIN						
.1000	2.685E4	1.478E4	1.170E4	4.049E4	1.486E4	6.760E5
.2155	2.070E4	1.422E4	7.277E3	6.983E4	6.319E4	8.390E5
.4642	1.141E4	1.399E4	1.673E4	2.816E4	4.050E4	2.765E5
1.000	1.292E4	1.626E4	2.042E3	2.828E4	4.155E4	3.089E5
2.155	9.098E3	1.376E4	2.846E3	3.464E4	4.913E4	3.307E5
4.642	1.557E4	7.225E3	5.598E3	3.524E4	5.306E4	3.304E5
10.00	7.532E3	7.972E3	5.337E3	3.473E4	4.844E4	3.368E5
21.54	8.082E3	8.168E3	5.412E3	3.510E4	4.747E4	3.467E5
46.41	8.400E3	7.936E3	5.943E3	3.509E4	5.150E4	4.125E5
100.0	8.812E3	7.600E3	5.542E3	3.316E4	4.750E4	3.459E5
1.0 PERCENT STRAIN						
.1000	1.988E4	1.466E4	1.221E4	3.754E4	4.684E4	5.791E5
.2155	1.404E4	1.606E4	2.969E2	4.183E4	5.321E4	5.532E5
.4642	1.424E4	1.476E4	6.733E3	4.388E4	4.898E4	5.733E5
1.000	1.183E4	9.019E3	6.930E3	4.361E4	5.043E4	5.370E5
2.155	9.892E3	9.690E3	5.244E3	4.374E4	5.690E4	6.117E5
4.642	9.069E3	9.729E3	7.130E3	4.490E4	5.939E4	6.302E5
10.00	8.800E3	9.920E3	7.340E3	4.658E4	6.140E4	6.485E5
21.54	8.552E3	1.031E4	7.362E3	4.736E4	6.268E4	6.892E5
46.41	7.904E3	1.061E4	7.548E3	4.809E4	6.578E4	8.130E5
100.0	8.569E3	1.123E4	8.323E3	5.018E4	6.627E4	8.632E5
5.0 PERCENT STRAIN						
.1000	1.781E4	1.141E4	9.960E3	6.185E4	4.913E4	1.762E5
.2155	1.529E4	1.016E4	9.547E3	6.217E4	4.872E4	1.630E5
.4642	1.664E4	1.043E4	9.459E3	6.378E4	5.257E4	0.000E0
1.000	1.585E4	1.040E4	9.344E3	6.712E4	5.890E4	1.920E5
2.155	1.632E4	1.055E4	1.006E4	7.059E4	6.344E4	2.059E5
4.642	1.679E4	1.107E4	1.056E4	7.474E4	6.867E4	2.298E5
10.00	1.708E4	1.220E4	1.167E4	7.688E4	7.240E4	2.594E5
21.54	1.702E4	1.400E4	1.328E4	7.925E4	7.478E4	3.082E5
46.41	1.662E4	1.689E4	1.586E4	8.343E4	7.595E4	3.659E5
100.0	1.593E4	2.028E4	1.894E4	8.848E4	7.784E4	4.352E5

Storage Moduli for PEA-PBLG Films at Various Weight Percent PBLG and Strains. (All Moduli values in Dynes per Centimeter Squared)

SAMPLE FREQ (rad/s)	6I	7I	8D	9I	10I	11D
0.3 PERCENT STRAIN						
.1000	4.889E5	7.815E5	8.451E5	1.174E6	1.096E6	7.374E5
.2155	4.670E5	8.669E5	8.359E5	1.226E6	1.224E6	7.652E5
.4642	5.037E5	8.694E5	8.843E5	1.316E6	1.290E6	8.180E5
1.000	5.138E5	9.401E5	9.468E5	1.387E6	1.373E6	8.778E5
2.155	5.083E5	9.803E5	9.761E5	1.447E6	1.420E6	9.101E5
4.642	5.289E5	1.043E6	1.026E6	1.531E6	1.528E6	9.569E5
10.00	5.397E5	1.115E6	1.086E6	1.623E6	1.600E6	1.026E6
21.54	5.579E5	1.196E6	1.163E6	1.745E6	1.713E6	1.107E6
46.41	5.834E5	1.305E6	1.280E6	1.919E6	1.846E6	1.225E6
100.0	6.320E5	1.459E6	1.396E6	2.125E6	2.000E6	1.364E6
1.0 PERCENT STRAIN						
.1000	4.676E5	7.083E5	6.417E5	1.086E6	9.244E5	5.517E5
.2155	4.744E5	7.484E5	6.683E5	1.135E6	9.688E5	5.732E5
.4642	4.732E5	7.824E5	7.142E5	1.185E6	1.021E6	6.143E5
1.000	4.787E5	8.286E5	7.501E5	1.235E6	1.073E6	6.340E5
2.155	4.836E5	8.765E5	7.984E5	1.299E6	1.118E6	6.818E5
4.642	4.855E5	9.300E5	8.416E5	1.349E6	1.169E6	7.226E5
10.00	4.942E5	9.940E5	9.015E5	1.420E6	1.183E6	7.754E5
21.54	5.085E5	1.077E6	9.768E5	1.518E6	1.219E6	8.421E5
46.41	5.376E5	1.195E6	1.075E6	1.534E6	1.188E6	9.330E5
100.0	5.856E5	1.357E6	1.209E6	1.642E6	1.255E6	1.058E6
5.0 PERCENT STRAIN						
.1000	4.132E5	4.937E5	3.266E5	5.172E5	4.105E5	2.957E5
.2155	4.215E5	5.143E5	3.451E5	4.675E5	3.823E5	3.042E5
.4642	4.285E5	5.464E5	3.742E5	4.727E5	3.862E5	3.223E5
1.000	4.376E5	5.827E5	4.066E5	4.785E5	3.915E5	3.445E5
2.155	4.476E5	6.202E5	4.396E5	4.769E5	3.923E5	3.666E5
4.642	4.579E5	6.581E5	4.672E5	4.643E5	3.944E5	3.898E5
10.00	4.713E5	6.968E5	4.891E5	4.309E5	4.055E5	4.153E5
21.54	4.915E5	7.385E5	5.117E5	4.022E5	4.251E5	4.456E5
46.41	5.246E5	7.925E5	5.414E5	3.781E5	4.600E5	4.884E5
100.0	5.778E5	8.691E5	5.854E5	3.777E5	5.155E5	5.468E5

Loss Moduli for PEA - PBLG Films at Various Weight Percent PBLG and Strains.
(All Moduli Values in Dynes per Centimeter Squared)

SAMPLE FREQ (rad/s)	6I	7I	8D	9I	10I	11D
0.3 PERCENT STRAIN						
.1000	2.102E4	1.302E5	1.128E5	1.387E5	2.917E5	1.725E5
.2155	4.564E4	1.446E5	1.075E5	1.626E5	2.661E5	1.721E5
.4642	3.970E4	1.378E5	1.396E5	1.570E5	2.487E5	1.769E5
1.000	1.311E4	1.188E5	1.216E5	1.748E5	2.642E5	2.172E5
2.155	4.644E4	1.301E5	1.588E5	1.891E5	2.533E5	2.332E5
4.642	3.775E4	1.595E5	1.580E5	2.359E5	3.046E5	2.598E5
10.00	5.677E4	2.017E5	2.060E5	2.832E5	3.289E5	2.963E5
21.54	9.023E4	2.670E5	2.625E5	3.602E5	3.918E5	3.513E5
46.41	1.453E5	3.633E5	3.498E5	4.589E5	4.595E5	4.368E5
100.0	2.350E5	5.151E5	4.877E5	6.289E5	5.636E5	5.609E5
1.0 PERCENT STRAIN						
.1000	4.110E4	1.450E5	1.588E5	1.768E5	2.472E5	1.703E5
.2155	3.594E4	1.427E5	1.625E5	1.619E5	2.503E5	1.779E5
.4642	3.536E4	1.456E5	1.646E5	1.776E5	2.460E5	1.808E5
1.000	2.767E4	1.517E5	1.811E5	1.950E5	2.571E5	1.896E5
2.155	3.501E4	1.671E5	1.846E5	2.169E5	2.807E5	1.989E5
4.642	3.956E4	1.826E5	2.060E5	2.515E5	3.008E5	2.265E5
10.00	5.677E4	2.196E5	2.364E5	2.950E5	3.373E5	2.536E5
21.54	8.695E4	2.747E5	2.836E5	3.618E5	3.699E5	2.982E5
46.41	1.362E5	3.649E5	3.629E5	4.989E5	4.263E5	3.691E5
100.0	2.196E5	5.093E5	4.918E5	6.253E5	4.930E5	4.766E5
5.0 PERCENT STRAIN						
.1000	3.636E4	1.560E5	1.755E5	2.445E5	2.206E5	1.543E5
.2155	3.083E4	1.570E5	1.790E5	2.654E5	2.229E5	1.511E5
.4642	2.776E4	1.616E5	1.839E5	2.756E5	2.345E5	1.569E5
1.000	2.731E4	1.660E5	1.873E5	2.827E5	2.470E5	1.668E5
2.155	2.998E4	1.729E5	1.901E5	2.901E5	2.706E5	1.764E5
4.642	3.731E4	1.908E5	1.983E5	3.004E5	2.875E5	1.904E5
10.00	5.293E4	2.197E5	2.121E5	3.121E5	3.066E5	2.103E5
21.54	8.266E4	2.647E5	2.362E5	3.299E5	3.280E5	2.390E5
46.41	1.324E5	3.373E5	2.754E5	3.611E5	3.539E5	2.859E5
100.0	2.105E5	4.496E5	3.351E5	3.976E5	3.838E5	3.536E5

Storage Moduli for PEA-PBLG Films at Various
Weight Percent PBLG and Strains.
(All Moduli Values in Dynes per Centimeter Squared)

SAMPLE FREQ (rad/s)	12I	13I	14I	14D	15I	15D
0.3 PERCENT STRAIN						
.1000	1.031E6	2.102E6	1.588E6	1.530E6	1.600E6	1.529E6
.2155	1.098E6	2.174E6	1.719E6	1.653E6	1.666E6	1.687E6
.4642	1.129E6	2.326E6	1.925E6	1.733E6	1.785E6	1.809E6
1.000	1.188E6	2.411E6	2.010E6	1.853E6	1.891E6	1.933E6
2.155	1.257E6	2.605E6	2.084E6	1.913E6	2.054E6	2.031E6
4.642	1.302E6	2.798E6	2.225E6	2.034E6	2.167E6	2.169E6
10.00	1.368E6	2.963E6	2.361E6	2.177E6	2.322E6	2.349E6
21.54	1.443E6	3.246E6	2.539E6	2.376E6	2.542E6	2.582E6
46.41	1.555E6	3.586E6	2.884E6	2.884E6	2.946E6	3.015E6
100.0	1.733E5	4.109E6	3.348E6	3.534E6	3.472E6	3.561E6
1.0 PERCENT STRAIN						
.1000	5.610E5	1.079E6	8.023E5	7.869E5	7.596E5	7.120E5
.2155	5.561E5	1.061E6	8.467E5	7.904E5	8.000E5	7.663E5
.4642	5.670E5	1.130E6	8.533E5	7.938E5	8.476E5	8.334E5
1.000	5.810E5	1.203E6	9.024E5	8.067E5	9.019E5	8.866E5
2.155	6.011E5	1.282E6	9.115E5	8.534E5	9.660E5	9.524E5
4.642	6.180E5	1.360E6	9.492E5	9.068E5	1.012E6	1.020E6
10.00	6.439E5	1.435E6	9.870E5	9.955E5	1.060E6	1.087E6
21.54	6.709E5	1.535E6	1.059E6	1.145E6	1.110E6	1.166E6
46.41	7.116E5	1.681E6	1.203E6	1.389E6	1.226E6	1.298E6
100.0	7.752E5	1.910E6	1.546E6	1.797E6	1.421E6	1.583E6
5.0 PERCENT STRAIN						
.1000	2.782E5	1.128E5	1.375E5	1.795E5	2.110E5	2.149E5
.2155	2.840E5	1.222E5	1.246E5	1.803E5	2.235E5	2.282E5
.4642	2.996E5	1.403E5	1.192E5	1.733E5	2.518E5	2.602E5
1.000	3.156E5	1.525E5	1.210E5	1.725E5	2.673E5	2.787E5
2.155	3.311E5	1.639E5	1.262E5	1.757E5	2.799E5	2.931E5
4.642	3.446E5	1.687E5	1.436E5	1.919E5	2.877E5	3.056E5
10.00	3.560E5	1.642E5	1.798E5	2.316E5	2.981E5	3.162E5
21.54	3.658E5	1.485E5	2.341E5	2.863E5	3.063E5	3.296E5
46.41	3.818E5	1.359E5	3.086E5	3.574E5	3.180E5	3.447E5
100.0	4.339E5	1.323E5	3.891E5	3.985E5	3.477E5	3.700E5

Loss Moduli for PEA - PBLG Films at Various Weight Percent PBLG and Strains.
(All Moduli Values in Dynes per Centimeter Squared)

SAMPLE FREQ (rad/s)	12I	13I	14I	14D	15I	15D
0.3 PERCENT STRAIN						
.1000	3.246E5	5.680E5	5.362E5	4.841E5	6.249E5	4.660E5
.2155	3.003E5	5.484E5	5.966E5	5.429E5	4.954E5	5.537E5
.4642	3.214E5	5.869E5	5.334E5	6.212E5	5.413E5	5.549E5
1.000	3.337E5	6.201E5	6.216E5	6.437E5	5.901E5	6.269E5
2.155	3.598E5	6.477E5	7.325E5	7.146E5	6.574E5	7.252E5
4.642	3.908E5	7.177E5	8.336E5	8.218E5	7.714E5	7.962E5
10.00	4.412E5	8.333E5	9.901E5	9.758E5	8.808E5	8.774E5
21.54	5.082E5	9.749E5	1.209E6	1.194E6	1.037E6	1.031E6
46.41	6.317E5	1.175E6	1.550E6	1.528E6	1.255E6	1.246E6
100.0	8.041E5	1.454E6	2.012E6	1.940E6	1.556E6	1.535E6
1.0 PERCENT STRAIN						
.1000	2.822E5	6.454E5	5.796E5	4.662E5	5.766E5	5.391E5
.2155	2.783E5	6.585E5	5.573E5	4.946E5	5.574E5	5.442E5
.4642	2.873E5	6.685E5	5.858E5	5.388E5	5.785E5	5.825E5
1.000	2.991E5	7.014E5	6.541E5	5.930E5	6.182E5	6.300E5
2.155	3.016E5	7.033E5	7.178E5	6.324E5	6.715E5	6.648E5
4.642	3.085E5	7.245E5	7.773E5	6.999E5	7.145E5	7.178E5
10.00	3.166E5	7.683E5	8.656E5	7.828E5	7.631E5	7.822E5
21.54	3.379E5	8.435E5	9.826E5	9.250E5	8.505E5	8.793E5
46.41	3.819E5	9.847E5	1.205E6	1.164E6	1.007E6	1.051E6
100.0	4.618E5	1.191E6	1.566E6	1.540E6	1.265E6	1.330E6
5.0 PERCENT STRAIN						
.1000	1.300E5	1.738E5	2.451E5	2.333E5	2.468E5	2.347E5
.2155	1.319E5	1.889E5	2.470E5	2.324E5	2.565E5	2.512E5
.4642	1.339E5	2.009E5	2.583E5	2.406E5	2.632E5	2.597E5
1.000	1.347E5	2.113E5	2.706E5	2.519E5	2.678E5	2.713E5
2.155	1.352E5	2.174E5	2.904E5	2.726E5	2.715E5	2.829E5
4.642	1.357E5	2.212E5	3.179E5	3.052E5	2.820E5	2.988E5
10.00	1.425E5	2.249E5	3.595E5	3.587E5	3.036E5	3.164E5
21.54	1.612E5	2.271E5	4.193E5	4.339E5	3.350E5	3.513E5
46.41	1.944E5	2.431E5	5.234E5	5.445E5	3.885E5	4.081E5
100.0	2.391E5	2.783E5	6.522E5	6.715E5	4.695E5	4.896E5

Storage Moduli for PEA-PBLG Films at Various Weight Percent PBLG and Strains.
(All Moduli Values in Dynes per Centimeter Squared)

SAMPLE FREQ (rad/s)	16I	16D	18I	18D	19I	19D
0.3 PERCENT STRAIN						
.1000	1.146E6	1.192E6	1.282E6	1.196E6	2.962E6	3.514E6
.2155	1.197E6	1.075E6	1.371E6	1.275E6	3.723E6	3.881E6
.4642	1.219E6	1.084E6	1.413E6	1.345E6	4.069E6	4.124E6
1.000	1.329E6	1.165E6	1.437E6	1.389E6	4.401E6	4.423E6
2.155	1.425E6	1.285E6	1.522E6	1.469E6	4.683E6	4.725E6
4.642	1.533E6	1.363E6	1.583E6	1.494E6	5.043E6	5.039E6
10.00	1.681E6	1.481E6	1.674E6	1.563E6	5.325E6	5.322E6
21.54	1.873E6	1.643E6	1.760E6	1.617E6	5.734E6	5.619E6
46.41	2.168E6	1.924E6	1.960E6	1.800E6	6.417E6	6.116E6
100.0	2.563E6	2.325E6	2.237E6	2.130E6	7.311E6	6.845E6
1.0 PERCENT STRAIN						
.1000	8.288E5	6.888E5	7.247E5	6.130E5	1.902E6	1.609E6
.2155	8.899E5	7.170E5	7.174E5	6.311E5	1.990E6	1.762E6
.4642	9.368E5	7.794E5	7.368E5	6.506E5	2.082E6	1.919E6
1.000	9.984E5	8.364E5	7.437E5	6.749E5	2.160E6	2.059E6
2.155	1.078E6	8.971E5	7.664E5	7.018E5	2.231E6	2.040E6
4.642	1.150E6	9.753E5	7.901E5	7.273E5	2.274E6	1.980E6
10.00	1.250E6	1.064E6	8.127E5	7.657E5	2.239E6	1.868E6
21.54	1.373E6	1.174E6	8.466E5	8.115E5	2.103E6	1.743E6
46.41	1.549E6	1.320E6	9.079E5	8.882E5	2.079E6	1.333E6
100.0	1.819E6	1.573E6	1.007E6	1.020E6	2.114E6	1.106E6
5.0 PERCENT STRAIN						
.1000	2.572E5	2.576E5	1.859E5	1.917E5	2.731E5	2.436E5
.2155	2.835E5	3.134E5	2.046E5	2.162E5	2.693E5	2.623E5
.4642	3.352E5	3.534E5	2.185E5	2.311E5	2.925E5	2.370E5
1.000	3.689E5	3.841E5	2.241E5	2.379E5	2.288E5	2.178E5
2.155	3.802E5	3.914E5	2.191E5	2.347E5	2.015E5	1.877E5
4.642	3.659E5	3.760E5	2.031E5	2.269E5	1.693E5	1.559E5
10.00	3.127E5	3.415E5	1.689E5	2.098E5	1.374E5	1.275E5
21.54	2.776E5	3.056E5	1.560E5	1.983E5	1.152E5	1.070E5
46.41	2.876E5	3.020E5	1.650E5	2.110E5	9.203E4	8.559E4
100.0	1.491E5	1.475E5	2.256E5	2.589E5	7.132E4	6.435E4

Loss Moduli for PEA - PBLG Films at Various Weight Percent PBLG and Strains.

(All Moduli Values in Dynes per Centimeter Squared)

SAMPLE FREQ (rad/s)	16I	16D	18I	18D	19I	19D
0.3 PERCENT STRAIN						
.1000	2.686E5	1.589E5	4.177E5	4.417E5	1.436E6	1.418E6
.2155	1.518E5	2.892E5	4.152E5	4.836E5	1.304E6	1.453E6
.4642	3.091E5	3.004E5	4.570E5	4.955E5	1.337E6	1.495E6
1.000	3.978E5	3.180E5	4.912E5	5.288E5	1.413E6	1.593E6
2.155	3.882E5	3.551E5	5.514E5	5.988E5	1.469E6	1.688E6
4.642	4.757E5	4.376E5	5.792E5	6.493E5	1.553E6	1.789E6
10.00	5.818E5	5.288E5	6.409E5	7.269E5	1.811E6	1.938E6
21.54	7.250E5	6.682E5	7.084E5	8.047E5	2.031E6	2.187E6
46.41	9.427E5	8.836E5	8.557E5	9.515E5	2.390E6	2.570E6
100.0	1.260E6	1.172E6	1.046E6	1.156E6	2.851E6	3.046E6
1.0 PERCENT STRAIN						
.1000	2.858E5	2.308E5	3.503E5	3.562E5	1.281E6	1.276E6
.2155	2.789E5	2.440E5	3.738E5	3.759E5	1.308E6	1.346E6
.4642	3.104E5	2.558E5	3.890E5	3.891E5	1.384E6	1.421E6
1.000	3.284E5	2.860E5	4.090E5	4.017E5	1.460E6	1.474E6
2.155	3.714E5	3.248E5	4.292E5	4.272E5	1.543E6	1.510E6
4.642	4.226E5	3.723E5	4.553E5	4.465E5	1.639E6	1.519E6
10.00	5.021E5	4.508E5	4.865E5	4.756E5	1.699E6	1.490E6
21.54	6.237E5	5.662E5	5.370E5	5.246E5	1.715E6	1.465E6
46.41	8.072E5	7.474E5	6.222E5	6.116E5	1.778E6	1.617E6
100.0	1.076E6	9.920E5	7.526E5	7.484E5	1.888E6	1.706E6
5.0 PERCENT STRAIN						
.1000	2.820E5	2.575E5	2.163E5	1.975E5	5.690E5	5.513E5
.2155	2.927E5	2.638E5	2.145E5	1.969E5	6.074E5	5.928E5
.4642	2.940E5	2.632E5	2.115E5	1.977E5	6.431E5	5.290E5
1.000	2.949E5	2.669E5	2.086E5	1.987F5	5.401E5	5.043E5
2.155	2.984E5	2.716E5	2.121E5	2.007E5	5.058E5	4.677E5
4.642	3.084E5	2.830E5	2.167E5	2.084E5	4.493E5	4.208E5
10.00	3.294E5	3.082E5	2.307E5	2.256E5	3.911E5	3.732E5
21.54	3.726E5	3.558E5	2.513E5	2.552E5	3.573E5	3.431E5
46.41	4.387E5	4.270E5	2.955E5	3.016E5	3.449E5	3.350E5
100.0	4.137E5	4.038E5	3.633E5	3.698E5	3.499E5	3.438E5

Storage Moduli for PEA - PBLG IPN's at Various Weight Percent PBLG and Strains.*
(All Moduli Values in Dynes per Centimeter Squared)

SAMPLE FREQ (rad/s)	17I	20I	21I	22I	23I	23D
0.3 PERCENT STRAIN						
.1000	1.489E6	4.131E5	4.496E5	2.150E5	6.097E5	3.788E5
.2155	1.569E6	4.175E5	4.674E5	2.352E5	5.409E5	5.085E5
.4642	1.628E6	4.326E5	4.931E5	2.580E5	5.234E5	5.547E5
1.000	1.691E6	4.433E5	5.139E5	2.697E5	5.579E5	5.945E5
2.155	1.739E6	4.635E5	5.356E5	2.932E5	5.990E5	5.783E5
4.642	1.825E6	4.724E5	5.601E5	3.030E5	6.326E5	6.219E5
10.00	1.890E6	4.944E5	5.956E5	3.269E5	6.915E5	6.737E5
21.54	1.986E6	5.246E5	6.363E5	3.577E5	7.589E5	7.450E5
46.41	2.115E6	5.839E5	6.984E5	4.003E5	8.642E5	8.517E5
100.0	2.236E6	6.538E5	7.789E5	4.512E5	9.871E5	9.686E5
1.0 PERCENT STRAIN						
.1000	1.250E6	3.995E5	4.544E5	2.296E5	4.601E5	4.654E5
.2155	1.301E6	4.063E5	4.682E5	2.423E5	5.145E5	4.899E5
.4642	1.345E6	4.183E5	4.819E5	2.575E5	5.223E5	5.107E5
1.000	1.395E6	4.222E5	4.942E5	2.714E5	5.608E5	5.408E5
2.155	1.455E6	4.394E5	5.198E5	2.854E5	5.877E5	5.696E5
4.642	1.515E6	4.534E5	5.411E5	3.031E5	6.273E5	6.103E5
10.00	1.576E6	4.752E5	5.713E5	3.251E5	6.798E5	6.620E5
21.54	1.656E6	5.077E5	6.117E5	3.550E5	7.516E5	7.294E5
46.41	1.747E6	5.587E5	6.699E5	3.962E5	8.476E5	8.243E5
100.0	1.813E6	6.355E5	7.532E5	4.519E5	9.841E5	9.529E5
5.0 PERCENT STRAIN						
.1000	6.601E5	3.474E5	4.676E5	2.133E5	4.597E5	4.476E5
.2155	6.507E5	3.469E5	4.850E5	2.219E5	4.727E5	4.640E5
.4642	6.630E5	3.582E5	5.075E5	2.317E5	4.872E5	4.815E5
1.000	6.751E5	3.704E5	5.319E5	2.421E5	5.071E5	5.028E5
2.155	6.839E5	3.844E5	5.593E5	2.544E5	5.344E5	5.306E5
4.642	6.930E5	4.012E5	5.918E5	2.699E5	5.719E5	5.683E5
10.00	7.036E5	4.247E5	6.347E5	2.910E5	6.190E5	6.158E5
21.54	7.185E5	4.609E5	6.897E5	3.189E5	6.803E5	6.781E5
46.41	2.300E5	5.138E5	7.658E5	3.568E5	7.608E5	7.591E5
100.0	1.672E5	5.921E5	8.741E5	4.078E5	8.758E5	8.714E5

* Sample 17I is a PEA-PBLG film which was carried over to this set of data.

Loss Moduli for PEA - PBLG IPN's at Various Weight Percent PBLG and Strains.*

(All Moduli Values in Dynes per Centimeter Squared)

SAMPLE FREQ (rad/s)	17I	20I	21I	22I	23I	23D
0.3 PERCENT STRAIN						
.1000	3.427E5	1.001E4	5.018E4	2.525E4	0.000E0	9.404E4
.2155	3.393E5	1.118E4	4.346E4	1.178E4	1.230E5	6.556E4
.4642	3.421E5	3.278E4	4.875E4	2.312E4	7.554E4	8.436E4
1.000	3.514E5	1.928E4	6.310E4	3.495E4	8.455E4	6.386E4
2.155	3.505E5	3.537E4	5.780E4	3.702E4	8.562E4	8.973E4
4.642	3.770E5	5.225E4	7.547E4	5.173E4	1.188E5	1.128E5
10.00	3.925E5	8.428E4	9.850E4	6.787E4	1.664E5	1.636E5
21.54	4.356E5	1.239E5	1.444E5	9.035E4	2.363E5	2.304E5
46.41	5.145E5	1.901E5	2.123E5	1.193E5	3.527E5	3.357E5
100.0	6.025E5	2.904E5	3.203E5	1.733E5	5.346E5	5.064E5
1.0 PERCENT STRAIN						
.1000	2.570E5	2.790E4	5.336E4	2.589E4	4.440E4	8.185E4
.2155	2.457E5	2.423E4	5.054E4	2.626E4	4.141E4	4.680E4
.4642	2.507E5	3.295E4	4.947E4	2.940E4	6.533E4	6.149E4
1.000	2.618E5	3.487E4	5.317E4	3.368E4	6.630E4	7.641E4
2.155	2.751E5	4.109E4	6.423E4	4.284E4	8.901E4	8.945E4
4.642	2.944E5	6.116E4	7.943E4	5.295E4	1.221E5	1.191E5
10.00	3.241E5	8.428E4	1.046E5	6.972E4	1.687E5	1.615E5
21.54	3.628E5	1.240E5	1.462E5	9.301E4	2.387E5	2.295E5
46.41	4.272E5	1.867E5	2.127E5	1.260E5	3.481E5	3.356E5
100.0	5.201E5	2.884E5	3.262E5	1.775E5	5.382E5	5.154E5
5.0 PERCENT STRAIN						
.1000	2.771E5	4.724E4	9.356E4	3.259E4	5.702E4	5.902E4
.2155	2.753E5	5.693E4	9.984E4	3.462E4	5.671E4	6.042E4
.4642	2.791E5	5.845E4	1.050E5	3.665E4	6.236E4	6.199E4
1.000	2.806E5	6.164E4	1.129E5	4.041E4	7.678E4	7.575E4
2.155	2.825E5	6.609E4	1.257E5	4.689E4	9.637E4	9.625E4
4.642	2.834E5	7.912E4	1.451E5	5.685E4	1.261E5	1.246E5
10.00	2.895E5	1.003E5	1.744E5	7.314E4	1.674E5	1.646E5
21.54	3.044E5	1.355E5	2.209E5	9.416E4	2.289E5	2.277E5
46.41	3.185E5	1.920E5	2.956E5	1.251E5	3.285E5	3.276E5
100.0	3.047E5	2.852E5	4.202E5	1.715E5	4.971E5	4.954E5

* Sample 17I is a PEA-PBLG film which was carried over to this set of data.

Storage Moduli for PEA - PBLG IPN's at Various
Weight Percent PBLG and Strains.
(All Moduli Values in Dynes per Centimeter Squared)

SAMPLE FREQ (rad/s)	24I	25I	26I	27I	28I
0.3 PERCENT STRAIN					
.1000	7.731E5	6.478E5	1.560E6	1.234E6	1.412E6
.2155	8.217E5	6.986E5	1.693E6	1.375E6	1.555E6
.4642	8.734E5	7.665E5	1.782E6	1.474E6	1.665E6
1.000	9.388E5	8.214E5	1.893E6	1.581E6	1.797E6
2.155	9.677E5	8.721E5	2.021E6	1.684E6	1.902E6
4.642	1.029E6	9.407E5	2.167E6	1.789E6	2.028E6
10.00	1.092E6	1.020E6	2.329E6	1.900E6	2.159E6
21.54	1.163E6	1.114E6	2.527E6	2.028E6	2.332E6
46.41	1.271E6	1.254E6	2.782E6	2.186E6	2.761E6
100.0	1.377E6	1.394E6	3.074E6	2.380E6	3.209E6
1.0 PERCENT STRAIN					
.1000	6.724E5	5.984E5	1.346E6	1.053E6	7.242E5
.2155	6.921E5	6.394E5	1.409E6	1.127E6	7.178E5
.4642	7.115E5	6.797E5	1.499E6	1.201E6	6.979E5
1.000	7.395E5	7.217E5	1.584E6	1.279E6	6.903E5
2.155	7.670E5	7.769E5	1.666E6	1.361E6	6.789E5
4.642	7.930E5	8.364E5	1.756E6	1.453E6	6.852E5
10.00	8.241E5	9.047E5	1.861E6	1.562E6	7.108E5
21.54	8.656E5	9.859E5	1.992E6	1.688E6	7.513E5
46.41	9.286E5	1.094E6	2.144E6	1.841E6	8.302E5
100.0	1.015E6	1.226E6	2.255E6	2.031E6	9.659E5
5.0 PERCENT STRAIN					
.1000	3.929E5	3.579E5	5.378E5	6.121E5	9.199E4
.2155	4.024E5	3.544E5	5.204E5	6.211E5	8.210E4
.4642	4.163E5	3.734E5	5.247E5	6.470E5	7.772E4
1.000	4.290E5	3.955E5	5.163E5	6.754E5	7.461E4
2.155	4.399E5	4.224E5	4.923E5	6.961E5	7.449E4
4.642	4.436E5	4.453E5	4.473E5	7.128E5	8.003E4
10.00	4.402E5	4.709E5	3.408E5	7.247E5	8.600E4
21.54	4.421E5	4.964E5	2.741E5	7.133E5	8.459E4
46.41	4.824E5	5.014E5	2.324E5	6.539E5	7.504E4
100.0	5.581E5	4.878E5	2.103E5	6.016E5	7.023E4

Loss Moduli for PEA - PBLG IPN's at Various Weight Percent PBLG and Strains. (All Moduli Values in Dynes per Centimeter Squared)

SAMPLE FREQ (rad/s)	24I	25I	26I	27I	28I
0.3 PERCENT STRAIN					
.1000	1.595E5	1.290E5	2.870E5	2.929E5	5.218E5
.2155	1.221E5	1.150E5	2.654E5	2.827E5	5.567E5
.4642	1.414E5	1.288E5	2.686E5	2.773E5	5.990E5
1.000	1.538E5	1.225E5	2.937E5	2.893E5	6.748E5
2.155	1.501E5	1.675E5	3.250E5	3.141E5	7.807E5
4.642	1.826E5	1.791E5	3.734E5	3.412E5	9.001E5
10.00	2.185E5	2.177E5	4.459E5	3.882E5	1.108E6
21.54	2.598E5	2.727E5	5.299E5	4.523E5	1.193E6
46.41	3.243E5	3.452E5	6.440E5	5.304E5	1.499E6
100.0	4.067E5	4.330E5	8.172E5	6.338E5	1.780E6
1.0 PERCENT STRAIN					
.1000	1.598E5	1.436E5	3.003E5	2.798E5	5.088E5
.2155	1.485E5	1.372E5	3.094E5	2.703E5	5.335E5
.4642	1.555E5	1.500E5	3.253E5	2.780E5	5.702E5
1.000	1.665E5	1.640E5	3.564E5	2.984E5	6.129E5
2.155	1.731E5	1.756E5	4.052E5	3.103E5	6.594E5
4.642	1.981E5	2.075E5	4.615E5	3.378E5	7.051E5
10.00	2.249E5	2.399E5	5.281E5	3.716E5	7.276E5
21.54	2.582E5	2.853E5	6.010E5	4.188E5	7.638E5
46.41	3.063E5	3.518E5	7.205E5	4.852E5	8.587E5
100.0	3.826E5	4.403E5	8.800E5	5.781E5	1.003E6
.0 PERCENT STRAIN					
.1000	1.278E5	1.468E5	3.512E5	2.570E5	2.040E5
.2155	1.269E5	1.582E5	3.594E5	2.546E5	2.027E5
.4642	1.297E5	1.663E5	3.752E5	2.615E5	2.053E5
1.000	1.351E5	1.788E5	3.865E5	2.726E5	2.077E5
2.155	1.439E5	1.926E5	3.936E5	2.904E5	2.121E5
4.642	1.568E5	2.109E5	3.985E5	3.113E5	2.138E5
10.00	1.773E5	2.371E5	4.086E5	3.350E5	2.142E5
21.54	2.005E5	2.709E5	3.965E5	3.728E5	2.139E5
46.41	2.294E5	3.220E5	4.016E5	4.069E5	2.149E5
100.0	2.791E5	3.661E5	4.241E5	4.199E5	2.253E5

Storage Moduli for PEA - PBLG IPN's at Various Weight Percent PBLG and Strains. (All Moduli Values in Dynes per Centimeter Squared)

SAMPLE FREQ (rad/s)	29I	29D	30I	30D
0.3 PERCENT STRAIN				
.1000	4.864E5	5.090E5	3.238E6	2.991E6
.2155	5.189E5	5.328E5	3.461E6	3.012E6
.4642	5.478E5	5.503E5	3.572E6	2.984E6
1.000	5.724E5	5.752E5	3.670E6	2.944E6
2.155	6.005E5	5.882E5	3.711E6	2.811E6
4.642	6.265E5	6.292E5	3.661E6	2.474E6
10.00	6.627E5	6.638E5	3.578E6	2.226E6
21.54	7.064E5	7.037E5	3.511E6	2.077E6
46.41	7.574E5	7.538E5	3.878E6	2.159E6
100.0	8.244E5	8.207E5	4.354E6	2.472E6
1.0 PERCENT STRAIN				
.1000	4.489E5	4.392E5	7.269E5	7.225E5
.2155	4.720E5	4.616E5	6.994E5	6.660E5
.4642	4.924E5	4.821E5	6.488E5	6.013E5
1.000	5.149E5	5.018E5	6.061E5	5.341E5
2.155	5.419E5	5.287E5	5.665E5	4.957E5
4.642	5.658E5	5.544E5	5.269E5	4.590E5
10.00	5.963E5	5.849E5	4.858E5	4.234E5
21.54	6.328E5	6.206E5	4.282E5	3.805E5
46.41	6.779E5	6.634E5	4.026E5	3.544E5
100.0	7.351E5	7.204E5	3.999E5	3.637E5
5.0 PERCENT STRAIN				
.1000	2.589E5	2.791E5	5.103E4	5.302E4
.2155	2.637E5	2.836E5	4.552E4	4.641E4
.4642	2.705E5	2.910E5	3.918E4	4.048E4
1.000	2.751E5	2.972E5	3.572E4	3.766E4
2.155	2.770E5	3.010E5	3.491E4	3.512E4
4.642	2.790E5	3.037E5	3.655E4	3.461E4
10.00	2.819E5	3.069E5	3.307E4	3.353E4
21.54	2.879E5	3.109E5	3.082E4	3.009E4
46.41	3.016E5	3.248E5	2.880E4	2.651E4
100.0	3.307E5	3.566E5	2.345E4	2.213E4

Loss Moduli for PEA - PBLG IPN's at Various Weight Percent PBLG and Strains. (All Moduli Values in Dynes per Centimeter Squared)

SAMPLE FREQ (rad/s)	29I	29D	30I	30D
0.3 PERCENT STRAIN				
.1000	8.119E4	6.396E4	1.201E6	1.312E6
.2155	7.288E4	6.079E4	1.209E6	1.365E6
.4642	6.233E4	6.084E4	1.307E6	1.429E6
1.000	6.975E4	5.706E4	1.387E6	1.487E6
2.155	7.172E4	7.366E4	1.556E6	1.519E6
4.642	7.996E4	8.421E4	1.698E6	1.627E6
10.00	9.608E4	9.628E4	1.788E6	1.597E6
21.54	1.193E5	1.180E5	1.963E6	1.621E6
46.41	1.532E5	1.531E5	2.199E6	1.849E6
100.0	2.034E5	2.071E5	2.442E6	2.166E6
1.0 PERCENT STRAIN				
.1000	8.442E4	7.315E4	1.043E6	8.641E5
.2155	8.136E4	7.479E4	1.020E6	8.458E5
.4642	8.207E4	7.782E4	9.986E5	8.257E5
1.000	8.718E4	8.148E4	9.778E5	7.881E5
2.155	8.977E4	8.772E4	9.343E5	7.448E5
4.642	1.015E5	9.672E4	8.769E5	7.044E5
10.00	1.155E5	1.110E5	8.050E5	6.603E5
21.54	1.352E5	1.316E5	7.713E5	6.438E5
46.41	1.668E5	1.634E5	8.208E5	6.841E5
100.0	2.168E5	2.124E5	8.977E5	7.644E5
5.0 PERCENT STRAIN				
.1000	1.123E5	9.367E4	2.143E5	1.840E5
.2155	1.119E5	9.906E4	2.032E5	1.744E5
.4642	1.152E5	1.041E5	1.923E5	1.672E5
1.000	1.192E5	1.095E5	1.818E5	1.599E5
2.155	1.262E5	1.161E5	1.675E5	1.526E5
4.642	1.356E5	1.256E5	1.583E5	1.451E5
10.00	1.461E5	1.383E5	1.476E5	1.403E5
21.54	1.624E5	1.566E5	1.439E5	1.386E5
46.41	1.857E5	1.801E5	1.470E5	1.429E5
100.0	2.179E5	2.147E5	1.562E5	1.525E5