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TRANSIENT PHENOMENA OF POLYMER SOLUTIONS

BY

NIKOLAUS ZWETKOW

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APPROVAL OF THESIS

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NIKOLAUS ZWETKOW

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEW JERSEY INSTITUTE OF TECHNOLOGY

BY

FACULTY COMMITTEE

APPROVED:

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ABSTRACT

With the aid of a rotational viscometer, several transient phenomena were studied with different polymer solutions. In order to be acquainted with the operations of the rotational viscometer, viscosity measurements were made on polystyrene solution of a 7.14 wt. % NBS-2-35967 in a 35 - 65 mixture of aroclor and TCP, polyisobutylene (16.5% in mineral spirits), Indopol H-1900 (polyisobutylene) and 4.5% polyisobutylene in Primol 355. All these were done at a temperature of 77°F, except for Indopol H-1900 which was done at different temperatures. The results are listed in the section of tables and graphs.

Viscosity was measured with a rotational viscometer. Its operational mechanism will be described in the chapter dealing with experimental equipment. Next the properties of a 4.5% polyisobutylene in Primol 355 was exclusively investigated in terms of shear stress versus rate of shear, recoverable shear at infinite time versus shear stress, displacement or flow history versus time and recoverable shear versus time as a function of shear stress. Having obtained the curves of displacement versus time and recoverable shear versus time of a 4.5% PIB solution and the 3% PIB solution available from previous experiments at Esso Research Center, the shear velocity profiles of displacement versus time and irreversible shear versus time was investigated.

Recoverable shear (recoil measurements) was measured by a stop-load mechanism described in detail in later sections. Also investigated were a series of unpublished flow histories of a 3% PIB in Primol 355, beginning at time zero with the aid of a hi-speed camera. Having transformed the flow curves into shear curves, the phenomena in question being investigated is the existance of zero shear that occurs during the interval between .1 to .2 seconds for loads ranging between 5 and 500 grams. With the aid of a mathematical model and working in the area of complete elasticity, it was found that the zero shear is the result of two phenomena. These phenomena are the vibrations due to the string holding the weight and also due to the elasticity of the polymer solution. It was also found that the vibration due to the elastic property of the polymer solution had a very significant effect on the zero shear. The extent of that effect was also found to be a function of the load. The mathematical model used resulted in the following conclusion; the calculated inertial effects of the viscometer are much higher than the initially measured value, it predicts the zero shear phenomena, the spring constant for the polymer solution is a function of weight and it also gives an indication of the nature of the flow curves free of vibrational phenomena. The final results are graphs and tables describing

viscosity measurements and transient phenomena occurring in the polymer solution.

TABLE OF CONTENTS

HISTORICAL DEVELOPMENT OF TRANSIENT PHENOMENA

The field of rheology was born a little over forty years ago, with its ancestors traced well back into the past. The first recording rheologist was Amenemhet, an Egyptian, who was on the staff of the pharoah about 1540 B.C.(1) He used the flow of water in a conical vessel to measure time, taking into account changes in viscosity and temperature. Eugene Bingham is called the father of rheology and it was he who gave the field its name deriving from the Greek word rheos meaning flow. The field of rheology increased its momentum with the help of K. Weissenberg and M. Reiner whose works dealt with the measurement of physical phenomena of materials and their theoretical understanding. Its uniqueness is that there is no such thing as a true rheologist, for the participants who engage in this field are made up of people of many disciplines and professions.

Rheology in its basic definition is the science of the study of deformations and flow of matter. Such a simple definition does not give justice to this ever growing field. It has been developed for the past thirty years predominantly in the United States.(2) Today the definition of rheology

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(1)E.T. Severs, Rheology of Polymers, (1962) p. 1

(2)W. Philippoff, "Present State of Rheology Theory", Esso Research and Engineering Co., Linden, (1970) is much more broader, and can be defined in two parts. The first part describes the response of all types of materials subjected to mechanical forces under specified conditions of flow or deformation. In the second part, a mathematical relationship is derived which connects stresses, strain and time. These are commonly called the rheological equation of state or constitutive equation. The beginnings of rheology was geared to the description of rheological phenomena, especially non-Newtonian viscosity which lead to the flow curve dependence of shear rate to shear stress. This in turn induced the idea of comparing experimental results with different types of laminar flow apparatus, capillary, rotational concentric cylinder and the cone and plate viscometer. In 1946 Weissenberg discovered the normal stresses, which indicate the shear stress was not the only stress that occurred in steady shear flow. As a result two parameters were needed to describe steady flow of viscoelastic liquids, one describing normal stress and the other describing viscosity. Today rheology is concerned with the interrelationship between deformation and the internal structure of materials. Much emphasis is placed on the internal structure because it affords a better understanding of the phenomenological properties of the material. The eventual goal of rheology is to be able to predict deformation or flow resulting from application of a given experimental conditions.

Two ideal extreme behaviors are observed in rheology, pure elastic deformation of solids and pure viscous flow of liquids. These two forms of ideal behavior are often called the Hookean solid and Newtonian fluid. Hooke's law states that stress is proportional to strain, while Newton's law states that shear stress is proportional to the shear rate. The vast number of materials exhibit both of these characteristics and are classified as viscoelastic materials. Mathematical models which describe the behavior of viscoelastic materials consist of combinations of elastic springs and viscous dashpots, of which the most common and basic ones are the Maxwell and Kelvin-Voigt models. The most important phenomena distinguishing viscoelastic substances from purely viscous fluids is the occurrence of recoil, or strain recovery when the stress is released. Viscoelastic materials which differ from the perfectly elastic solid is the phenomena of flow. Viscoelastic materials are treated as time dependent, while Newtonian liquid are not. Pure elasticity occurs when the body returns to its original form after release of stress. Pure viscosity occurs when liquid flows under any amount of stress applied and that it does not retake the shape after release of stress. Viscoelastic materials combine both of these effects simultaneously. In viscoelastic materials there is a combination of elastic and viscous deformations. At all stresses, but usually at low stresses and short times of observation, the elastic phenomena are predominant. When the time of force is increased, more flow occurs and the gradual transition to viscous flow takes over. Thus total deformation which occurs in viscoelastic materials is the sum of viscous and elastic deformation.

$$\gamma_{\text{total}} = \gamma_{\text{viscous}} + \gamma_{\text{elastic}}$$

In other words, energy is partly stored in a body undergoing stress and partly dissipated as heat. Unlike Newton's or Hooke's Law the properties of viscoelastic materials are dependent on time.

Rheology is concerned with different types of methods where one measures and predicts the property of materials that flow. Its major target is with non-Newtonian viscoelastic fluid. Investigations of rheological phenomena of viscoelastic materials falls into two classes - steady state and vibrational. Examples of steady state experiments consist of the capillary and rotational viscometer. Vibrational techniques involve mechanical oscillations on viscoelastic fluids. However the major concern will be focused on simple shear flow where there is a component velocity in only one direction. Two types of deformations studied in viscoelastic materials are: reversible deformation (elasticity) and irreversible deformation (viscous flow). Energy is required continuously for flow, work not recoverable will be dissipated as heat. Most experiments are being done on non-Newtonian viscoelastic materials in which the relationship between shear rate and shear stress is dependent on time of shear. The time dependence of the viscoelastic material shows itself molecularly in the following way.(3) The liquid that is being sheared must adjust itself internally to absorb the energy reversibly within itself by the formation or destruction of transient spatial configuration of its consistent molecules. The new spatial arrangement will be different energetically from that of the random ground state. In time it will revert back to its ground state upon removal of stress. All this represents stored potential energy or elasticity. The recoverable stored energy will not be instantaneous especially where there is 100% recoverable shear. As a result, recoverable shear comes in two parts, instantaneous and delayed. The ultimate is thus the sum of these two parts. It was Weissenberg who first observed that recoverable strain is proportional to normal stress:

$$S = \frac{\tau_{11} - \tau_{22}}{\tau_{12}}$$

where; $\tau_{11} - \tau_{22}$ is normal stress (dynes/cm^2)

τ_{12} is shear stress (dynes/cm^2)

S is recoverable shear (dimensionless)

Up to now, the gap between phenomenological theory and

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(3)R.S. Lenk, Plastics Rheology, New York: John Wiley and Sons, Inc., (1968) p. 2

molecular theory in viscoelastic behavior has not been completely resolved yet.

The type of flow that have been used experimently in the investigation of viscoelastic fluids are of the following type: poiseuille flow, couette flow, the parallel plate torsion flow and the cone and plate torsion flow. The cone and plate instrument has been recently the most widely used instrument for the study of transient phenomena of polymer solution. With this instrument viscosity is measured and stress growth as a function of shear rate is studied. With the advent of the Weissenberg rheogoniometer; normal stresses were also studied as functions of time and constant shear rate.

The first comprehensive study on recoverable shear was made by Braunbeck (1929) on cable compound. It was A. A. Trapeznikov(4) who first measured elastic properties of viscoelastic materials with an instrument based on coaxial cylinders. The outer cylinder would turn at constant shear rate, while the stoppage angle was preset. Then stress growth was studied as a function of time. After the outer cylinder has been stopped, the inner cylinder is released,

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(4)A.A. Trapeznikov and B. A. Fedotova, "Fluidity and Strength of Oleogels," Doklady Akad-Nauk, SSSR, 81, 1101-4, (1951) and the elastic recoil as a function of the angle of the inner cylinder rotation is measured. He first studied the growth of shearing stress as a function of deformation time at various shear rates on a 4% oleogel of al-naphthenate in decahydronaphtalene. A.A. Trapeznikov was the first one to observe a maximum shear before reaching an equilibrium value as rate of shear is increased. He called this the "strength of the system," and pointed out that the maxima can only be explained in terms of its elastic properties, while the steady state shear stress characterizes the viscous properties of the system. In 1956, A.A. Trapeznikov and T.G. Shalopalkina(5) studied recoverable strain as a function of deformation time. Since then, A.A. Trapeznikov and associates have investigated many types of solutions.

In 1957, Philippoff, Gaskins, and Brodnyan were first to measure recoverable shear versus shear rate of a polymer solution (100% polyisobutylene).(6) They also measured shear strain as a function of shear stress. Dependence of recoverable shear strain on stress was essentially linear.

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(5)A.A. Trapeznikov and T.G. Shalopalkina, "Elastic Deformation and its Relaxation in an Al-Naphthenate Gel," Doklady Akad Navk., SSSR 111, 380-3, (1956)

(6)W. Philippoff, F.H. Gaskins, and J.G. Brodnyn, "Flow Birefringence and Stress. V. Correlation or recoverable shear strains with other rheological properties of polymer solutions," Journal of Applied Physics, Vol. 28, No. 10, (1957) Using the formula of:

$$P_{11} = Gs^2$$

where P_{11} is normal stresses (dynes/cm^2)

G is shear modulus

s is recoverable shear,

The data obtained by the rotational viscometer, flow birefringence and the rheogoniometer were compared and were found to be consistant with each other. However, the study of stress growth at constant shear rate of a polymer solution was first investigated by A.A. Trapeznikov in 1964. The existance of normal stress and normal stress growth at constant shear rate were first observed by Weissenberg and the manufacturers of the Weissenberg Rheogoniometer, respectively.

During the last half of the past decade till now, many similar and broader investigations have been carried out. Most of this type of investigation have been carried out by G.V. Vinogradov and Associates. In 1965, G.V. Vinogradov and I.M. Belkin(7) investigated polymer melts and solutions and observed that shear stress growth became non-monotonic with rising deformation rates. He used a rotational

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(7)G.V. Vinogradov and I.M. Belkin, "Elastic, Strength, and Viscous Properties of Polymer Melts," Journal of Polymer Science, Part A, Vol. 3, 917-32, (1965) elastoviscometer with a rigid dynamometer, which is basically of the cone and plate type of instrument. In 1967, J.D. Huppler(8) and Associates using a Weissenberg Rheogoniometer studied shear growth, normal stress growth as a function of shear rate. They found that shear stress and normal stress not only overshoot but also undershoot the steady state value. Normal stress growth increased more slowly then shear stress growth and reaches its maximum at a later time. A.A. Trapeznikov(9) also in 1967 observed stress growth undershoot as well as overshoot, but no mention or explanation was made of this phenomena. It was only till 1970 that A.A. Trapeznikov and A.A. Pylaeva(10) made known that shear stress undershoot exist for very high shear rates. Another time that the phenomena of overshoot as well as undershoot appearing in experimental data was in 1972, when

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(8)J.D. Huppler, I.F. MacDonald, E. Ashare, T.W. Spriggs, R.B. Bird and L.A. Holmes, "Rheological Properties of three solutions. Part II. Relaxation and growth of shear and normal stresses," Transactions of the Society of Rheology, Vol. 11:12, 181-204, (1967)

(9)A.A. Trapeznikov, "Role of the pre-steady state deformation stage in the rheological properties of dispersed systems and concentrated solutions of polymers," Zn. Fiz. Khim. 41 (6) 1247-56, (1967)

(10)A.A. Trapeznikov and A.T. Pylaeva, "Structural changes in concentrated solutions of polyisobutene," Vysokomol Soedin., Ser. A, 12(6), 294-307, (1970) I-Jen Chen and D.C. Bogue(11) investigated high and low density polyethylene and polystyrene melts. However, G.V. Vinogradov and I.M. Belkin also investigated polyethylene and polystyrene of comparable constant shear rates and did not observe any undershoot phenomena in the study of shear stress growth. The discrepancy may be traced to the instrument used or to the difference in the material. J.D. Huppler and Associates(12) and I-Jen Chen and D.C. Bogue(13) who both observed undershoot used a Weissenberg Rheogoniometer, while G.V. Vinogradov used a rotational elastoviscometer with a very rigid dynamometer. Other investigators (see references) have done similar types of investigations, but have not observed any undershoots. However the following conclusions were drawn from the investigations:

A. For low shear rates, both shear stress and normal stress growth reaches monotonically to a equilibrium vales.

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(11)I-Jen Chen and D.C. Bogue, "Time dependent stress in polymer melts and review of viscoelastic theory," <u>Transactions of the Society of Rheology</u>, Vol. 16:1, 59-78, (1972)

(12)J.D. Huppler, I.F. MacDonald, E. Ashare, T.W. Spriggs, R.B. Bird and L.A. Holmes, Op. Cit.

(13)I-Jen Chen and D.C. Bogue, Op. Cit.

B. For higher shear rates, shear stress, normal stress growth and recoverable strain becomes non-monotonic. In all cases there appears a maximum in the curve which is related to the elasticity of the solution, followed by steady flow conditions.

C. With increasing deformation rates, the time for attaining the maxima is decreased and also to some degree, the time for attainment of steady flow.

D. As shear rate increase, the maxima in shear stress, normal stress and recoverable strain becomes more pronounced.

E. Depending on the material and at high shear rates, undershoot as well as overshoot occurs.

F. Shear stress maxima is not necessarily accompanied by a maxima in normal stresses. Steady state flow depends on constancy of the normal stresses and not on shear stress.(14)

It should be pointed out that Charles Goldstein(15) in 1974 investigated the transient properties S.B.R. Polymers and

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(14)G.V. Vinogradov and I.M. Belkin, Op. Cit.

(15)G. Goldstein, "Transient and steady shear behavior of SBR Polymers," <u>Transactions of the Society of Rheology</u>, Vol. 18, Issue 3, 357-69, (1974) observed no overshoot in the shear stress growth. However, his range of shear rate was low. Whether the same phenomena will exist for higher shear rate is not known.

Up to now, the method of studying the behavior of a polymer solution in transient regions consisted in applying a constant shear rate and observing the changes in the various properties of the material. When a constant shear rate is applied to the material, three responses of viscoelastic material are observed: Shear stress, normal stress and high elastic recoverable strain. The method of investigation employed in this thesis is one of constant shear stress with the aid of a rotational viscometer. It permits the study of the flow history curve as a function of time and shear stress. It permits the determination of high elastic deformation as a function of stress and time. The transition from elastic deformation to steady viscous flow can also be observed. Transient shear rate phenomena will also be observed at constant shear stress. The constant stress method will also determine observable separation of irreversible and reversible flow curves. With the optical system used in conjunction with the rotational viscometer, the the maximum error obtainable is $\pm 2.24 \times 10^{-3}$ shear units. With the use of the cone and plate method, G.V. Vinogradov, Malkin and Shumsky(16) gives an error of ± .2 units.

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(16)G.V. Vinogradov, A.YA. Malkin, and V.F. Shumsky, "High Elasticity, Normal and Shear Stresses on Shear Deformation of low-molecular-weight polyisobutylene," Rheologica Acta, Vol. 9, p. 2, 155-63, (1970)

EQUIPMENT AND MATERIALS

I. EXPERIMENTAL EQUIPMENT

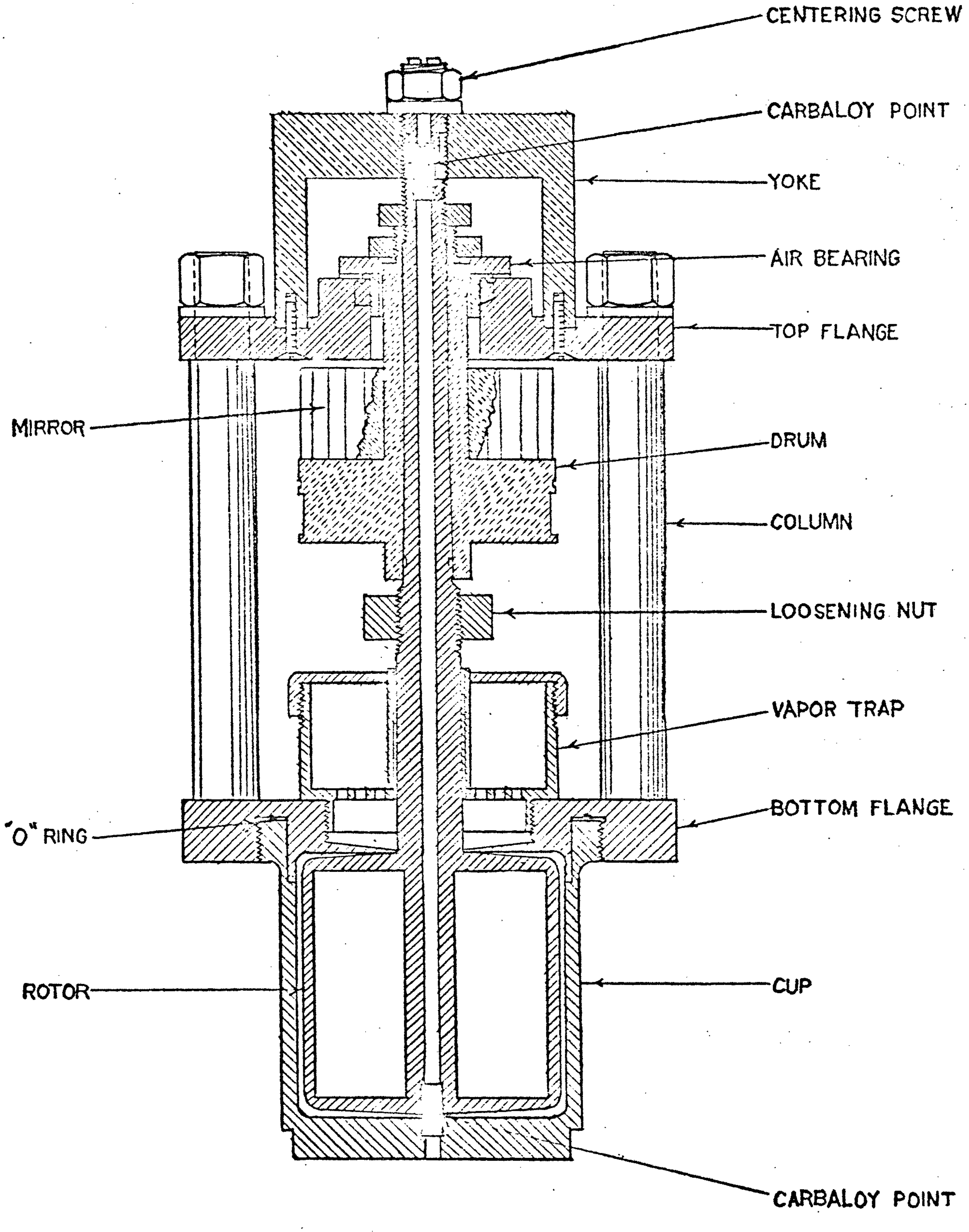
Rotational Viscometer

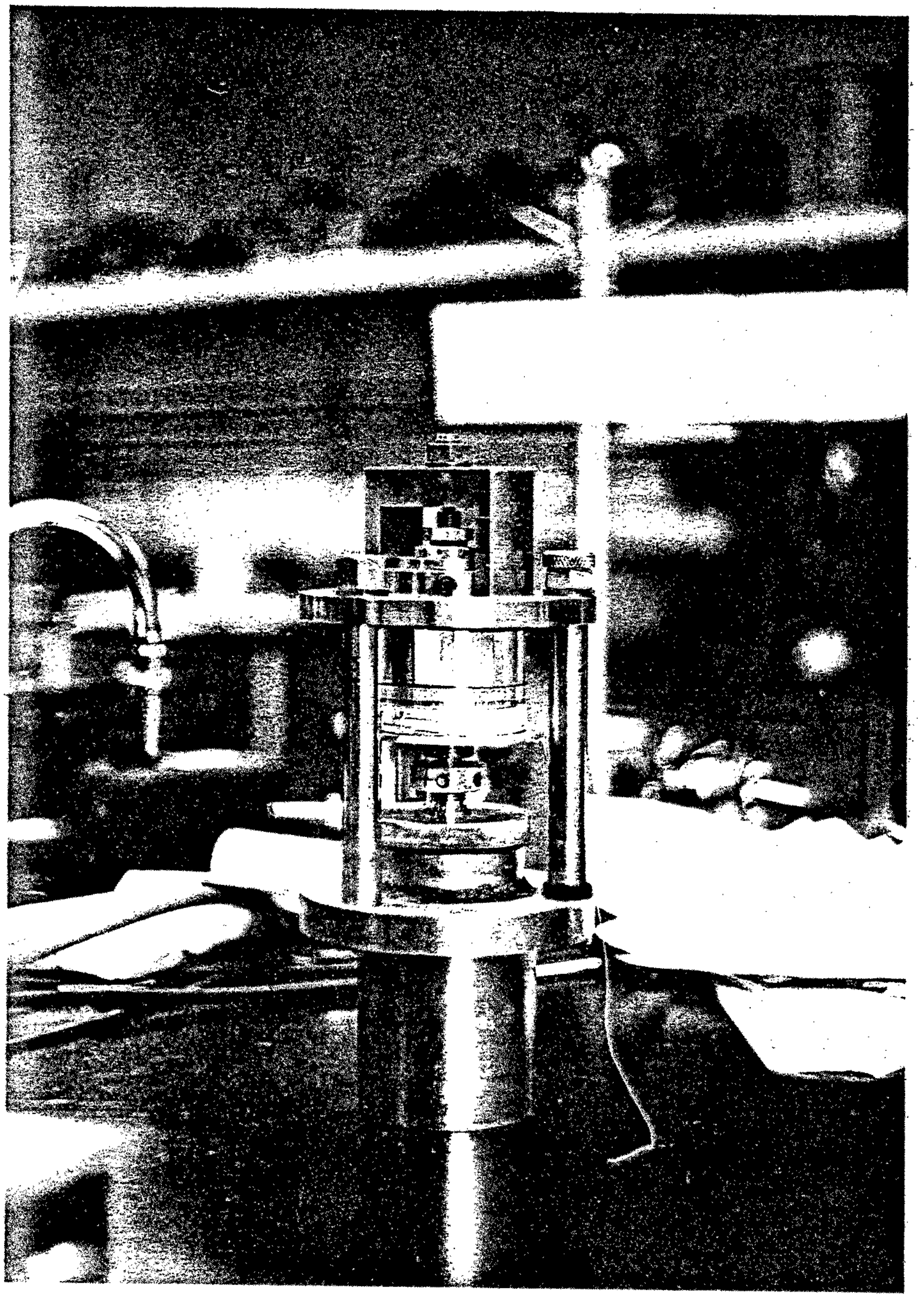
The components of the rotational viscometer, which was designed by Dr. Philippoff, are shown on figures (1, 2). It is made up of a hollow cylinder rotor with two three degree ends which rotate in a cup. The clearance between rotor and cup is .079 inches. The rotor was specifically designed to eliminate end effects by curving the ends of the bob. This will cause a constant shear rate to be maintained on the entire surface of the rotor. The sharp edge of the cup on top of the rotor will cause very low shear rates to occur, so as to eliminate the Weissenberg effect.

The driving force of the viscometer is achieved by attaching a weight to a nylon string which in turn is wound around the drum. The drum in turn is attached to the shaft on the rotor. The speed of the angular rotation of the rotor is used to measure the shear rate of the polymer solution. The rotor and stationary components are shown in figure (4).

The unique feature of the rotational viscometer is that the entire weight of the rotating components of the

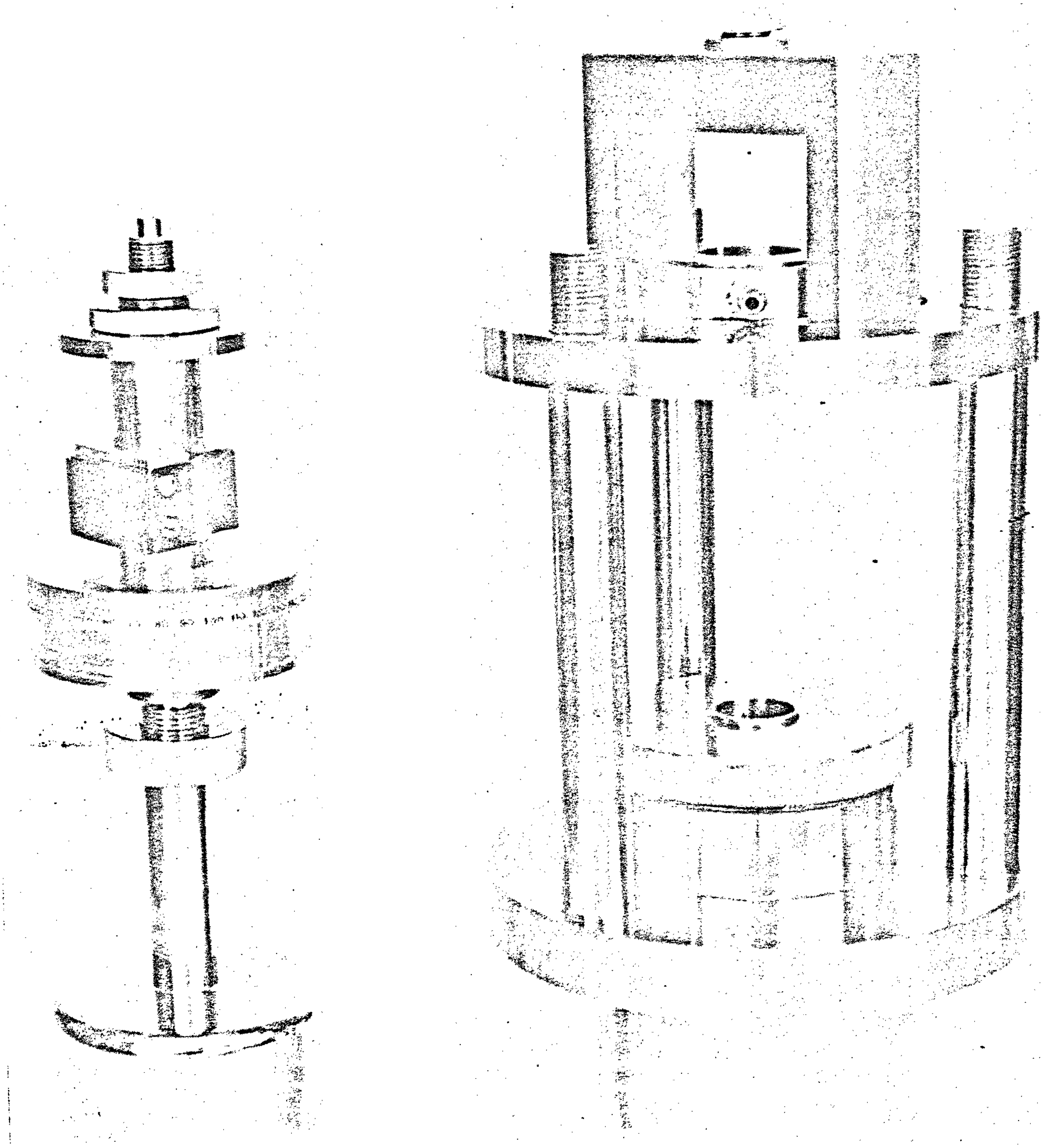
ROTATIONAL VISCOMETER





FIQURE 2

FIGURE 4



viscometer is supported by an air bearing. This is shown in detail in figure (5). The rotational viscometer works in the following way. Air at a pressure of sixty PSIG is forced out through the holes of the stationary component of the viscometer against the bearing plate of the rotor. The resultant effect is that the friction between the moving air bearing plate and the stationary plate is drasticly reduced to an equivalent in shear stress of a few thousandths of a dyne/cm^2. This was later measured and was found to be approximately .006 ± .0002 dynes/cm^2.(17)

The shear stress in the rotational viscometer is measured by the following equation:

$$\Upsilon = \frac{981Wr}{2\pi R_1^2 L_o} = K_1 W \text{ (dynes/cm}^2\text{)}$$

where: W is the driving load (grams)

r is the radius of the drum where the thread is wound (cm)

R_1 is the radius of the inner cylinder (cm)

L_o is the equivalent length of the conical cylinder (cm)

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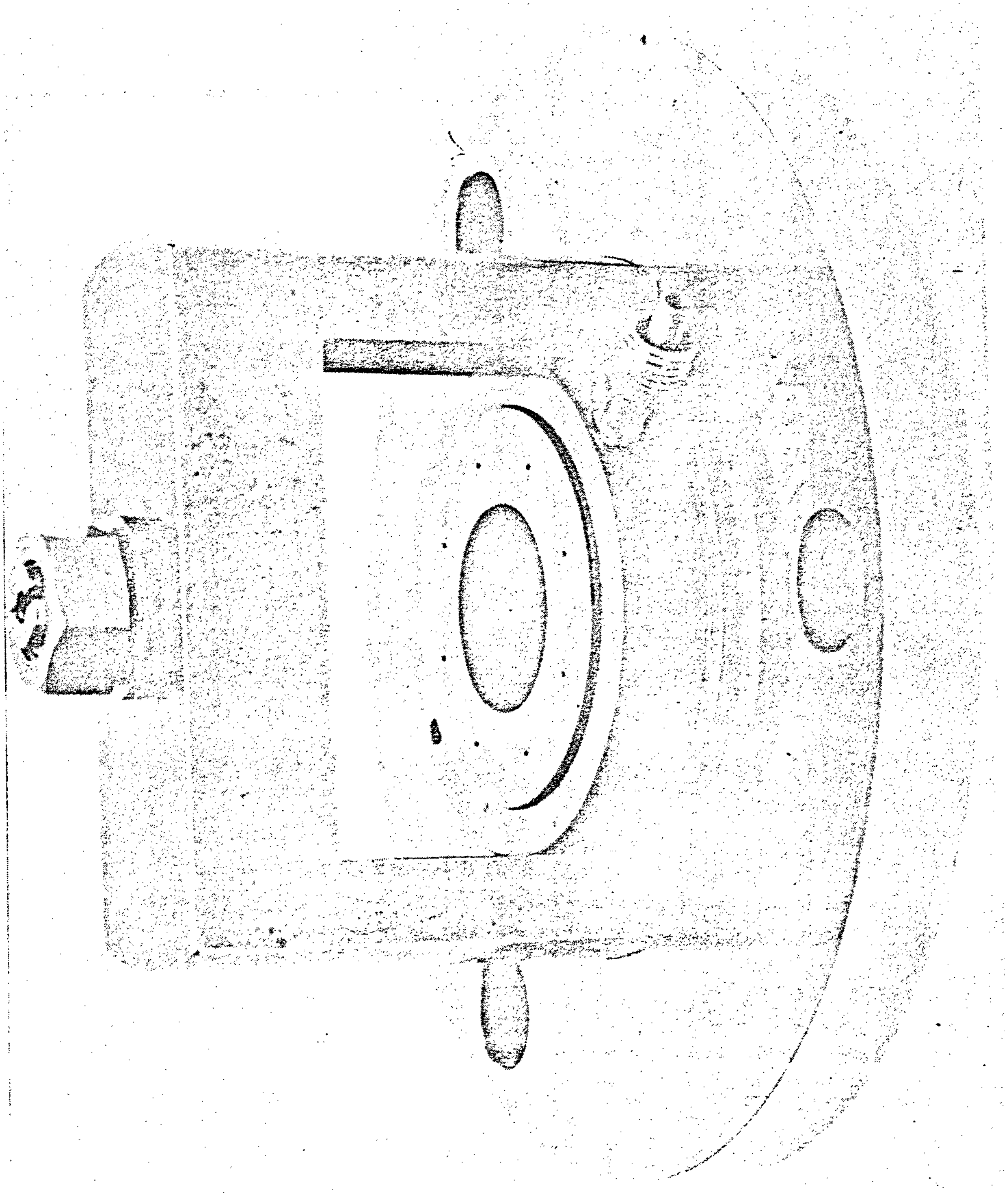
(17)A.G. Birkhimer, "Two new viscometers for measuring viscosity at recoverable shear over a wide range of shear rates," Esso Research, Linden, N.J. (1960)

FIGURE 5.



The rate of shear, $\dot{\gamma}$, is given by:

$$\dot{\gamma} = \frac{2W}{1-C^2} = \frac{K_2}{t_{10^o}}$$

where t_{10^o} is the time required to transverse ten degrees.

C is the ratio of the radius of the inner to outer cylinders

W is the angular velocity in radians/sec.

The viscosity is then given by:

$$N = \frac{\tau}{\dot{\gamma}} = \frac{k_1 W t_{10}}{k_2} = kwt10$$

The constant K was determined by calibration with a reference oil (Bureau of Standards Oil 03). The result was a value of 11.17 as oppose to the calculated value of 10.92. The error of one % was due to the calculation of the equivalent length. K_1 and K_2 was calculated to give 4:00 and 3.58

$$\tau = 4.00W$$
$$\dot{\gamma} = 3.58/t_{10}$$ (18)

Using low rates of shear, a mirror over the drum on the shaft with a simple optical system was used to increase the accuracy of the measurements. This idea of the mirror was later refined by using 36 mirrors, 1/4" x 1/4" x 1 1/16" in size, which reflect the light of the lamp on a curved

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(18)A.C. Birkhimer, Op. Cit.

scale at a distance of 229 cm. Each mirror was approximated to be equivalent to ten degrees in angular displacement. Limitations of the viscometer was set by the ability of the operator. The next step is to compare the measurements made with the rotational, capillary, and a common ubbelohde viscometer. This was done by E. A. Birkhimer and Associates in the summer of 1960. All the results were consistent.(19)

All viscoelastic materials are characterized by having recoverable shear. They have the properties that is situated between pure elastic solid when stretched will return to its original shape, so long as its elastic limit has not been exceeded. Newtonian fluids on the other hand has no recoil whatsoever. One of the unique advantages of the rotational viscometer is its ability to measure recoverable shear, for example, when a constant shear stress is suddenly removed with the aid of a stop-load mechanism, the material stops moving forward and recoils towards its original position. Recoverable shear is measured in shear units and a shear unit (dimensionless) is defined as a recoil of 1 cm by a moving infinite-plate which is at a distance of one cm from a stationary infinite-plate. The usual procedure of measuring recoil is to set the rotational viscometer in motion by

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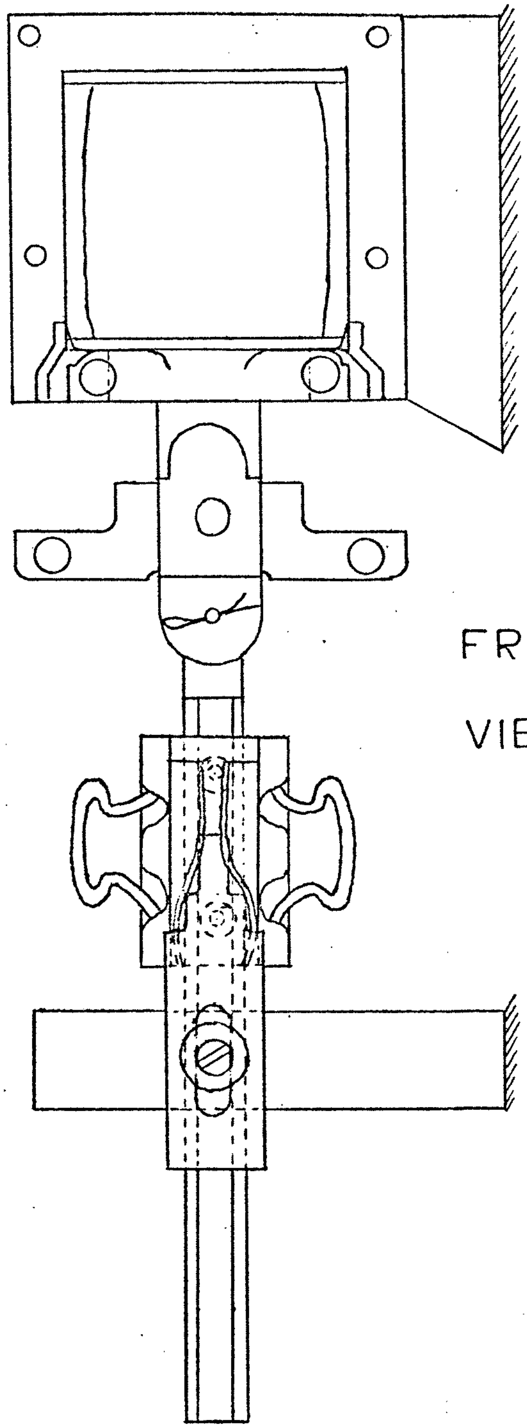
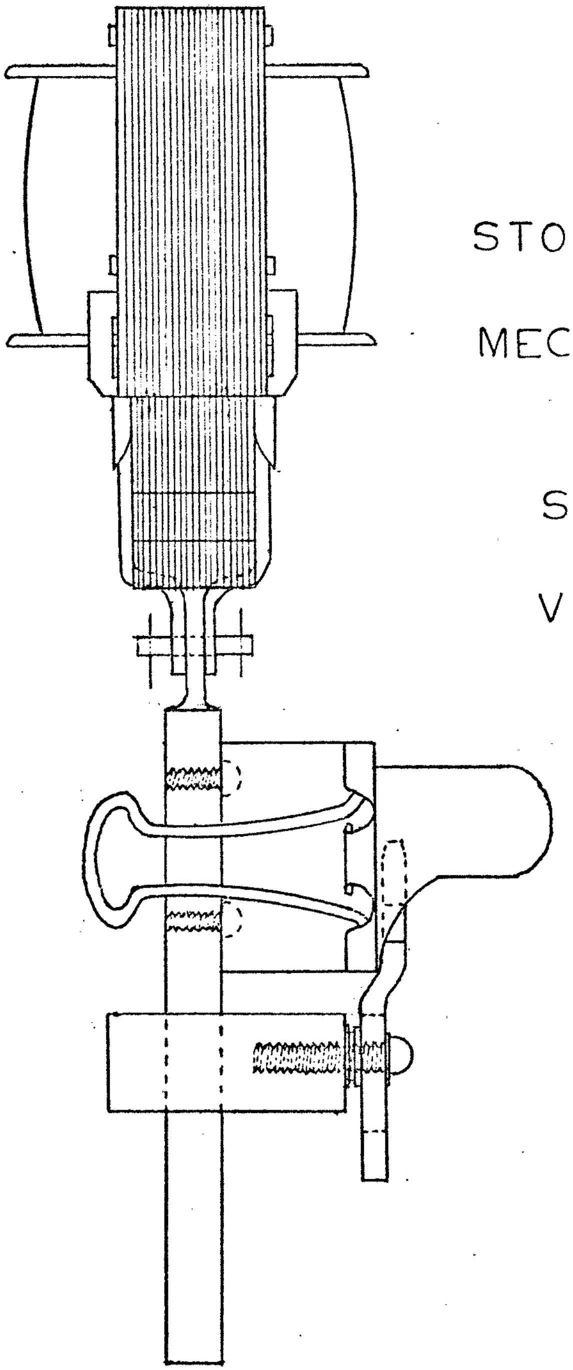
(19)A.E. Birkhimer, Op. Cit.



STOP-LOAD MECHANISM

FRONT VIEW

FIQURE 6



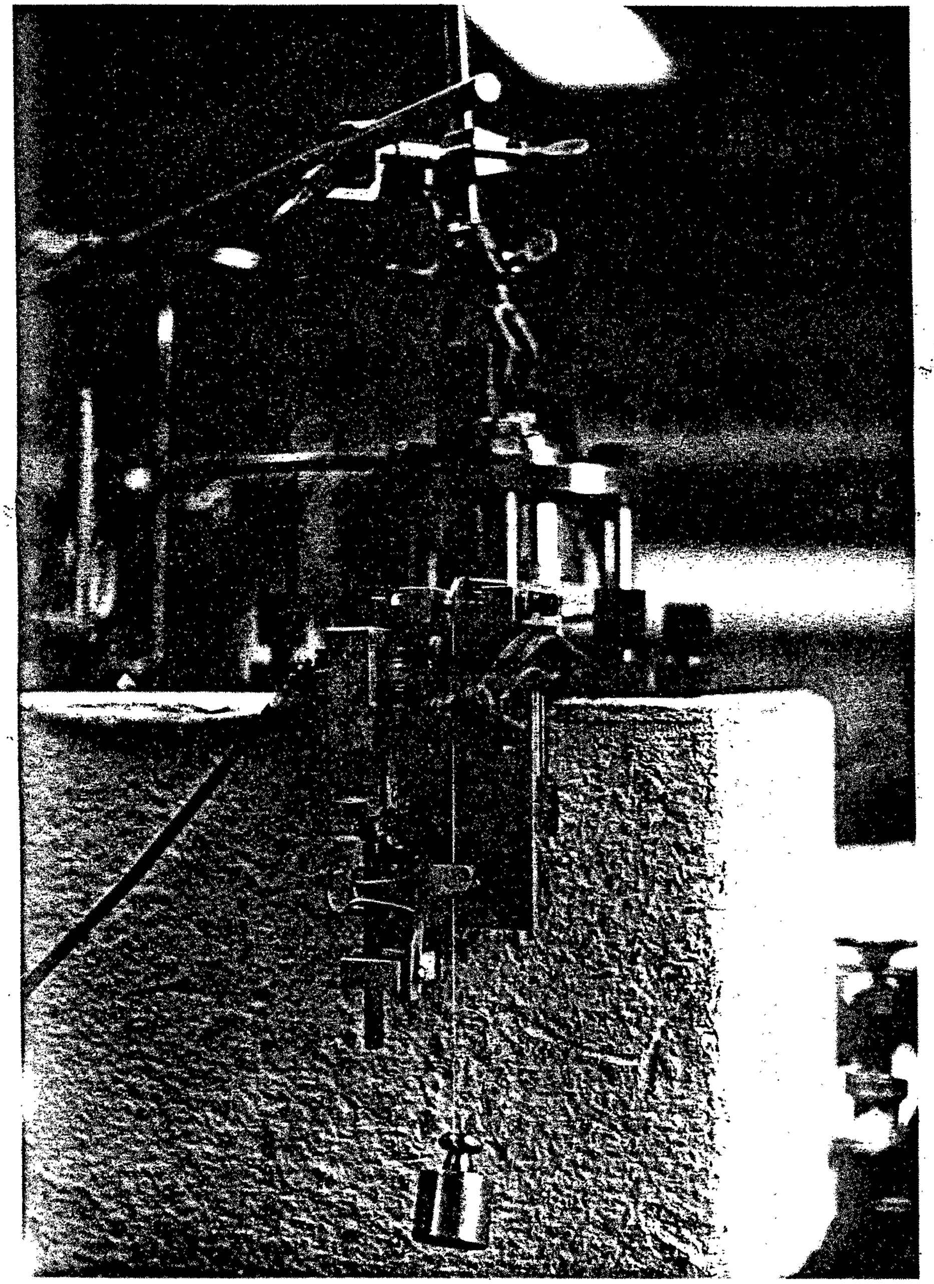
STOP-LOAD

MECHANISM

SIDE

VIEW

FIQURE 7



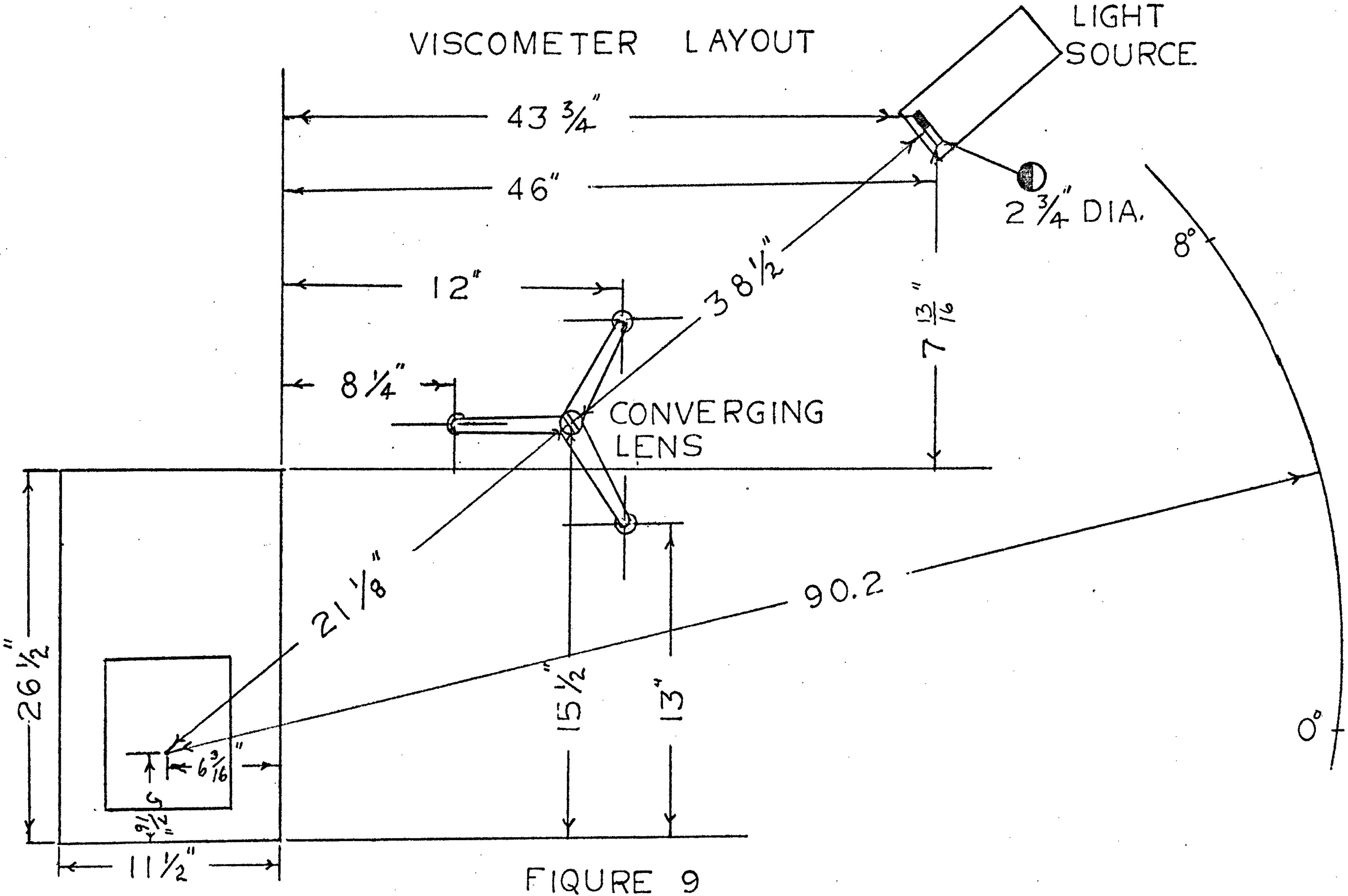
FIQURE 8

applying a constant shear stress and attaining a steady-state condition or as a function of time, and then suddenly removing the shear stress. In some of the experiments undertaken recoils of over ten degrees were observed.

Optical System

The component layout of the optical system is shown on figure (9). The light source used is from a type 31-33-37 model, manufactured by Bausch and Lomb Incorporated of Rochester, New York. The transformer used in conjunction with the lamp is manufactured by Jefferson Electric Corporation of Bellwood, Illinois (cat. no. 969-001-069). The lamp is mounted on a jack which allows it to be translated in a vertical plane. This mechanism is a Ceno-Lerner-Lab-Jack (#19089). The beam of light enters a 888 mm. focal converging lens which is mounted 38 1/2 inches from the lamp. The converging lens was manufactured by Bausch and Lomb Optical Company of New York, Cat. #L-117, Item #DCX-6-011. A glass lens in front of the lamp is one-half covered to give a vertical semi-circular image on a curved scale 229 cm. from the viscometer. The converging lens was used to increase the sharpness of the semi-circular image so that readings of ± 1/4 mm. can be read off the scale. The beam emerging from the converging lens is then reflected off one of the 36 mirrors on the viscometer drum to a curved scale at 229 cm. away giving a total resolution of eighty mm per degree. There are also two photocells eight degrees apart, which will shut on or

OPTICAL SYSTEM AND ROTATIONAL VISCOMETER LAYOUT



FIQURE 9

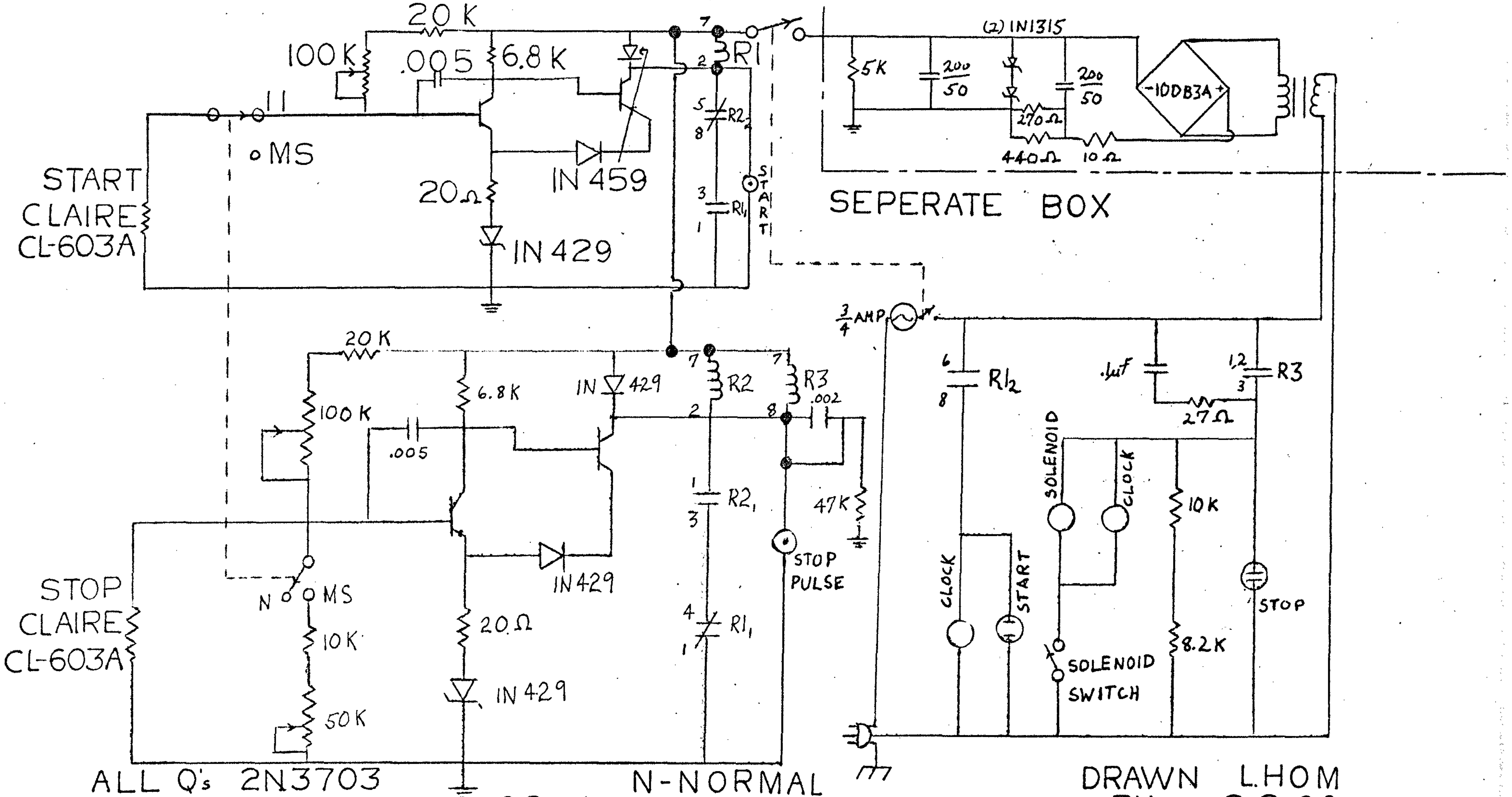
off the elctronic timing mechanism which increases the accuracy of the viscosity and recoil measurements. This optical system, when used for measuring viscosity, is primarily used for low constant stresses. This in turn is dependent on how viscous the polymer solution is. The operator here is left to his discretion on his own ability in determining the cut-off point between using the optical system for low constant stresses or by measuring off the displacement in degrees on the drum of the viscometer for high constant stresses. The optical system is also used for measuring recoil, in that it helps to increase the accuracy of the readings by measuring mm. This is done when the image from the lamp hits the photocell at the 0° point and simultaneously triggers a stop-load mechanism in which the constant stress is suddenly removed, then the image will reverse itself in direction to some equilibrium valve.

Timing and Heating Mechanism

The constant temperature bath in which the viscometer is placed is controlled by a heat input device (Haake R21) and a thermostat both manufactured by Haake of Berlin, Germany. Care must be taken so that the polymer solution is not contaminated by water which can seep in through the flanges. Much experimental time and data was sacrified because of this oversight. This unfortunate situation can easily be remedied by placing a water resistant putty around the flanges. This will prevent any water from coming in. In order to insure that the temperature of the polymer solution inside the viscometer is the same as the constant water temperature. It is best to determine several runs until values become constant. The switching mechanism for the viscometer has the following characteristics. When reflected light hits the first photocell it activates a timer which records the time to travel a distance of eight degrees. Upon reaching the second photocell, the first timer is stopped and the recoil timer is activated which at the same time a stop-load mechanism goes into effect which picks up the falling weight. Either one or both operations can be worked at the same time. Measuring time for larger distance than eight degrees can be utilized by covering up the stop time photocell for any amount of displacement desired.

The switching circuit layout for the viscometer is shown on figure (10), which has been drawn by L. Hom of Esso Research. It works in the following way, when light hits the first photocell, the relay 7-2-R1 is activated, this in turn opens 5-8-R$^{2}_{2}$, closes 3-1-R1$_1$, and closes 6-8-R1$_2$. The first clock is started with the closing of 6-8-R1$_2$. When the light reaches the second photocell, which is also the stop light, the 7-2-R2 relay is activated and this in turn closes 5-8-R2$_2$, opens 6-8-R1$_2$, closes 1-3-R2, and closes 4-1-R1$_1$. With the opening of 5-8-R2$_2$, this will stop the first timer. When R2 is activated this not only stops the first clock but also

SWITCHING CIRCUIT FOR VISCOMETER



ALL Q's 2N3703
R1, R2 SIGMA 42R06 1000G-SIL
R3 HGP 1010

N-NORMAL
MS-MANUAL STOP

DRAWN BY: L.HOM 2-2-68

FIQURE 10

activates the second relay, R3, which in turn starts the recoil clock and activates the solenoid, which removes the clamp from its unlock position.

Apparatus Setup

The apparatus setup is shown previously on figure (9). It functions in the following manner. The light rays from the light source first goes through an image lens which is next to and directly in front of the light bulb. The image lens is an ordinary circular glass plate in which one-half of it is covered up by untransparent tape. This will allow a semi-circular image to be projected on the degree scale with its vertical edge used for reading measurements and for starting and stopping the timing mechanism by the use of photocells placed eight degrees apart. After the light rays goes through the image lens, it goes through a converging lens, which converges the light rays onto the mirror of the drum on the viscometer. The light rays are then reflected off the mirror onto the measuring scale. The measuring units used on the measuring scale are degrees and mm. One degree contains a finite number of mm. The measuring scale was originally designed so that one degree was equal to 64 mm. However, in this experiment 80 mm was used to represent one degree. The difference in design specification from 64 mm to 80 mm will result in negligible experimental error as indicated by the following error analysis.

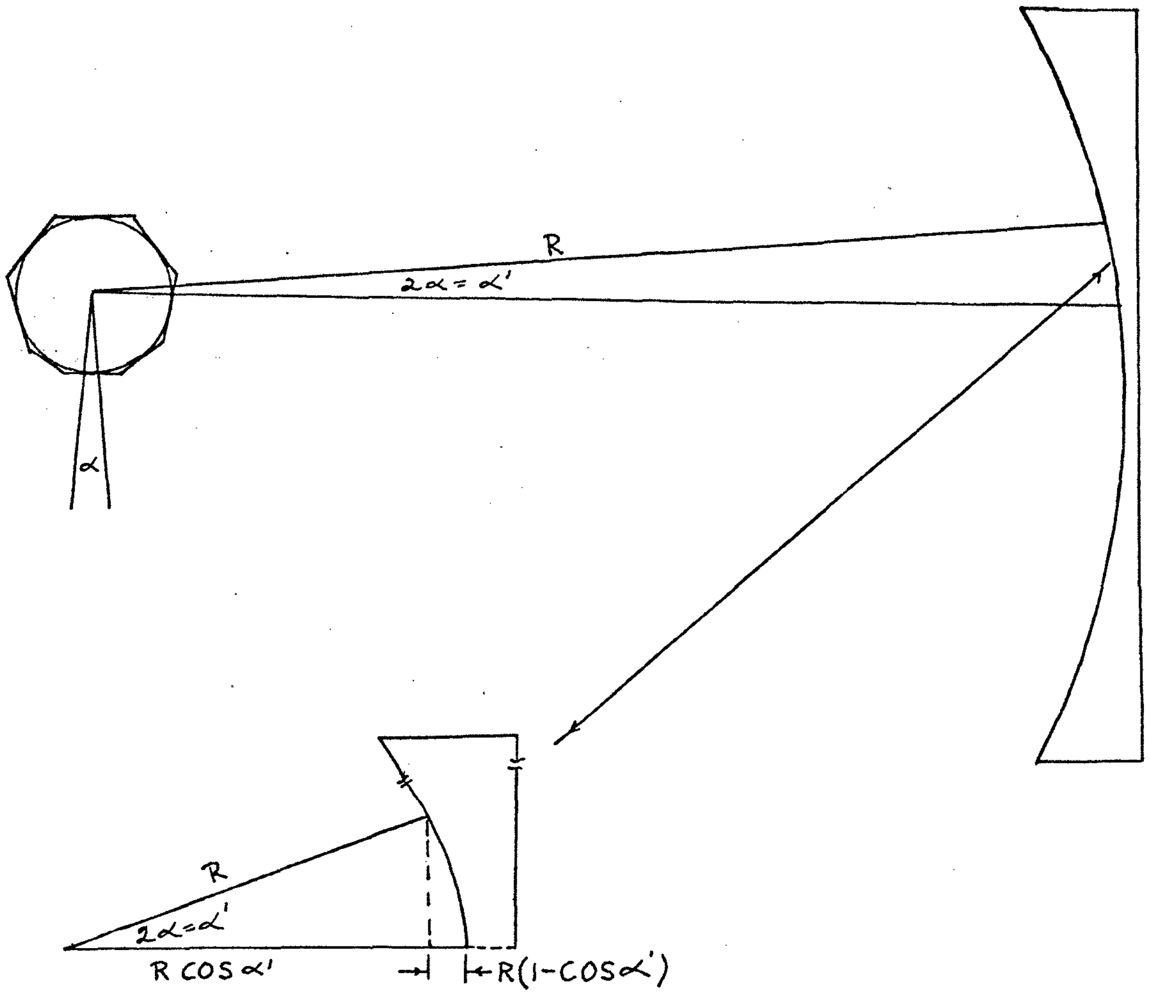


FIGURE (11)

the following relationship is used;

$$L = R \cdot \frac{\pi}{180} \alpha'$$

where: L = Length of Arc

R = Radius of curvature

α' = Angle of rotation of arc

Since the original design specifications calls for one degree to equal 64 mm (6.4 cm), one can compute the actual design radius of curvature for the measurement scale. It is important to note that when the angle of the drum on the viscometer makes a rotation of one degree, the angle α' made by the viscometer and measurement scale is two degrees or twice the angle made by the drum as shown on figure (11). Using the above formula, the actual radius of curvature was 183.439 cm.

One can now determine the change in α' due to the difference in radius and allowing one degree to equal to 80 mm instead of 64 mm. Let the angle of the drum rotate one degree, therefore α' will be two degrees. Substituting the values into the following equation:

$$229 \cdot \frac{2}{180}\pi = 80 = 183 \cdot \frac{\alpha'}{180}\pi$$

α' results in an answer of 2.5°. Therefore, the following conclusion can be drawn. For a radius of 229 cm and a corresponding α' of 2° will relate to a 183 cm radius by an α' increase of $.5^\circ$ or an α' equal to 2.5°. It is now possible to determine how this effects the radius of the beam of light as it travels along the measurement scale. Using the following error equation.

$$(1 - \cos\theta_1) - (1 - \cos\theta_1^1)\,\frac{183}{229} = \frac{|\Delta R_1| \times 100}{229} = \%\ \text{Error}$$

The readings from 0° - 4° will only be considered because the results of 4° - 8° will be symmetrical with the first results.

From 0° - 1°:

$$(1 - \cos 2^\circ) - (1 - \cos 2\ 1/2^\circ)\,\frac{183}{229} = \frac{|\Delta R_1| \times 100}{229} = .01987\%$$

From 0° - 2°:

$$(1 - \cos 4^\circ) - (1 - \cos 5^\circ)\,\frac{183}{229} = \frac{|\Delta R_2| \times 100}{229} = .0634\%$$

From 0° - 3°:

$$(1 - \cos 6^\circ) - (1 - \cos 7\ 1/2^\circ)\,\frac{183}{229} = \frac{|\Delta R_3| \times 100}{229} = .1375\%$$

From 0° - 4°:

$$(1 - \cos 8^\circ) - (1 - \cos 10^\circ)\,\frac{183}{229} = \frac{|\Delta R_4| \times 100}{229} = .2225\%$$

Since the errors involved is small we are justified in using a measurement scale with a design radius specification of 183 cm to one of 229 cm radius used in the experiment.

II. MATERIALS

The test fluids used in the investigation were of the following type. For the viscosity measurement polystyrene NBS-2-35967 was used. Polystyrene is mixed in a solution consisting of 65% TCP (Tri-Cresyl-Phosphate) and 35% Aroclor with $N_{d25} = 1.5910$. The molecular weight polystyrene is 450,000. The concentration of polystyrene in the solution is 7.14% weight and the density of the solution is 1.213. Polystyrene NBS-2-35967 is manufactured by Pressure Chemical Company of Pittsburgh, Pennsylvania and the solution was made up by the National Bureau of Standards. Polyisobutylene in 16.5% mineral spirits were also used. After that, Indopol H-1900 (polyisobutylene) was used to measure viscosity as a function of temperature. Polyisobutylene was obtained from Amoco Chemical of Whiting, Indiana. It has a molecular weight of 2893 and a density of .88. Then Vistanex L-200 in Primol 355 was investigated in terms of its viscosity and transient phenomena. Vistanex L-200 (SL-64480, 16F6-2) has a molecular weight of 5.5×10^6 and was obtained from Esso in Linden, New Jersey. Vistanex was mixed in Primol 355 in the ratio of 3% and 4.5%. The properties of Primol 355 are listed on the following page. Vistanex L-200 has a density of .92. The 16.5% solution was made at New York University in "Mineral Spirits".

VISCOSITY-TEMPERATURE RELATION FOR PRIMOL 355

Temp. °F.	Temp. °C.	Kim. Vis. v cSt	Density g/cc	Viscosity cp
32	0	1256.6	(0.8954)	1125
59	15.00	340.46	0.8853	301.5
77	25.00	166.81	0.8788	146.6
100	37.78	77.49	0.8704	67.5
130	54.45	34.65	(0.8580)	29.75
210	98.89	8.202	(0.8275)	6.80

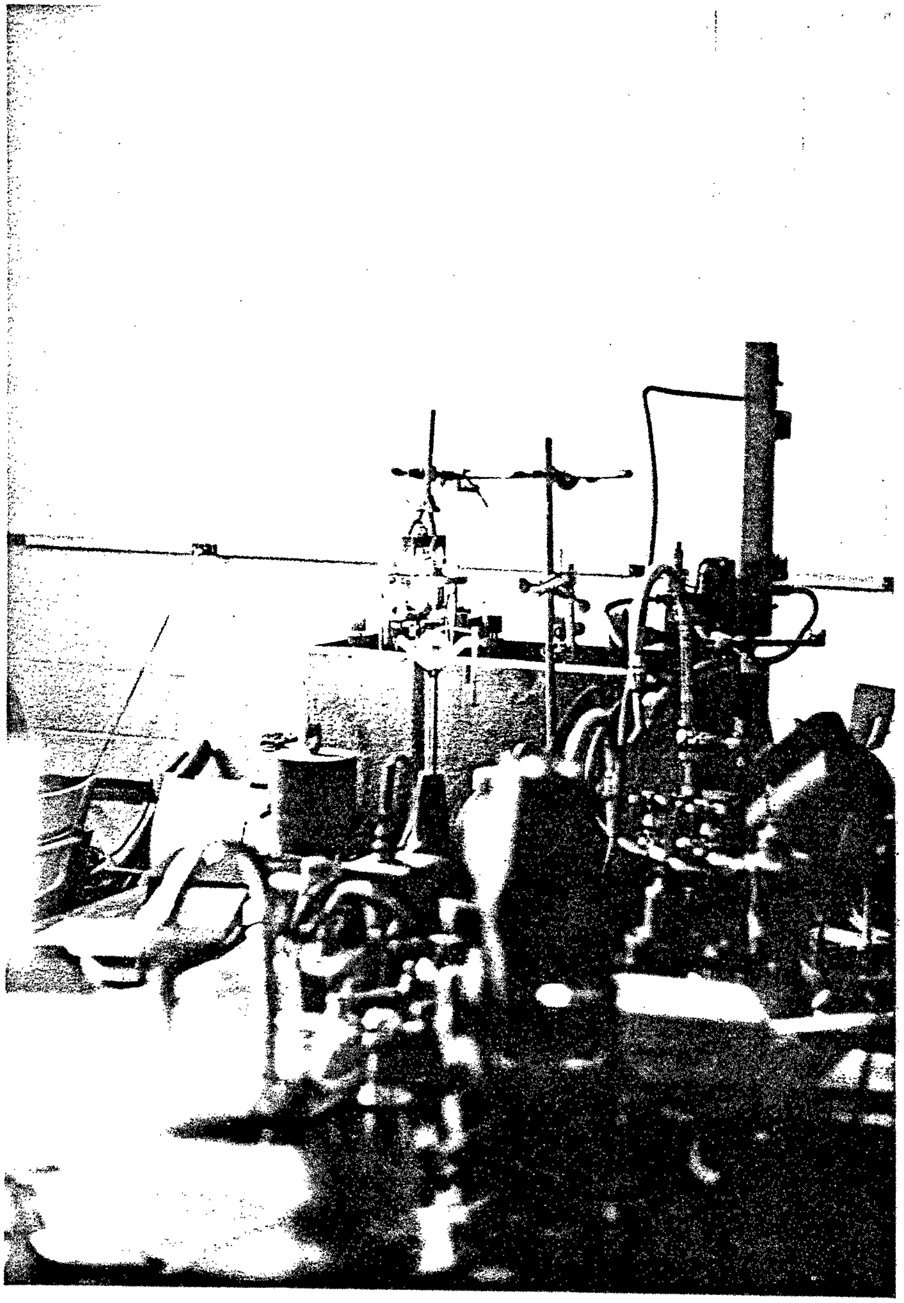
(Interpolated Values)

W. Philippoff/dm
1/29/62

EXPERIMENTAL PROCEDURES

Viscosity Measurements in Terms of Stress and Shear Rate

The apparatus setup of the experimental equipment have been shown previously. Referring back to the diagram of the components of the rotational viscometer, approximately sixty grams of a polymer solution is added to the cup. It is important to note that the level of the polymer solution should be safely below the vapor trap holes. Otherwise a higher than normal viscosity reading will be observed owing to a decrease in the rate of shear. It is also imperative that the rotary shaft in the section of the vapor trap compartment is completely free of any polymer solution, for it too will tend to give a higher than normal viscosity readings. Referring back to the optical settings of figure (9), viscosity was measured in the following way. A weight is attached to a string which in turn is wound around the drum of the rotational viscometer. When the air pressure is released to sixty PSIG, the weight is pulled down due to gravity causing the drum and bob to rotate. The mirror which is situated on top of the drum will also rotate. At the same time light rays from a light source passing through a converging lens will reflect off the mirror onto the measuring scale figure (12). Two photocells are placed eight degrees apart on the measurement scale. The photo cells are used to trigger on and off a timing mechanism to record time versus



FIQURE 12

displacement. Knowing the weight and the displacement time for eight degrees, the viscosity can be calculated using the follwoing equation:

$$N = \frac{\tau}{\dot{\gamma}}$$

$$\dot{\gamma} = \frac{3.58}{1.25 t_{8^o}} = \frac{2.864}{t_{8^o}}$$

where: N = Viscosity Measured in Poise (dynes sec/cm^2)

τ = Shear Stress - 4 x Weight (dynes/cm^2)

$\dot{\gamma}$ = Rate of Shear (sec^{-1})

t_{8^o} = Time for Displacement of Eight Degrees (secs)

All viscosities were measured at 77^{o}F except for Indopol H-1900 which was measured at a variety of temperatures. The viscometer containing the polymer solution is submerged into a constant temperature water bath with water level 3/4 of the way up the vapor trap component. To insure that the temperature of the polymer solution is the same as the water bath temperature, eight degree time measurements should be taken at regular intervals until constant readings are obtained. When measuring viscosities using higher weights, degree readings can be taken right off the drum of the viscometer. This procedure is used only when the time measured for eight degrees becomes too small to measure accurately. When measuring viscosities, the centering screw is adjusted in the following manner. For low weights with the air pressure turned off the centering screw is turned on all the way until contact is made between the carbaloy point and the rotational shaft. After having done this the centering screw is reversed one quarter of a turn. With air bearing plate on, the viscometer is now ready for viscosity measurements. The air bearing plate is used with lower weights because the air pressure will force the bob up from its carbaloy point making the rotational viscometer virtually frictionless. For higher weights the air bearing plate nut must be loosened completely. With the air bearing plate off there will be much more play between the carbaloy points and therefore the centering screw should be adjusted as outlined before. For high weights the rotational viscometer is insensitive to the small friction that may arise from the carbaloy points. The cutoff point between the high and low weights can be determined by measuring the viscosity using intermediate weights with the air plate on and with the air plate off. At the point when the viscosity starts to deviate between using the air plate on and off will determine the cutoff point. Leaving the air plate on after the cutoff point will tend to increase the viscosity readings. The cutoff point for this particular rotational viscometer was between 200 and 500 gms. It is also important to check if the rotational viscometer is leveled. It is also important that the contact surface between the air bearing and the top flange should always be smooth and clean.

Angular Displacement Versus Time Measurements

For small weights the optical setup and the measurement scale are used. The air pressure is initially off and the weight is allowed to hang freely from the viscometer. The viscometer by the use of reflected light is then positioned on the zero degree line slightly to the left of the "on timer mechanism" photocell. To insure that the viscometer will remain stationary, the yoke of the viscometer is clamped down by a series of connecting rods. As the air pressure valve is turned on, the lighted image will trigger the photocell which in turn will start the timing mechanism. Depending on how slow the weight moves, millimeters or degrees versus time is recorded at regular intervals. If the displacement span required moves more than eight degrees, the stop time photocell is covered up and the degrees measured beyond eight are read off the drum of the viscometer. This procedure is used rather then waiting for the reflected light to come around the measurement scale again because the mirrors on the drum are not exactly spaced ten degrees apart. To do so would be an expensive venture. Since the results are to be plotted on log-log scale, smaller time intervals should be taken initially and larger time intervals can be taken toward the end of the experiment.

For high weights with the air pressure valve off, if the air bearing plate cannot hold the weight stationary, then the weight is held by hand with the air pressure on. The weight is then released simultaneously with the timer, or the timer can be started with the help of the photocell. The readings can be taken off the drum of the viscometer. A small magnifying glass may be used to increase the accuracy of the readings for small and large weights where applicable. All of angular displacement versus time experiments were measured at 77°F. All polymer solutions must be stress free at the start of the experiment. This can be achieved when the viscometer with no weight on is allowed to rotate freely with the air pressure on. If the reflected light remains stationary on the measurement scale or has very negligent amount of movement, it is then stress free. Stress free implies that there is no elastic movement. If the polymer solution is not elastic free it will tend to shift the displacement versus time line to the left. The degree of the shift is dependent on the amount of elastic stress stored in the polymer solution.

Recoil Measurements

Recoil measurements are made with the aid of a stop-load mechanism (figure 6, 7, 8). Recoil measures the amount of recoverable shear when applied by a constant stress load. In this experiment recoverable shear was measured as a a function of displacement versus time. The viscometer is set up with the air pressure off. For small weights where the displacement versus time is low, the viscometer with the aid of reflected light is positioned at regular intervals to the left of the "stop time" photocell. For small weights with the air pressure valve off, the weights are allowed to hang freely. The air pressure is released simultaneously with the timer. When the reflected light from the viscometer hits the "off" photocell, it shuts off the timer and at the same time it triggers on the stop load mechanism. Once the weight is picked up by the clamp, the bob of the viscometer or the reflected light will reverse direction. It will continue to move in that direction until all its elastic potential is released. Sometimes it takes as long as one or two hours before the movement completely stops or becomes very negligent. All of its elastic potential must be eliminated before the next reading can be taken. If not, recoil measurement will then be less then what they truly are. It can change as much as 22.4%. High weights can be released by hand, since the friction of the air bearing plate is not high enough to hold the weight in place. The stop-load mechanism clamp will also not be able to hold onto the weight, but can be supplemented together with the hand.

Recoverable shear at infinite time versus shear stress is obtained by the following equation:

$$\%\ S_r = R \times \frac{3.58}{800} \times 100 = 0.448R$$

where: R = Millimeter recoil at infinite time

S_r = Percent recoverable shear measured in shear units

To determine recoverable shear at infinite time for a specific weight, one only has to keep taking recoil measurement as a function of time until recoil becomes constant. In order to save time, recoil measurements can be taken in conjunction with two prior experiments. In the experiment involving displacement versus time, when enough data has been obtained, one can take a recoil measurement to end the experiment. In the other experiment involving recoverable shear versus time, recoil measurement will reach a constant equilibrium which will remain the same at infinite time. All recoil measurements were taken at 77°F.

Determination of Shear Velocity Profiles from Displacement Versus Time

The velocity profile of total reversible shear and recoverable shear was determined with the use of a computer program. The computer program generated a best fit polynomial equation by the least mean square method. The velocity is then obtained by taking the differential of the best fit polynomial equation. The other method employed made use of the fact that the reversible and recoverable shear versus time was plotted on log-log graph paper. Since the lines also appeared smoother on a log-log plot, the following differential equation was used:

$$\frac{d\alpha}{dt} = \frac{\alpha}{t}\left(\frac{d\ln\alpha}{d\ln t}\right)$$

let α and t be converted into logs. The following polynomial is then generated:

$$\mathrm{Log}\,\alpha = A(\mathrm{Log}\ t)^{n} + b(\mathrm{Log}\ t)^{n-1} + c(\mathrm{Log}\ t)^{n-2} \ldots. + F(0)$$

Let $\alpha' = \mathrm{Log}\,\alpha$ and $t^{1} = \mathrm{Log}\ t$

$$= At^{\prime n} + bt^{\prime n-1} + ct^{\prime n-2} \ldots.\ F(0)$$

taking the differential of the equation:

$$\frac{d\alpha'}{dt'} = Ant^{\prime n-1} + b(n-1)t^{\prime n-2} + c(n-2)t^{\prime n-3} \ldots. + 0$$

Substituting:

$$\frac{d\ \mathrm{Log}\,\alpha}{d\ \mathrm{Log}\ t} = An(\mathrm{Log}\ t)^{n-1} + b(n-1)(\mathrm{Log}\ t)^{n-2} + c(n-2)(\mathrm{Log} t)^{n-3} + 0$$

Since: $\frac{d\mathrm{LN}\,\alpha}{d\mathrm{LN}t} = \frac{d\mathrm{Log}\,\alpha}{d\mathrm{Log}t}$

Therefore:

$$\frac{d\alpha}{dt} = \frac{\alpha}{t}\left(\frac{d\mathrm{Log}\,\alpha}{d\mathrm{Log}t}\right)$$

The differentiation of total reversible and recoverable shear versus time plot were divided into three sections to obtain better accuracy. These sections consist of the acceleration due to gravity, vibrations due to the string and the polymer solution, and the remaining reversible and recoverable shear versus time plot. The first part may be differentiated mathematically. Since everyone of these lines has the form of $\alpha = At^2$, substituting values for and t will give A. After that, it is just a simple matter of differentiation and plugging in values for t to obtain $d\alpha/dt$. The second and third part is handled by the computer. A smaller interval of points is needed for the second part as oppose to the third part owing to more flucuations in the curve. There must be considerable overlapping of all three parts to allow for continuity of the shear velocity curves. One may also take certain parts of the curve and plot it on linear graph paper to obtain a closer look or to obtain more accurate data points.

Determination of Flow History Free from Angular Vibration

Observance of the plot of angular displacement versus time, one questions the existance of zero or negative displacement after the fall of the weight due to gravity. This phenomena is the result of the following factors; vibration due to the elastic properties of the polymer solution, vibration of the nylon string and the inertia caused by the drum of the viscometer. All these inevitable factors come into play as a direct result of the weight as it is allowed to fall from rest. To verify that the zero shear phenomena is the result of the above factors, a mathematical model was used to calculate the dynamic response of the viscometer on step-loading working in the area of complete recoverable shear. The following model and equation was derived:

where M_2 = Equivalent Mass of Viscometer drum =

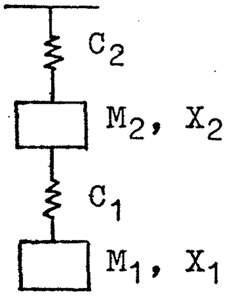
$$\frac{I}{R^2} = \frac{12{,}000 \text{ gm cm}^2}{3.825^2 \text{ cm}} = 820 \text{ gm}$$

M_1 = Amount of Loading Used - Grams

C_1 = Spring Constant for the Nylon String - $1.08 \times 10^6 \, \frac{\text{Dynes}}{\text{CM}}$

C_2 = Spring Constant for the Polymer Solution $.4 \times 10^6 \, \frac{\text{Dynes}}{\text{CM}}$

(20)



$$(1)\quad M_1\ddot{X}_1 = M_1G - C_1(X_1-X_2)$$

$$(2)\quad M_2\ddot{X}_2 = C_1(X_1-X_2) - C_2X_2$$

at $t = 0$

$$X_1(0) = \frac{M_1}{C_1} G;\; X_2(0) = \dot{X}_1(0) = \dot{X}_2(0) = 0$$

Laplace transform of equation (1) and (2)

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(20)W. Philippoff, Unpublished Mathematical Responses of the Rotational Viscometer Due to Loading.

(3) $$\frac{M_1G}{S} = M_1S^2X_1(S) - M_1X_0S + S^2M_2X_2(S) + C_2X_2(S)$$

(4) $$C_1X_1(S) - C_1X_2(S) = S^2M_2X_2(S) + C_2X_2(S)$$

Solve for $X_1(S)$

(5) $$X_1(S) = X_2(S)\ (1 + \frac{C_2}{C_1} + \frac{M_2S^2}{C_1})$$

Substitute (5) into (3)

$$\frac{M_1G}{S} = M_1S^2(1 + \frac{C_2}{C_1} + \frac{M_2}{C_1}S^2)X_2(S) - M_1X_1(0)S + C_2X_2(S)$$
$$+ S^2M_2X_2(S)$$

Solve for $X_2(S)$:

$$X_2(S) = \frac{\frac{M_1G}{S} + M_1X_oS}{M_1S^2(1 + \frac{C_2}{C_1} + \frac{M_2}{C_1}S^2) + S^2M_2 + C_2}$$

$$X_2(S) = \frac{\frac{M_1G}{S} + M_1X(0)S}{S^2(M_2 + (1 + \frac{C_2}{C_1})M_1) + \frac{M_1M_2}{C_1}S^4 + C_2}$$

$$X_2(S) = \frac{M_1}{S} \cdot \frac{G + X_1(0)S^2}{\frac{M_1M_2}{C_1} S^4 + (M_2 + (1 + \frac{C_2}{C_1})M_1)S^2 + C_2}$$

$$\frac{M_1M_2}{C_1} S^4 + (M_2 + (1 + \frac{C_2}{C_1})M_1)S^2 + C_2 = (S^2 + A^2)\ (S^2 + B^2)$$

$$\frac{M_1M_2}{C_1}\left[S^4 + \frac{M_2 + (1 + \frac{C_2}{C_1})M_1}{M_1M_2} C_1S^2 + \frac{C_1C_2}{M_1M_2}\right] = S^4 + (A^2 + B^2)S^2 + A^2B^2$$

$$A^2 + B^2 = \frac{M_2 + (1 + \frac{C_2}{C_1})\ M_1}{M_1M_2} C_1$$

$$A^2B^2 = \frac{C_1C_2}{M_1M_2} \qquad B^2 = \frac{1}{A^2} \cdot \frac{C_1C_2}{M_1M_2}$$

$$A^2 + \frac{1}{A^2} \frac{C_1C_2}{M_1M_2} = \frac{M_2 + (1 \frac{C_2}{C1})M_1}{M_1M_2} C_1$$

$$A^4 - A^2 \left[\frac{M_2 + (1 + \frac{C_2}{C_1})M_1}{M_1 M_2}\right] C_1 + \frac{C_1 C_2}{M_1 M_2} = 0$$

$$A^4 + CA^2 + D = 0$$

$$A^2 = -\frac{C}{2} \pm \sqrt{\frac{C^2}{4} - D}$$

$$B^2 = -\frac{C}{2} \pm \sqrt{\frac{C_2}{4} - D}$$

$$A = +\sqrt{-\frac{C}{2} + \sqrt{\frac{C_2}{4} - D}}$$

$$B = +\sqrt{-\frac{C}{2} - \sqrt{\frac{C^2}{4} - D}}$$

$$A,B = +\sqrt{\frac{1}{2}\,\frac{C_1 M_2 + (C_1 + C_2)M_1}{M_1 M_2} \pm \sqrt{\frac{\frac{1}{4}\,(C_1 M_2 + (C_1 + C_2)M_1)^2}{M_1{}^2 M_2{}^2} - \frac{C_1 C_2}{M_1 M_2}}}$$

$$X_2(S) = \frac{M_1C_1}{SM_1M_2} \cdot \frac{G + X(0)S^2}{(S^2+A^2)(S^2+B^2)}$$

$$X_2(S) = \frac{C_1}{M_2}\left[\frac{GS}{S^2(S^2+A^2)(S^2+B^2)} + \frac{X(0)S}{(S^2+A^2)(S^2+B^2)}\right]$$

$$X_2(S) = \frac{C_1}{M_2}\left[C_1I_1(S) + X_0I_2(S)\right]$$

$$I_2(S) = \frac{S}{(S^2+A^2)(S^2+B^2)}$$

$$\mathcal{L}^{-1}\left[I_2(S)\right] = I_2(t) = \frac{1}{B^2 - A^2}\left[\text{Cos } A\,t - \text{Cos } B\,t\right]$$

Expand to partial fractions:

$$I_1(S) = \frac{1}{S(S^2+B^2)(S^2+A^2)} = \frac{K_0}{S} + \frac{K_1B}{S^2+B^2} + \frac{K_2S}{S^2} + \frac{K_3A}{S^2+A^2} + \frac{K_4S}{S^2+A^2}$$

Multiply by S and let S → 0

$$K_0 = \frac{1}{A^2B^2}$$

Multiply by S^2+B^2 and let $S^2 \pm iB$

$$\frac{1}{S(S^2+A^2)} = k_1B + K_2\ B$$

$$\frac{1}{iB(A^2-B^2)} = K_1B + K_2iB$$

$$\frac{1}{iB^2(A^2 - B^2)} = K_1 + iK_2$$

Multiply by its conjugate

$$\frac{1}{iB^2(A^2-B^2)} \quad \frac{-i(B^2)(A^2 - B^2)}{-i(B^2)(A^2 - B^2)} = \frac{-B^2(A^2 - B^2)\ i}{B^4(A^2 - B^2)^2}$$

$$K_1 = 0 \quad , \quad K_2 = -\frac{1}{B^2(A^2 - B^2)}$$

Multiply by $S^2 + A^2$ and let $S = \pm iA$

$$\frac{1}{S\ (S^2+B^2)} = K_3A + K_4S$$

$$\frac{1}{iA(B^2 - A^2)} = A\left[K_3 + K_4 i\right]$$

Using same proceudre as above.

$$K_3 = 0 \;, \quad K_4 = \frac{1}{-A^2(B^2 - A^2)}$$

$$\mathcal{L}^{-1}\left[\frac{1}{S(S^2 + B^2)(S^2 + B^2)}\right] = \mathcal{L}^{-1}\left[\frac{K_o}{S}\right] + \mathcal{L}^{-1}\left[\frac{K_1 B + K_2 S}{S^2 + B^2}\right] + \mathcal{L}^{-1}\left[\frac{K_3 A + K_4 S}{S^2 + A^2}\right]$$

$$\mathcal{L}^{-1}\left[\frac{1}{S(S^2+B^2)(S^2+A^2)}\right] = \frac{1}{A^2B^2} - \frac{1}{B^2(A^2-B^2)} \quad \text{Cos At}$$

$$I_1(t) = \frac{1}{A^2B^2} + \frac{1}{B^2-A^2}\left[+\frac{\text{COS Bt}}{B^2} - \frac{\text{COS At}}{A^2}\right]$$

Rearranging:

$$I_1(t) = \frac{B^2-A^2}{(B^2-A^2)A^2B^2} + \frac{\text{COS Bt}}{(B^2-A^2)B^2} - \frac{\text{COS At}}{(B^2-A^2)A^2}$$

$$I_1(t) = \frac{1}{(B^2-A^2)A^2} - \frac{1}{(B^2-A^2)A^2}\text{COS At} - \frac{1}{(B^2-A^2)B^2}$$

$$+ \frac{1}{(B^2-A^2)B^2}\text{COS Bt}$$

$$I_1(t) = \frac{1}{B^2-A^2}\left[\frac{1-\text{COS } At}{A^2} - \frac{1-\text{COS } Bt}{B^2}\right]$$

$$X_2(t) = \frac{C_1}{M_1}\left\{G \cdot \frac{1}{B^2-A^2}\left[\frac{1-\text{COS } At}{A^2} - \frac{(1-\text{COS } Bt)}{B^2}\right] + \frac{X_1(0) \cdot (\text{COS } At - \text{COS } Bt)}{B^2-A^2}\right\}$$

$$X_2(t) = \frac{C_1}{M_2} \cdot \frac{1}{B^2-A^2}\left(\frac{G}{A^2} - \frac{G}{A^2}\text{ COS } At - \frac{G}{B^2} + \frac{G}{B^2}\text{ COS } Bt + X(0)\text{COS } At - X_1(0)\text{COS } Bt\right)$$

$$X_2(t) = \frac{C_1}{M_2}\,\frac{1}{B^2-A^2}\left[\left(-X_1(0) + \frac{G}{A^2}\right) + \left(X_1(0) - \frac{G}{A^2}\right)\text{ COS } At + \left(X_1(0) - \frac{G}{B^2}\right) - \left(X_1(0) + \frac{G}{B^2}\right)\text{ COS } Bt\right]$$

(6)

$$X_2(t) = \frac{C_1}{M_2}\,\frac{1}{A^2-B^2}\left[\left(X_1(0) - \frac{G}{A^2}\right)(1-\text{COS } At) - \left(X_1(0)- \frac{G}{B^2}\right)(1-\text{COS } Bt)\right]$$

It is now possible with the help of equation (6), to predict the displacement of the viscometer drum as a function of time. However to compare the velocity in shear units between the experimental with the calculated curves, certain correction factors must be employed. First equation (6) is differentiated with respect to t to obtain the velocity equation. To convert the velocity $(\frac{dx_2}{dt})$ from cm/sec. into degrees/sec the following relationship is used:

$$X_2 = R \cdot \alpha \text{ or } dx_2/dt = R \cdot d\alpha/dt$$

where $\frac{dx_2}{dt}$ = Velocity of the arc in cm/sec

R = Radius of the viscometer drum in cm.

$\frac{d\alpha}{dt}$ = Radians per sec.

To convert $d\alpha/dt$ into degrees, the following correction factors are used.

$$\frac{dx_2}{dt} = R \cdot \frac{\pi}{180^\circ} \frac{d\alpha^\circ}{dt}$$

solving for $d\alpha/dt$:

$$\frac{d\alpha^\circ}{dt} = \frac{dx_2}{dt} \cdot \frac{180}{\pi R} = \frac{dx_2}{dt} \cdot \frac{180}{\pi \cdot 3.825} = \frac{dx_2}{dt} \cdot 15$$

$\frac{dx_2}{dt}$ is also multiplied by .358 to convert it into shear units.

The differentiated equation with its correction factors gives the following results:

$$(7) \quad \frac{d\alpha^{o}}{dt} = .358 \cdot 15 \cdot \frac{C_1}{M_2} \cdot \frac{1}{A^2-B^2} \left[A(X_1(0) - \frac{G}{A^2}) \right.$$

$$\left. \text{SIN } At - B\,(X_1(0) - \frac{G}{B^2})\ \text{SIN } Bt \right]$$

Values of time are now substituted into the equation to observe the comparison between the experimental curve and the calculated curves for the different weights used in the experiment. Upon doing this certain preliminary conclusion were drawn. The calculated and experimental curves do not coincide, however the zero shear phenomena do exist in both of the curves. The procedure is to find out why the curves do not coincide, and also can the curves be made to coincide with each other by changing the constants. Having changed the constant, what physical interpretation can be drawn from it. There are only three possible constants that can be changed in the equation, namely C_1, C_2 and M_2. In manipulating these constants, certain observations were made. In changing the M_2 value it was possible to move the calculated curves vertically up or down with no change in horizontal translation. Changing C_2 has the only effect of shifting the zero shear velocity horizontally. C_1 was also changed and was found to have very little effect upon the curves. In other words C_2 (spring constant for polymer solution) is much more sensitive to changes than C_1 (spring constant for the nylon string).

These observations mentioned above was made using the following procedure. The equation describing the free fall component of the displacement versus time curve is:

$$(8) \qquad X_2 = \tfrac{1}{2} G\, t^2 \frac{M_1}{M_1 + M_2}$$

Where: X_2 = Displacement in cm.

G = Acceleration due to gravity (981 cm/sec)

t = Time in secs.

M_1 = Loading mass used on viscometer (Gms)

M_2 = Equivalent mass of rotational drum (Gms)

Differentiating equation (8) and transforming the equation from centimeters into degrees and into shear units gives the following result.

$$(9) \quad \dot{\gamma} = .358 \cdot \frac{180}{\pi \cdot R} \, \frac{dx_2}{dt} = \frac{M_1 t}{M_1 + M_2} \cdot 5270$$

In comparing the shear curves of the calculated and experimental curves, it was found that the calculated curves were higher than the experimental curves. Therefore the calculated curves can be lowered and made to coincide with the experimental curve by rewriting equation (9) in the following manner:

$$(10) \quad = 5270 \cdot \frac{M_1 t}{M_1 + M_2 + \Delta M_2}$$

By solving for $M_2 + \Delta M_2$ and substituting into equation (7) will give the calculated curve which will coincide with the experimental curve only in vertical translation. In physical terms, the ΔM_2 implies that the viscometer reacts with a higher inertial effect then the one previously calculated. To get the calculated zero shear to coincide with the experimental zero shear, the constant C_1 (spring constant for nylon string) and C_2 (spring constant for polymer liquid) were both examined for their effects on the calculated curves. C_2 was held constant and the value of C_1 was changed from $.4 \times 10^6$ to $.3 \times 10^8$. It was found no significant changes took place in the calculated curves. C_1 was then held constant and C_2 was subjected to change. It was observed that by increasing C_2 that the zero shear curve would move to the left and to the right if C_2 decreased. All calculated zero shear curves except for one appears to be on the right of the experimental shear curve. This would imply that the vibration due to the polymer liquid is much more pronounced than what one has previously believed to be.

The next step was to determine the history of the flow curve free from vibrational effects. Once the calculated and experimental curves were made to coincide as much as possible, the difference between the calculated and experimental curves were calculated and plotted only for the area before the zero shear curve. The difference curve was then extrapolated into the experimental flow curve after the zero shear and the hypothetical curve was then intergrated by the least square method with a computer program so that it may be compared with the flow curve of displacement versus time. The hypothetical curve was only intergrated to its highest peak of the differentiated curve and then replotted on linear graph paper. The intergrated curve was then extrapolated to the zero point on linear graph paper. The extrapolated curve was then replotted on log-log graph paper of angular displacement versus time so that the intergrated flow curve may be extended to areas of low times. The results are listed in the sections on conclusions.

PRESENTATION AND DISCUSSION OF RESULTS

Viscosity Data

Listed in the following tables are the results of viscosity measurements taken on a number of polymer solutions. All were taken at a temperature of 77°F except for Indopol H-1900 (polyisobutylene) which was done as a function of temperatures. From the results obtained from polystyrene NBS-2-35967, it behaves as a non-Newtonian liquid. Polyisobutylene in Primol 355 also behaves as a non-Newtonian liquid. Its recoverable shear as a function of shear stress have also been determined. Viscosity measurements were carried out on Indopol H-1900 as a function of temperature. It behaves as a Newtonian liquid. The following formula was used for the error calculations for Indopol H-1900.

$$\sigma_x = \sqrt{\frac{(X_i - X_{Avg.})^2}{n}}$$

$$\sigma_{\bar{x}} = \frac{\sigma_x}{\sqrt{n}}$$

where: $N_{Avg} = \sigma_x \pm \sigma_{\bar{x}}$

Viscosity measurements of Indopol H-1900 was plotted as a function of temperature which was also compared with the viscosity measurements taken at Esso Research Center using an ubbelohde viscometer. The two results agreed with each other well within reason, as can be observed from the graph. An empirical equation was developed by Russell Biss to relate

POLYSTYRENE NBS-2-35967

Wt. Gms.	Shear Stress (τ) $\frac{\text{Dynes}}{\text{CM}^2}$	Time Secs.	Displacement	Time (10^o) Secs.	Rate of Shear Sec^{-1}	Viscosity (N) Poise
2	8	259.62	8^o	324	.01103	725.216
3	12	164.27	8^o	205.33	.01743	688.282
4	16	121.98	8^o	152.48	.02347	681.489
5	20	94.52	8^o	118.22	.0302	660.451
6	24	79.39	8^o	99.23	.03607	665.279
8	32	58.94	8^o	73.67	.0486	657.547
10	40	47.0	8^o	60.01	.05965	657.3
15	60	31.32	8^o	39.15	.0914	656.145
20	80	23.175	8^o	28.96	.1235	647.346
30	120	15.36	8^o	19.2	.1865	643.435
50	200	9.15	8^o	11.43	.313	638.96
70	280	6.536	8^o	8.17	.4381	639.06

POLYISOBUTYLENE 16.5% IN MINERAL SPIRITS

Wt.	Shear Stress	Time	Displacement	Time (10°)	Rate of Shear	Viscosity (N)	Recoil	S_R
Gms	Dynes/CM^2	Secs		Secs	Sec^{-1}	Poise	mm	%
20	80	25,100	8°	31,400	.000114	702,000	6	2.66
50	200	9,380	8°	11,720	.000305	656,000	14	6.3
100	400	4,340	8°	5,425	.000661	605,000	25.5	11.4
200	800	2,061	8°	2,580	.00139	576,000	43.4	19.4
500	2,000	622.5	8°	778	.0046	435,000	85	38
1000	4,000	231	8°	288.5	.0124	323,000	136.5	61.2
5 lbs.	9,080	77	8°	96.25	.0372	244,000	241.5	108
4.62 kg	18,480	13.92	8°	17.4	.206	89,600	391	175
15 lbs	27,550	3.78	8°	4.72	.759	36,200	487	218
9136	36,544	1.385	8°	1.73	2.07	17,650	494	221

INDOPOL H-1900 (POLYISOBUTYLENE) 77°F

Wt. Gms.	Shear Stress $\frac{Dynes}{CM^2}$	Time Secs.	Displacement	Time (10^8) Secs.	Rate of Shear Sec^{-1}	Viscosity (N) Poise
1	4	56.48	10 mm	4,510.8	.000793	5040
2	8	28.05	10 mm	2,244.2	.001595	5015
5	20	89.95	1°	898.58	.00398	5050
10	40	44.90	1°	449.02	.00797	5017
20	80	22.52	1°	225.22	.01589	5033
50	200	76.39	8°	95.49	.0374	5035
100	400	36.01	8°	45.01	.0795	5030
200	800	18.00	8°	22.50	.1590	5030
500	1,000	7.21	8°	9.02	.3969	5039
1000	4,000	3.59	8°	4.49	.7965	5022
1200	4,800	3.00	8°	3.75	.9535	5034
1500	6,000	2.40	8°	3.00	1.1914	5036
2000	8,000	1.79	8°	2.23	1.605	5020

$N_{Avg.} = 5051.61 \pm 22.80$

INDOPOL H-1900 (POLYISOBUTYLENE) 86°F

Wt. Gms.	Shear Stress $\frac{\text{Dynes}}{\text{CM}^2}$	Time Secs.	Displacement	Time (10°) Secs.	Rate of Shear Sec^{-1}	Viscosity (N) Poise
1	4	35.91	10 mm	2872.95	.001246	3210
2	8	17.92	10 mm	1434.23	.002496	3205
5	20	57.24	1°	572.44	.006254	3198
10	40	28.64	1°	286.49	.01249	3201
20	80	12.35	1°	143.55	.02493	3208
50	200	45.91	8°	57.38	.06238	3206
100	400	22.89	8°	28.62	.12507	3198
200	800	11.39	8°	14.24	.25125	3184
500	2,000	4.57	8°	5.71	.6269	3190
1000	4,000	2.29	8°	2.87	1.246	3209
1200	4,800	2.38	10°	2.38	1.502	3195
1500	6,000	3.82	20°	1.91	1.868	3212
2008	8,032	2.86	20°	1.43	2.503	3208

$N_{Avg} = 3201.84 \pm 2.25$

INDOPOL H-1900 (POLYISOBUTYLENE) 100°F

Wt.	Shear Stress	Time	Displacement	Time (10°)	Rate of Shear	Viscosity (N)
Gms.	$\frac{\text{Dynes}}{\text{CM}^2}$	Secs.		Secs.	Sec^{-1}	Poise
1	4	18.68	10 mm	1494.65	.002395	1670
2	8	9.28	10 mm	742.85	.00482	1660
5	20	29.80	1°	298.03	.01201	1665
10	40	14.92	1°	149.28	.02398	1668
20	80	59.85	8°	74.82	.04784	1672
50	200	23.74	8°	29.67	.1206	1658
100	400	11.99	8°	14.99	.2388	1675
200	800	6.01	8°	7.52	.4761	1680
500	2,000	6.02	20°	3.01	1.189	1681
1000	4,000	2.96	20°	1.48	2.411	1659
1200	4,800	3.72	30°	1.24	2.889	1661
1500	6,000	3.968	40°	.992	3.608	1663
2008	8,032	7.42	100°	.742	4.824	1665

$N_{Avg} = 1667.46 \pm 2.06$

INDOPOL H-1900 (POLYISOBUTYLENE) 113°F

Wt. Gms	Shear Stress $\frac{\text{Dynes}}{\text{CM}^2}$	Time Secs	Displacement=	Time (10°) Secs	Rate of Shear Sec^{-1}	Viscosity (N) Poise
1	4	10.40	10 mm	832.43	.0043	930.1
2	8	41.87	1°	418.77	.008548	935.8
5	20	16.73	1°	167.31	.02139	934.7
10	40	66.82	8°	83.53	.0428	933.3
20	80	33.65	8°	42.07	.08509	940.1
50	200	13.45	8°	16.82	.2128	939.8
100	400	6.66	8°	8.33	.4295	931.1
200	800	3.32	8°	4.15	.8626	927.37
500	2,000	3.32	20°	1.66	2.152	929.1
1000	4,000	2.508	30°	.836	4.28	934.6
1200	4,800	6.95	100°	.695	5.15	932.1
1500	6,000	5.62	100°	.562	6.367	942.3
2008	8,032	4.18	100°	.418	8.552	939.2

$N_{Avg} = 934.58 \pm 1.24$

INDOPOL H-1900 (POLYISOBUTYLENE) 130°F

Wt. Gms.	Shear Stress $\frac{\text{Dynes}}{\text{CM}^2}$	Time Secs.	Displacement	Time (10°) Secs.	Rate of Shear Sec^{-1}	Viscosity (N) Poise
1	4	41.19	1°	411.96	.00869	460.3
2	8	20.57	1°	205.76	.01739	459.8
5	20	8.25	1°	82.52	.04338	461.03
10	40	32.73	8°	40.92	.0874	457.2
20	80	16.58	8°	20.73	.1726	463.3
50	200	6.56	8°	8.2	.4365	458.1
100	400	3.27	8°	4.09	.8749	457.17
200	800	4.12	20°	2.06	1.737	460.58
500	2,000	8.32	100°	.832	4.303	464.8
1000	4,000	4.12	100°	.412	8.671	461.3
1200	4,800	3.42	100°	.342	10.46	458.7
1500	6,000	5.54	200°	.277	12.90	465.1
2008	8,032	4.06	200°	.203	17.6	456.3

$N_{Avg} = 460.28 \pm 7.57$

INDOPOL H-1900 (POLYISOBUTYLENE) 149°F

Wt.	Shear Stress	Time	Displacement	Time (10°)	Rate of Shear	Viscosity (N)
Gms.	$\frac{\text{Dynes}}{\text{CM}^2}$	Secs.		Secs.	Sec^{-1}	Poise
1	4	19.89	1°	198.95	.018	222.3
2	8	10.20	1°	102.07	.03507	228.1
5	20	33.02	8°	41.27	.08673	230.6
10	40	15.78	8°	19.72	.1814	220.41
20	80	7.85	8°	9.81	.3648	219.3
50	200	3.25	8°	4.06	.8810	227.0
100	400	4.08	20°	2.04	1.7544	227.99
200	800	10.1	100°	1.01	3.540	225.95
500	2,000	4.09	100°	.409	8.749	228.6
1000	4,000	4.0	200°	.2006	17.84	224.21
1200	4,800	5.16	300°	.172	20.76	231.2
1500	6,000	4.174	300°	.1358	26.35	227.68
2008	8,032	3.12	300°	.1040	34.398	233.5

$N_{Avg} = 226.68 \pm 1.11$

INDOPOL H-1900 (POLYISOBUTYLENE) 167°F

Wt.	Shear Stress	Time	Displacement	Time (10°)	Rate of Shear	Viscosity (N)
Gms.	$\frac{\text{Dynes}}{\text{CM}^2}$	Secs.		Secs.	Sec^{-1}	Poise
1	4	84.91	8°	106.14	.03372	118.6
2	8	44.86	8°	56.07	.06384	125.3
5	20	17.49	8°	21.86	.1637	122.16
10	40	9.04	8°	11.30	.3165	126.35
20	80	4.64	8°	5.8	.6163	129.8
50	200	1.72	8°	2.15	1.665	120.11
100	400	10.7	100°	1.07	3.321	120.42
200	800	5.34	100°	.534	6.693	119.52
500	2,000	10.54	300°	.218	16.38	122.1
1000	4,000	3.65	300°	.115	31.1	128.6

$N_{Avg} = 124.47 \pm 1.11$

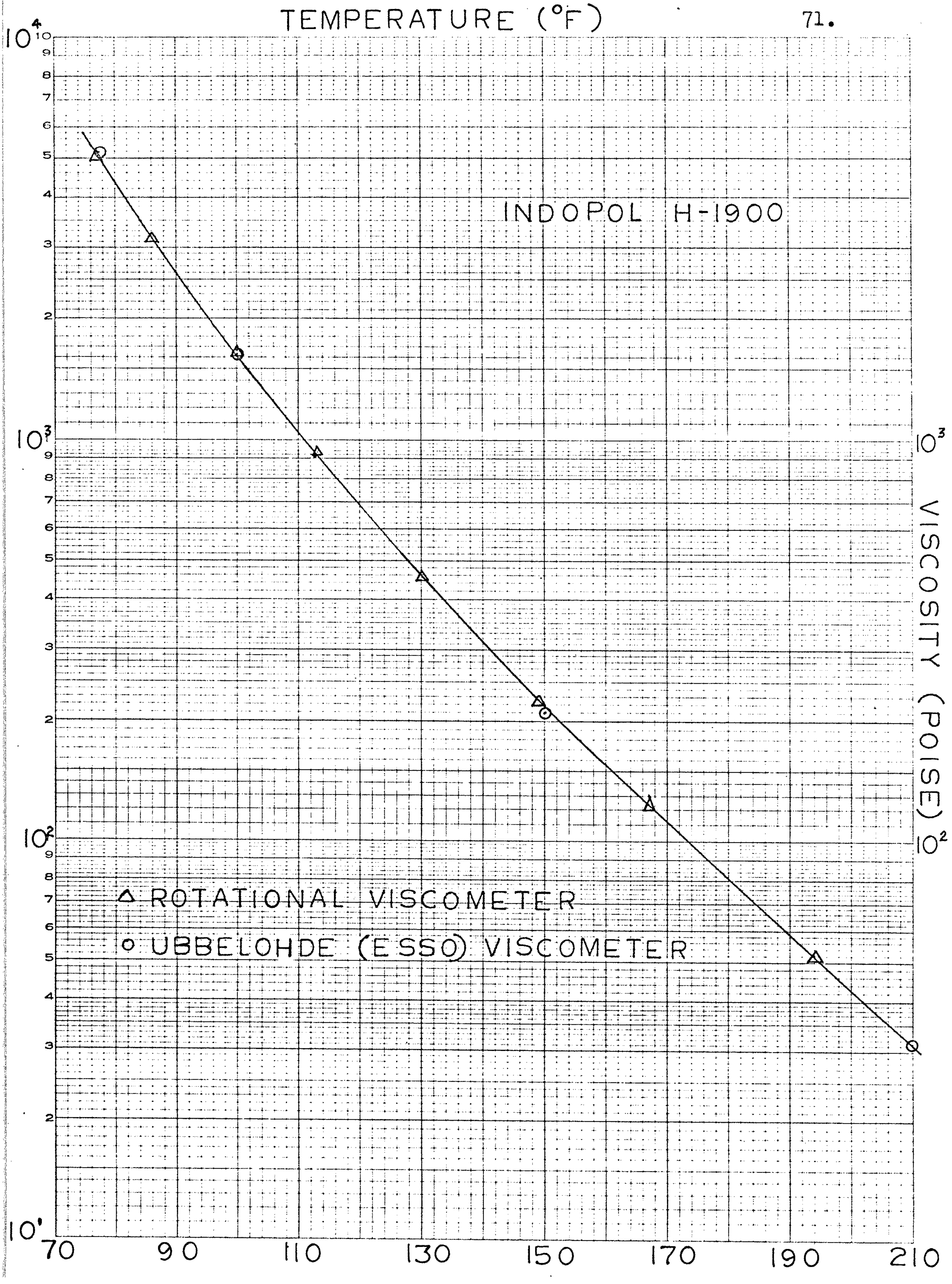
INDOPOL H-1900 (POLYISOBUTYLENE) 194°F

Wt.	Shear Stree	Time	Displacement	Time (10°)	Rate of Shear	Viscosity (N)
Gms.	$\frac{\text{Dynes}}{\text{CM}^2}$	Secs.		Secs.	Sec^{-1}	Poise
1	4	36.7	8°	45.87	.07803	51.251
2	8	18.12	8°	22.65	.158	50.631
5	20	7.71	8°	9.64	.3714	53.851
10	40	3.98	8°	4.98	.719	55.633
20	80	4.56	20°	2.28	1.567	51.052
50	200	9.43	100°	.943	3.796	52.685
100	400	4.69	100°	.469	7.626	52.452
200	800	7.08	300°	.236	15.162	52.762
500	1,000	2.868	300°	.0959	37.3	53.615

$N_{Avg} = 52.36 \pm .46$

4½% POLYISOBUTYLENE IN PRIMOL 355 77°F

Wt.	Shear Stress	Time	Displacement	Time (10°)	Rate of Shear	Viscosity (N)
Gms.	$\frac{\text{Dynes}}{\text{CM}^2}$	Secs.		Secs.	Sec^{-1}	Poise
1	4	450.65	10 mm	36,052	$.993 \times 10^{-4}$	40,282
2	8	206.2	10 mm	16,495	$.217 \times 10^{-3}$	36,861
5	20	72.19	10 mm	5,775	$.619 \times 10^{-3}$	32,263
10	40	30.75	10 mm	2,460.4	.001455	27,491
20	80	92.22	1°	922.2	.003881	20,608
50	200	19.98	1°	199.83	.01791	11,164
100	400	36.61	8°	45.77	.07821	5,114
200	800	6.72	8°	8.4	.4262	1,877
400	1,600	2.66	20°	1.33	2.69	594.8
531	2,124	6.02	100°	.602	5.946	357.2
731	2,924	8.13	300°	.271	13.2	221.5


TEMPERATURE (°F)
VISCOSITY (POISE)
INDOPOL H-1900
△ ROTATIONAL VISCOMETER
○ UBBELOHDE (ESSO) VISCOMETER
10^4
10^3
10^2
10^1
70
90
110
130
150
170
190
210

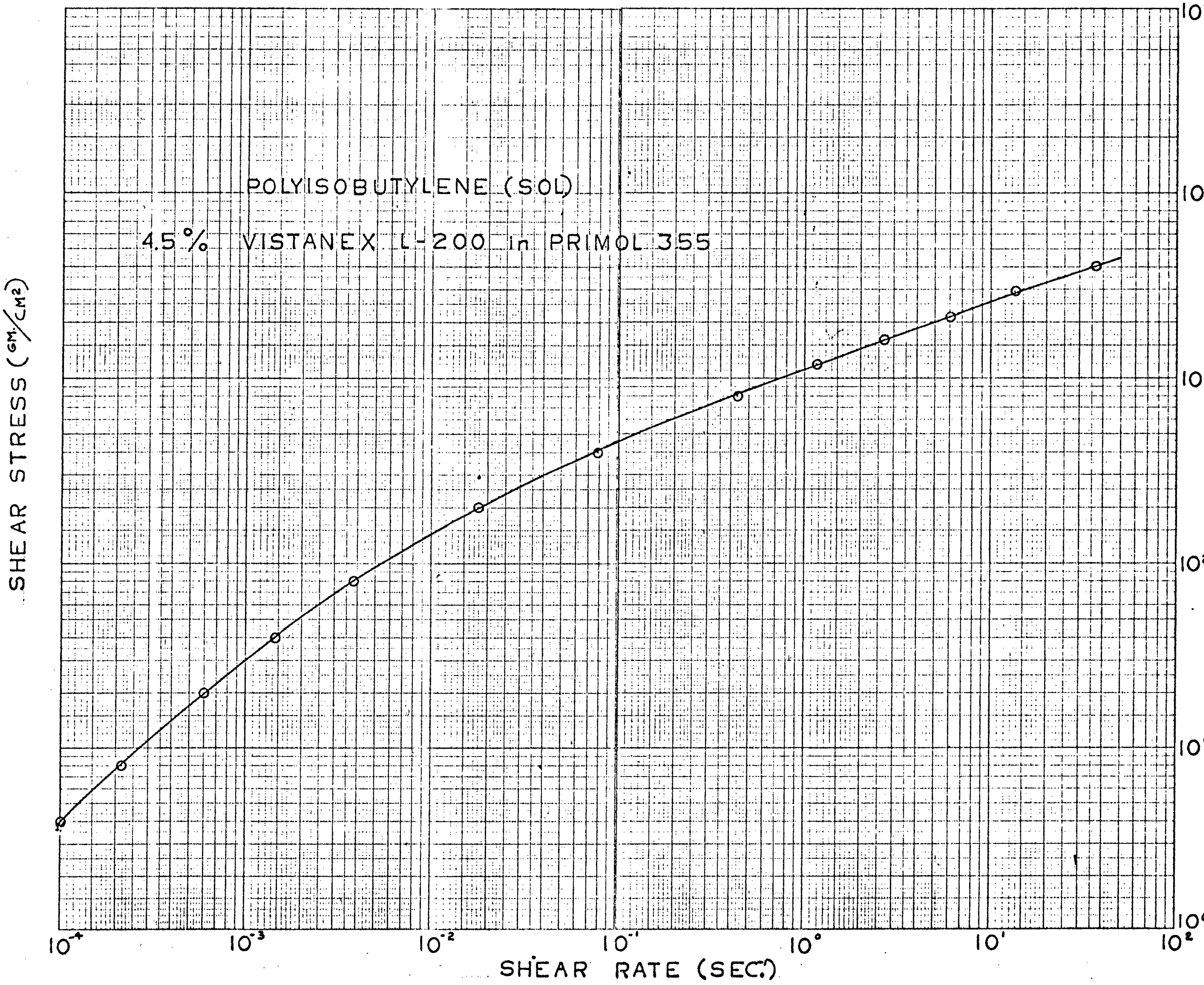
the viscosity of Indopol H-1900 with temperature.

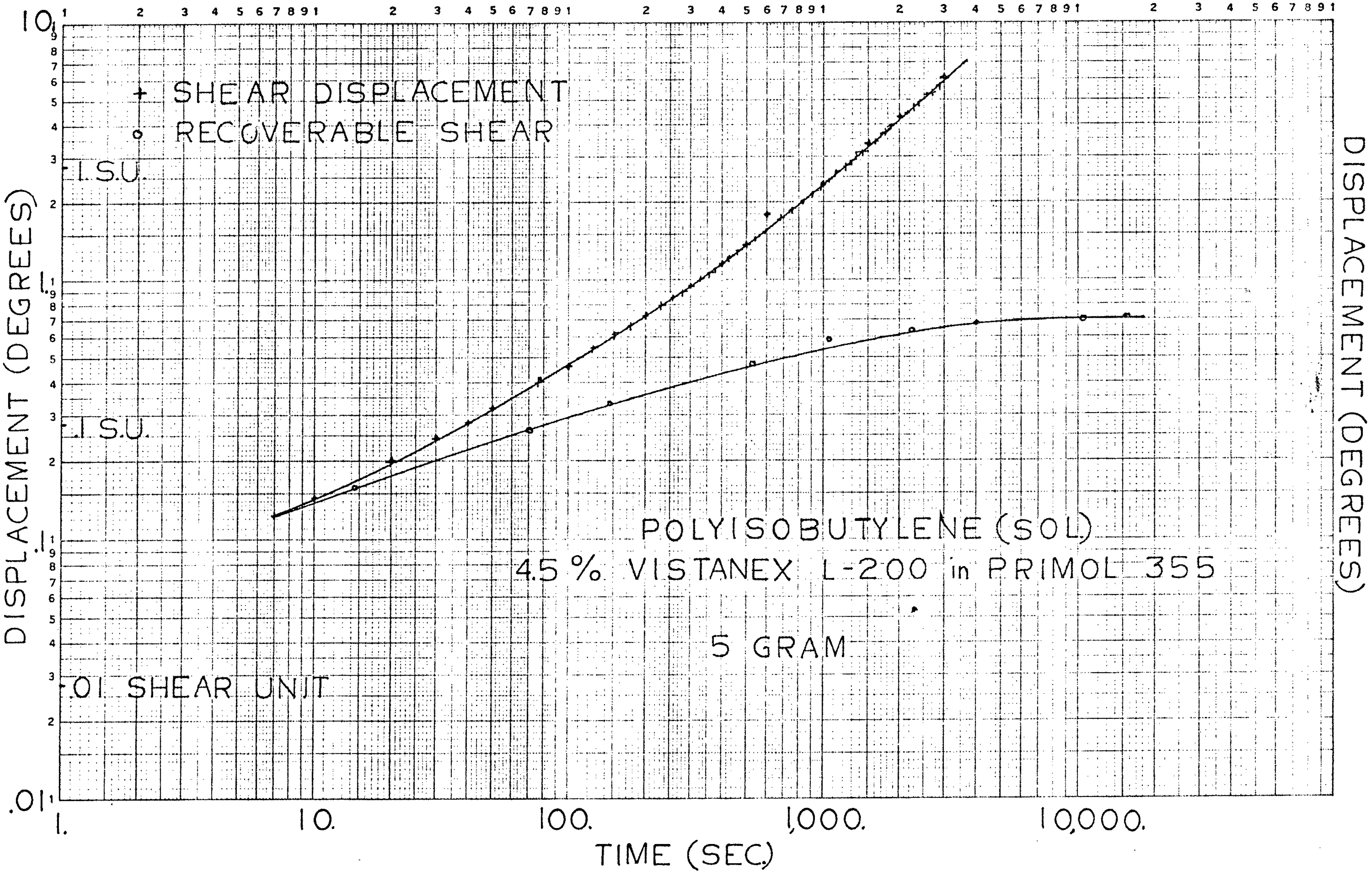
$$\text{Log } N = 2870 \quad 1/(280 + T^{\circ}F) - 1/(280 + 77^{\circ}F) \quad + \text{Log } N_{77^{\circ}F}$$

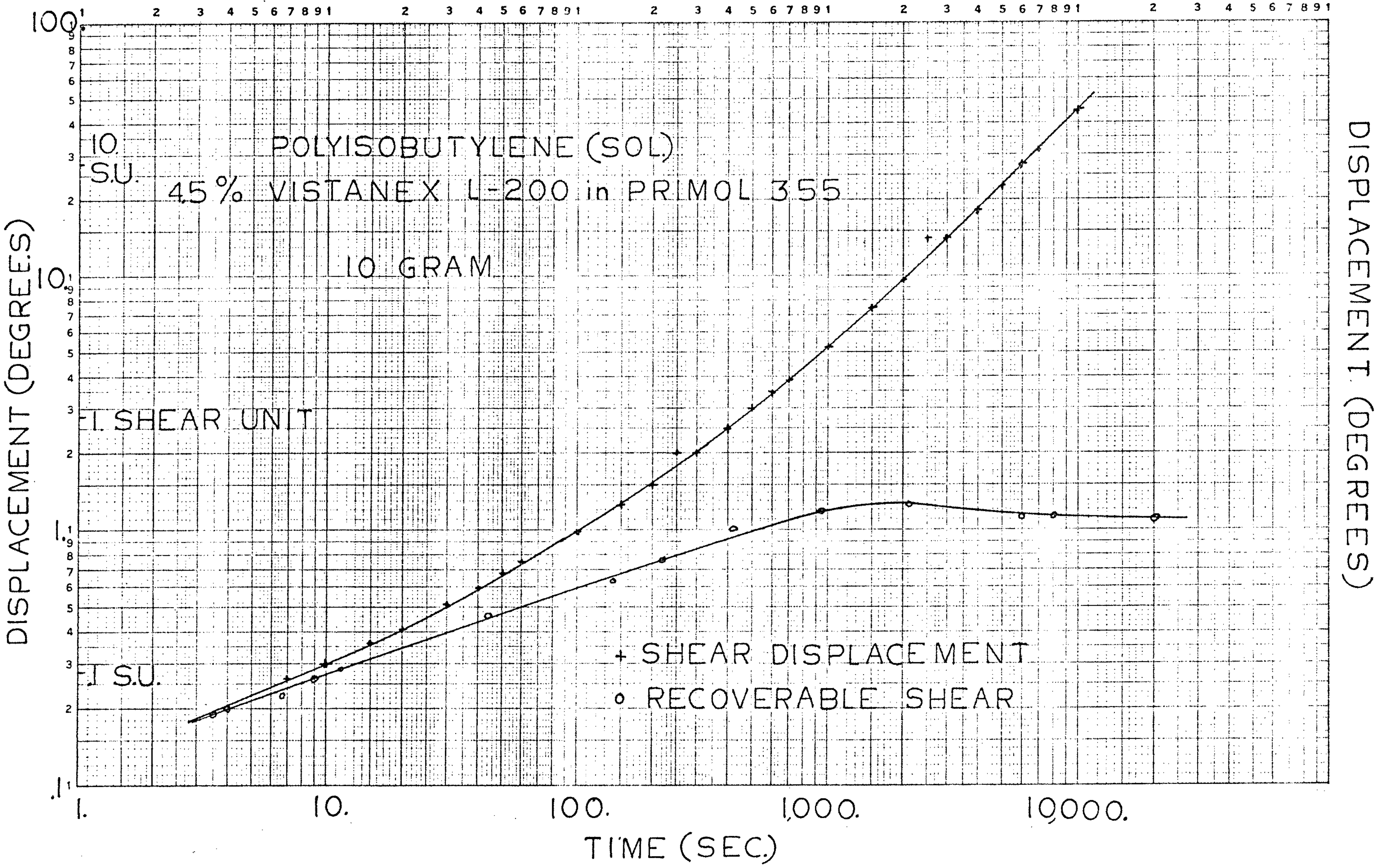
Viscosity measurements were also done on a solution of 4 1/2% polyisobutylene in Primol 355, which are presented in the following page. In non-Newtonian fluids a constant rate of shear must be attained before viscosity measurements may be taken. The time required for steady state is a function of the loading used. This can be easily determined by obtaining fairly constant time measurements for eight degree displacements or for that matter any amount of displacement. Shear rate as a function of shear stress was also determined for the 4 1/2% PIB in Primol 355 to obtain an overall view of viscosity at intermediate shear stresses.

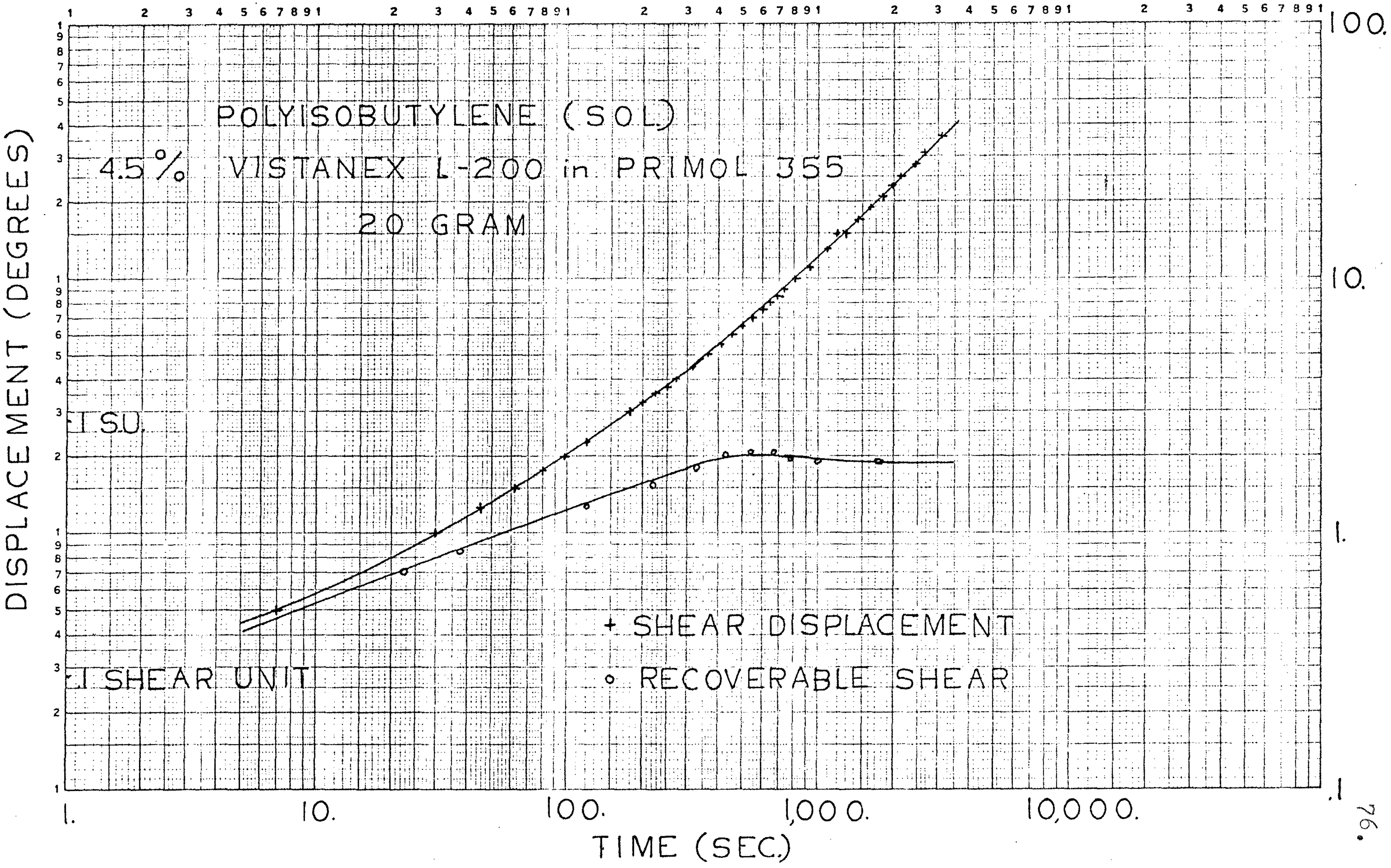
Flow History Curves and Recoil Measurements Results

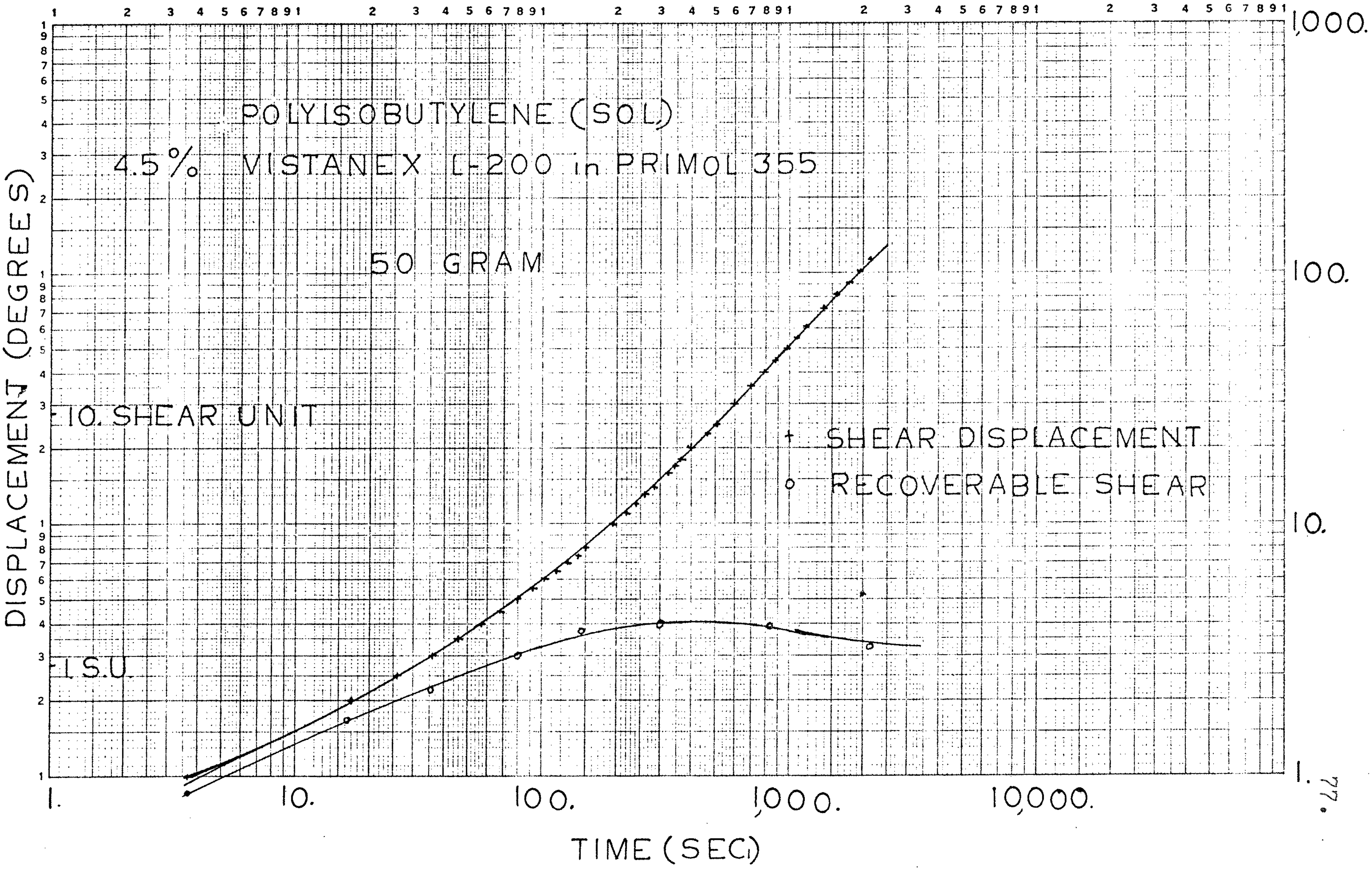
4 1/2% PIB Solution. Displacement flow curves and recoverable shear was determined for the 4.5% PIB in Primol 355 for intermediate and long times as a function of loading used. From the flow history curves, it can be observed that the slope of the displacement slowly rise until an equilibrium slope is attained. The rate of increase in the rise of the slope tends to rise as the amount of loading increased. The equilibrium slope is reached sooner as the amount of load is increased as contrasted between the 5 GM and 200 GM load.

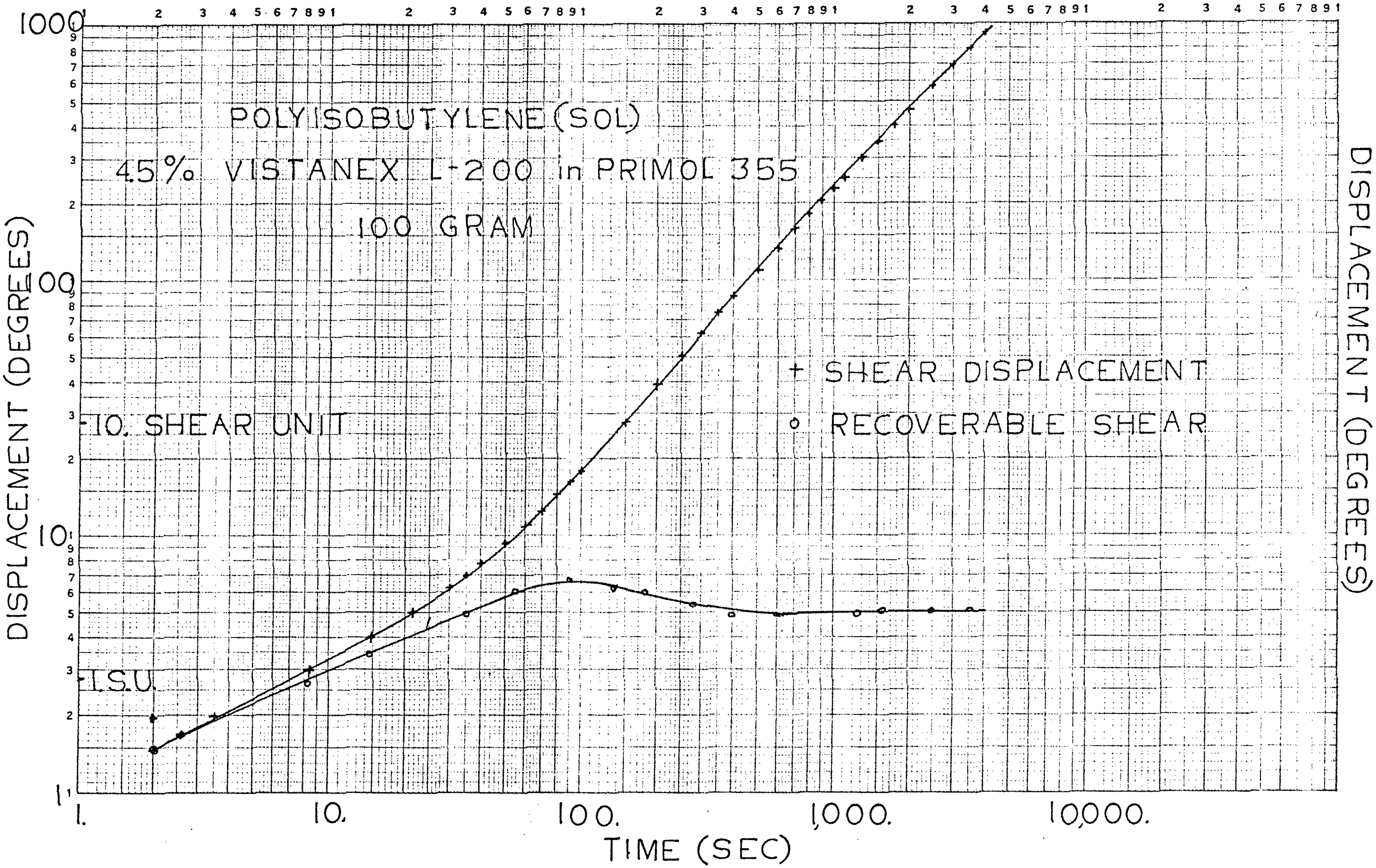

POLYISOBUTYLENE (SOL)
4.5% VISTANEX L-200 in PRIMOL 355
SHEAR STRESS (GM./CM²)
SHEAR RATE (SEC.⁻¹)
10⁻⁴
10⁻³
10⁻²
10⁻¹
10⁰
10¹
10²
10⁰
10¹
10²
10³
10⁴
10⁵

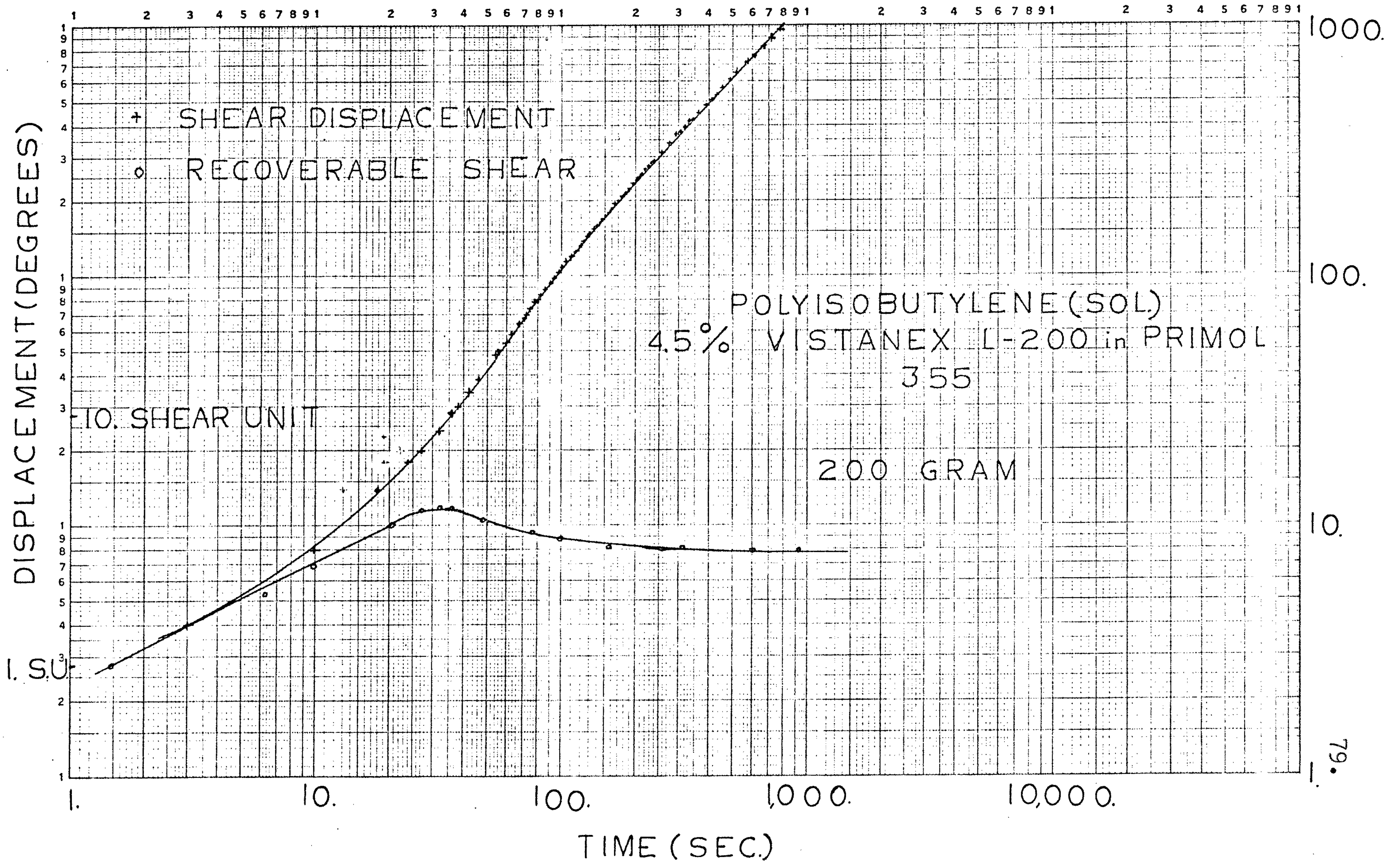

+ SHEAR DISPLACEMENT
o RECOVERABLE SHEAR
1 S.U.
.1 S.U.
.01 SHEAR UNIT
POLYISOBUTYLENE (SOL)
4.5 % VISTANEX L-200 in PRIMOL 355
5 GRAM
DISPLACEMENT (DEGREES)
DISPLACEMENT (DEGREES)
TIME (SEC.)
10
1.
.1
.01
1.
10.
100.
1,000.
10,000.


POLYISOBUTYLENE (SOL.)
45% VISTANEX L-200 in PRIMOL 355
10 GRAM
10. S.U.
1. SHEAR UNIT
.1 S.U.
+ SHEAR DISPLACEMENT
○ RECOVERABLE SHEAR
DISPLACEMENT (DEGREES)
DISPLACEMENT (DEGREES)
TIME (SEC.)
100.
10.
1.
.1
1.
10.
100.
1,000.
10,000.


POLYISOBUTYLENE (SOL)
4.5% VISTANEX L-200 in PRIMOL 355
20 GRAM
+ SHEAR DISPLACEMENT
o RECOVERABLE SHEAR
1 S.U.
.1 SHEAR UNIT
DISPLACEMENT (DEGREES)
TIME (SEC.)
1.
10.
100.
1,000.
10,000.
.1
1.
10.
100.


POLYISOBUTYLENE (SOL)
4.5% VISTANEX L-200 in PRIMOL 355
50 GRAM
10. SHEAR UNIT
1.S.U.
+ SHEAR DISPLACEMENT
o RECOVERABLE SHEAR
DISPLACEMENT (DEGREES)
TIME (SEC)
1.
10.
100.
1000.
10,000.
1.
10.
100.
1,000.


POLYISOBUTYLENE (SOL)
45% VISTANEX L-200 in PRIMOL 355
100 GRAM
+ SHEAR DISPLACEMENT
o RECOVERABLE SHEAR
10. SHEAR UNIT
1.S.U.
DISPLACEMENT (DEGREES)
DISPLACEMENT (DEGREES)
TIME (SEC)
1.
10.
100.
1,000.
10,000.
1
10
100
1000


+ SHEAR DISPLACEMENT
o RECOVERABLE SHEAR
POLYISOBUTYLENE (SOL.)
4.5% VISTANEX L-200 in PRIMOL 355
200 GRAM
10. SHEAR UNIT
1. S.U.
DISPLACEMENT (DEGREES)
TIME (SEC.)
1.
10.
100.
1000.
10,000.
1.
10.
100.
1000.

Recoverable shear was also investigated as a function of time. The following observations were observed from the graphs. All recoverable shear lines and displacement flow curves merge together at low times, proving that the liquid solution is completely elastic similar to the Hookean solid at low times. For intermediate and high loading, recoverable shear increases linearly until a maximum peak is reached and then decreases to some equilibrium value. For small loadings of 5 GM and under, the maximum peak is non-existant.

Also noticeable is that when the amount of loading is increased, the maxima peak in the recoverable shear curve tends to become more pronounced and moves to the left. The displacement time required for these peaks to occur also decreased with increase in loading.

3% PIB Solution. Also available are unpublished flow history curves for a 3% PIB in Primol 355 which was done previously at Esso Research Center in Linden, New Jersey. The flow curve for this solution was extended to low times with the help of a hi-speed camera. The recoverable flow curves were incomplete for this solution, but the results obtained from the 4.5% PIB solution shows unquestionably that the recoverable shear curve merges into the flow curve. The recoverable shear curve was then extended by dash lines into the flow curve. The 3% flow curves were later investigated in reference to its zero of negative displacement phenomena. (See following graphs.) The amount of loading for the 3% and 4½% solution was then plotted against the reciprical time of their maximum peaks. For the 3% solution a smooth curve could be drawn through the points except for the 500 GM load which was not consistent with the rest of the results. However if more data points were available for loads ranging between 300 and 500 GM, it would then determine if the 500 GM point was an experimental error or if the nature of the curve started to rise sharply. The results for the 4.5% solution was similar with the 3% solution except that the 4.5% solution showed more of a curvature which can be readily observed on the graphs. Recoil measurements (S_r) at infinite time as a function of shear stress was investigated on the 4.5% PIB solution. From the graph it can be seen that there exists two lines of different slopes which curves into each other at a shear stress of approximately 80 dynes/cm^2. This indicates a shear modulus of $G = 80$ dynes/cm^2 for shear stress less than 40 dynes/cm^2, increasing to 294 dynes/cm^2 for shear stress of 200 or more dynes/cm^2. Professor G.C. Berry(20) indicated that when displacement strain is divided by shear stress as function of time, the curves will merge together at low times and deviate as time increases. The deviation will move to the left as shear stress increases. γ/τ versus time was plotted for the 3% and 4 ½% PIB Solution. The

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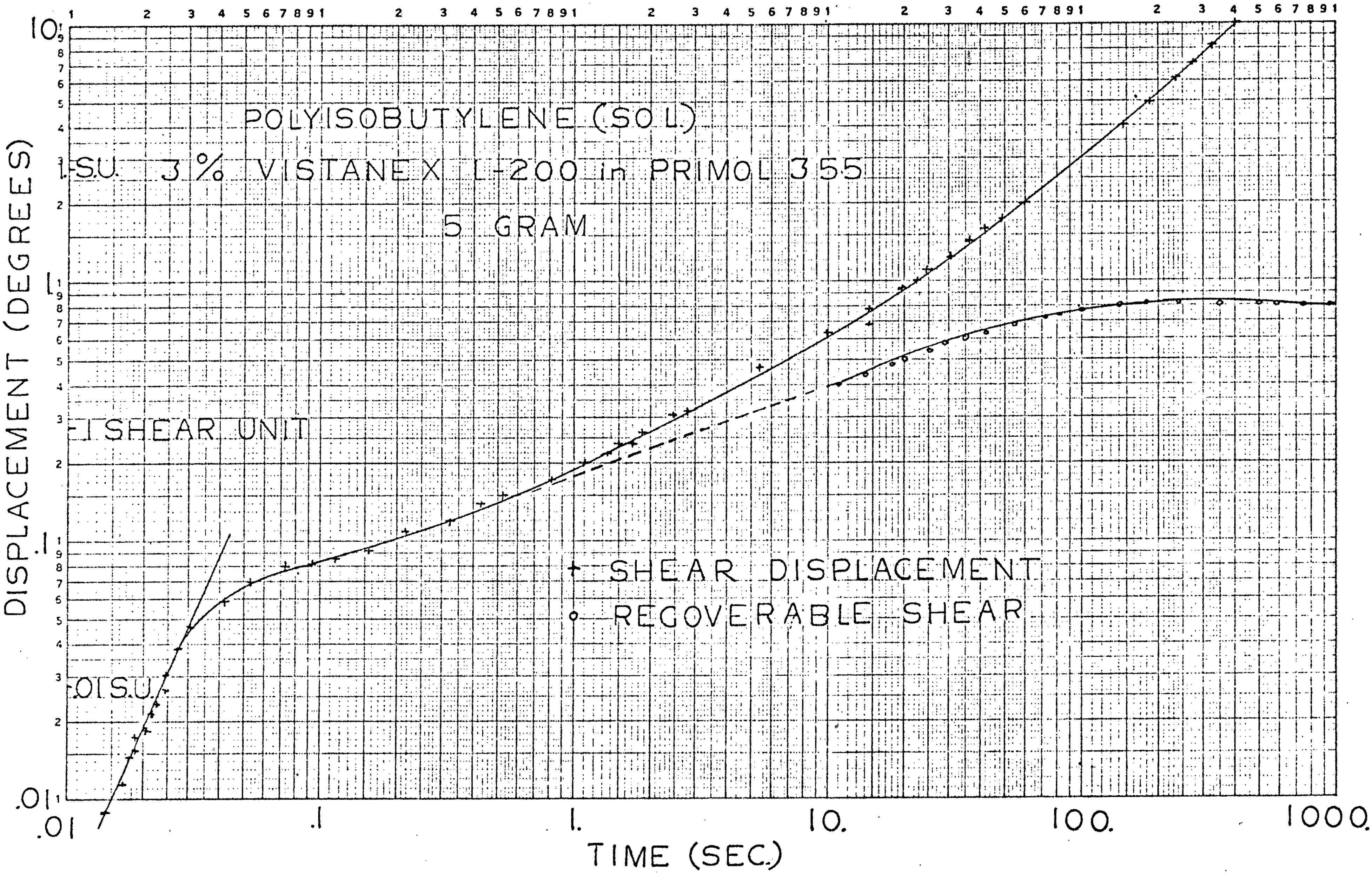
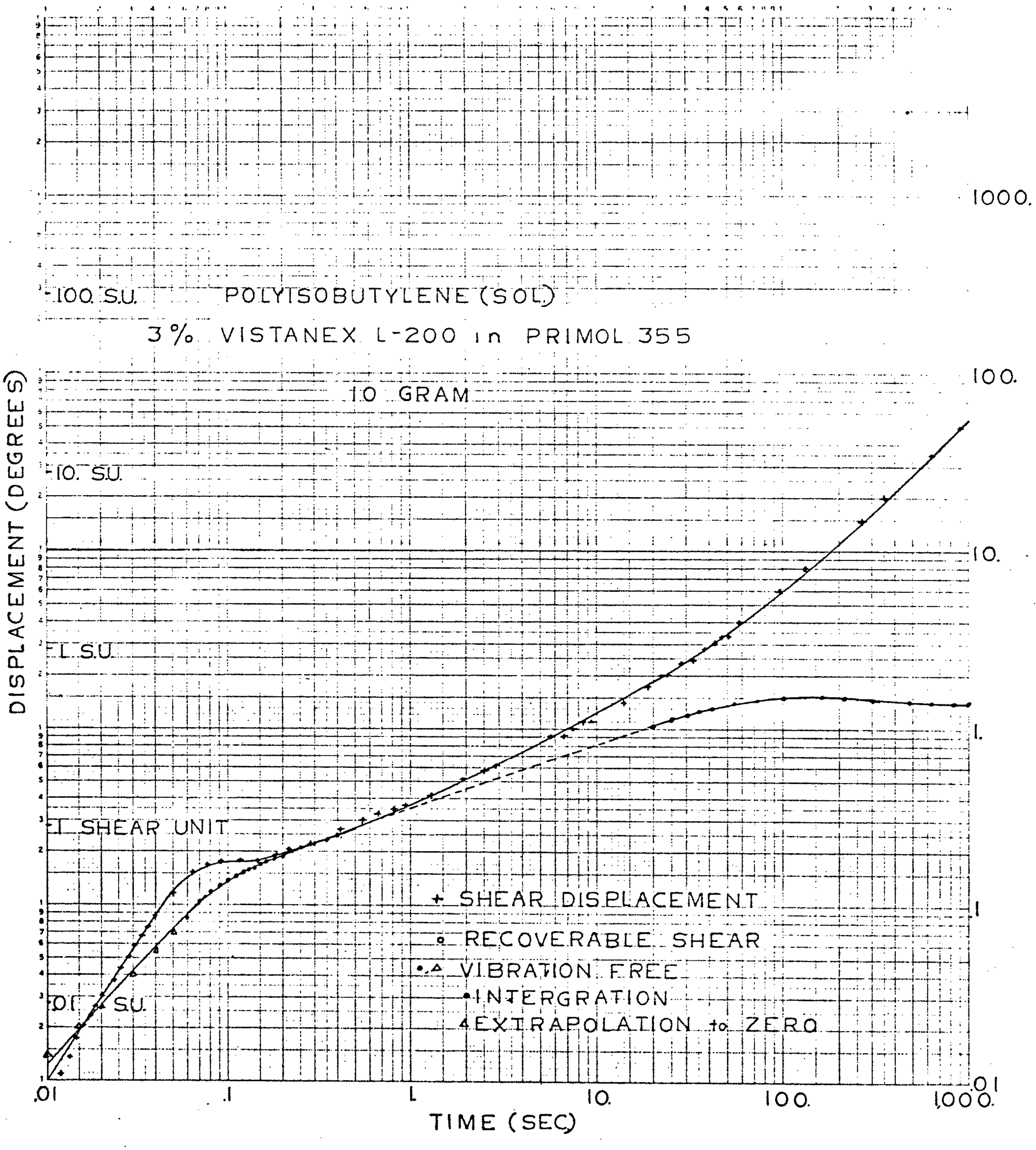
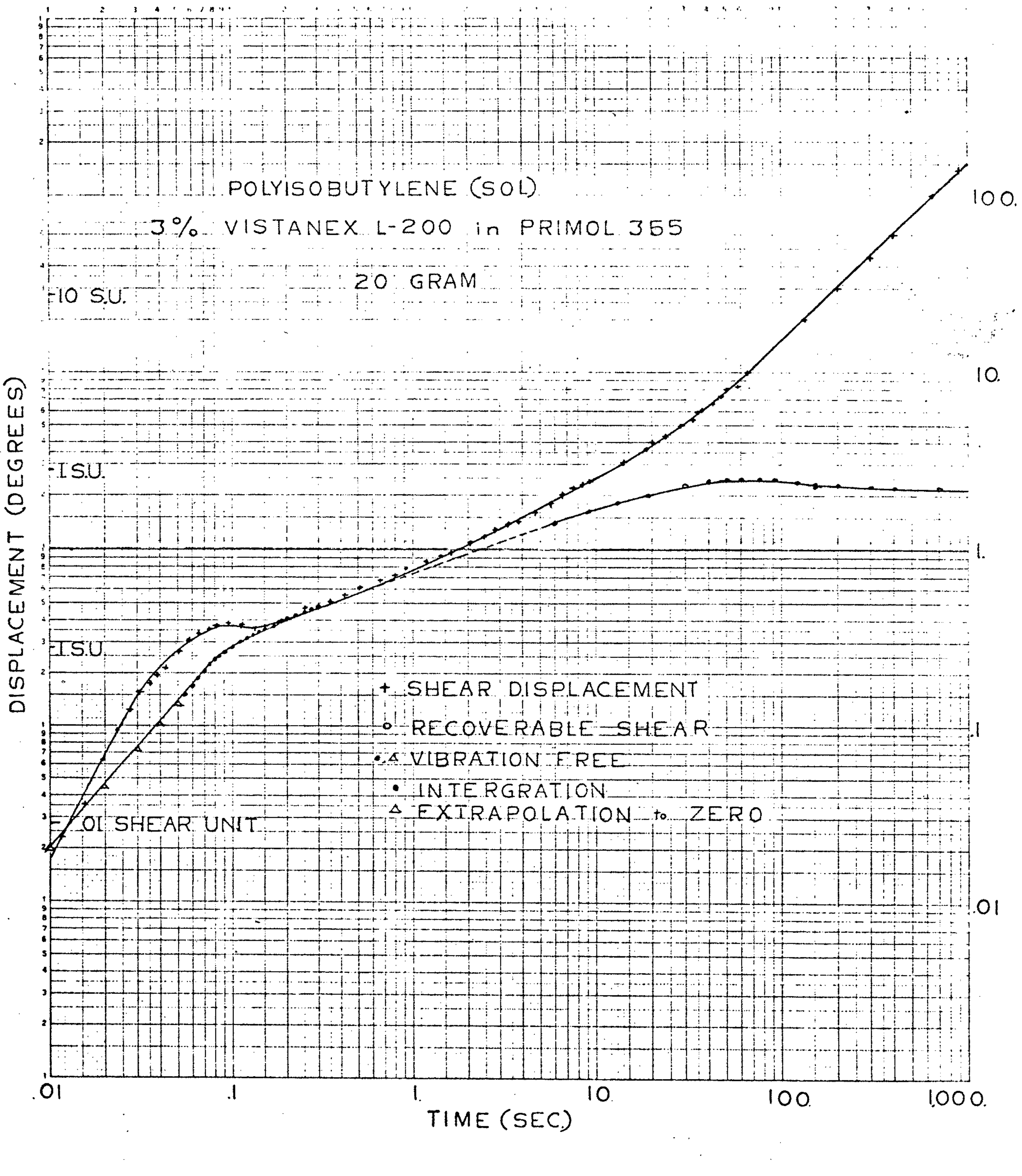
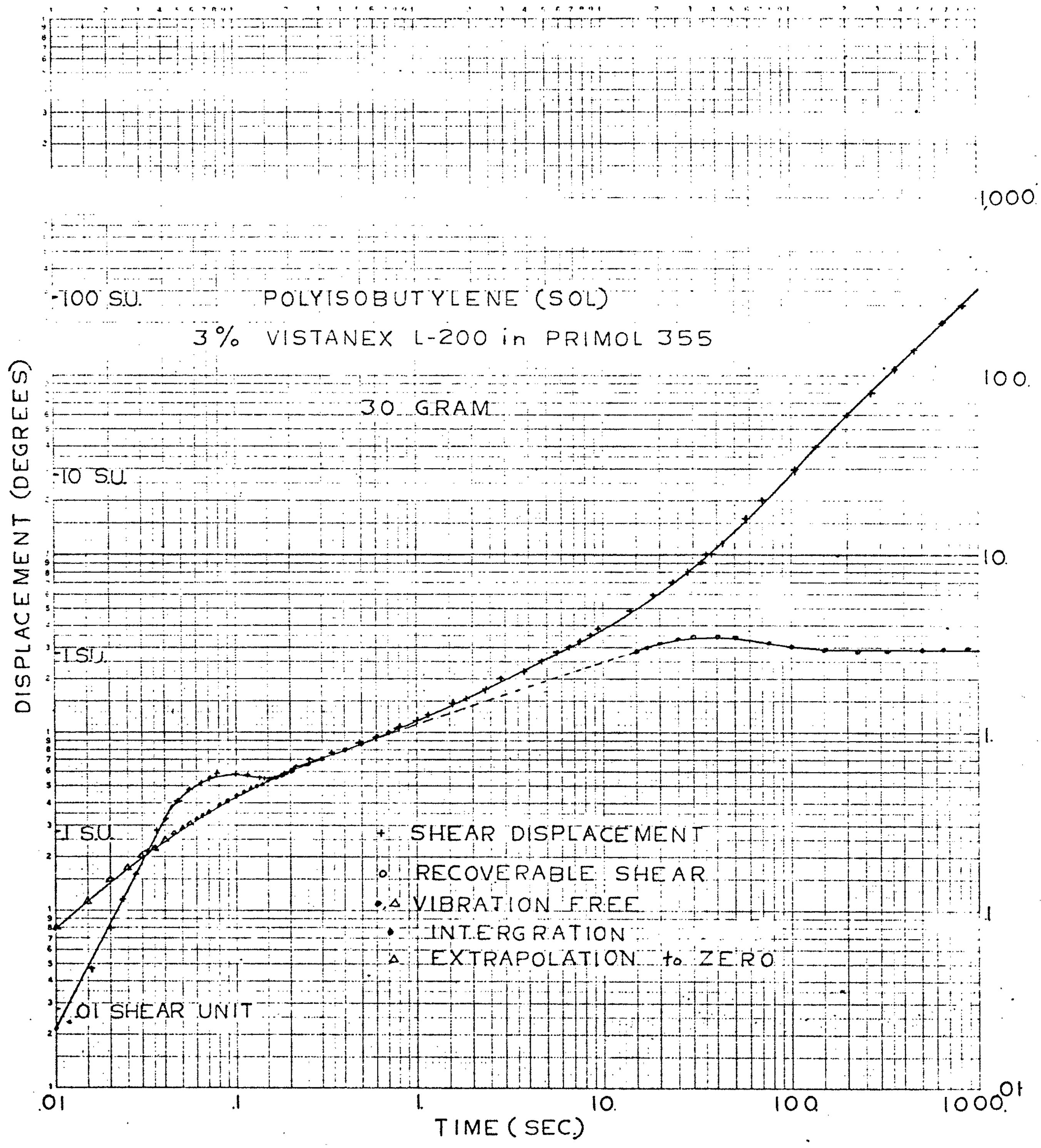
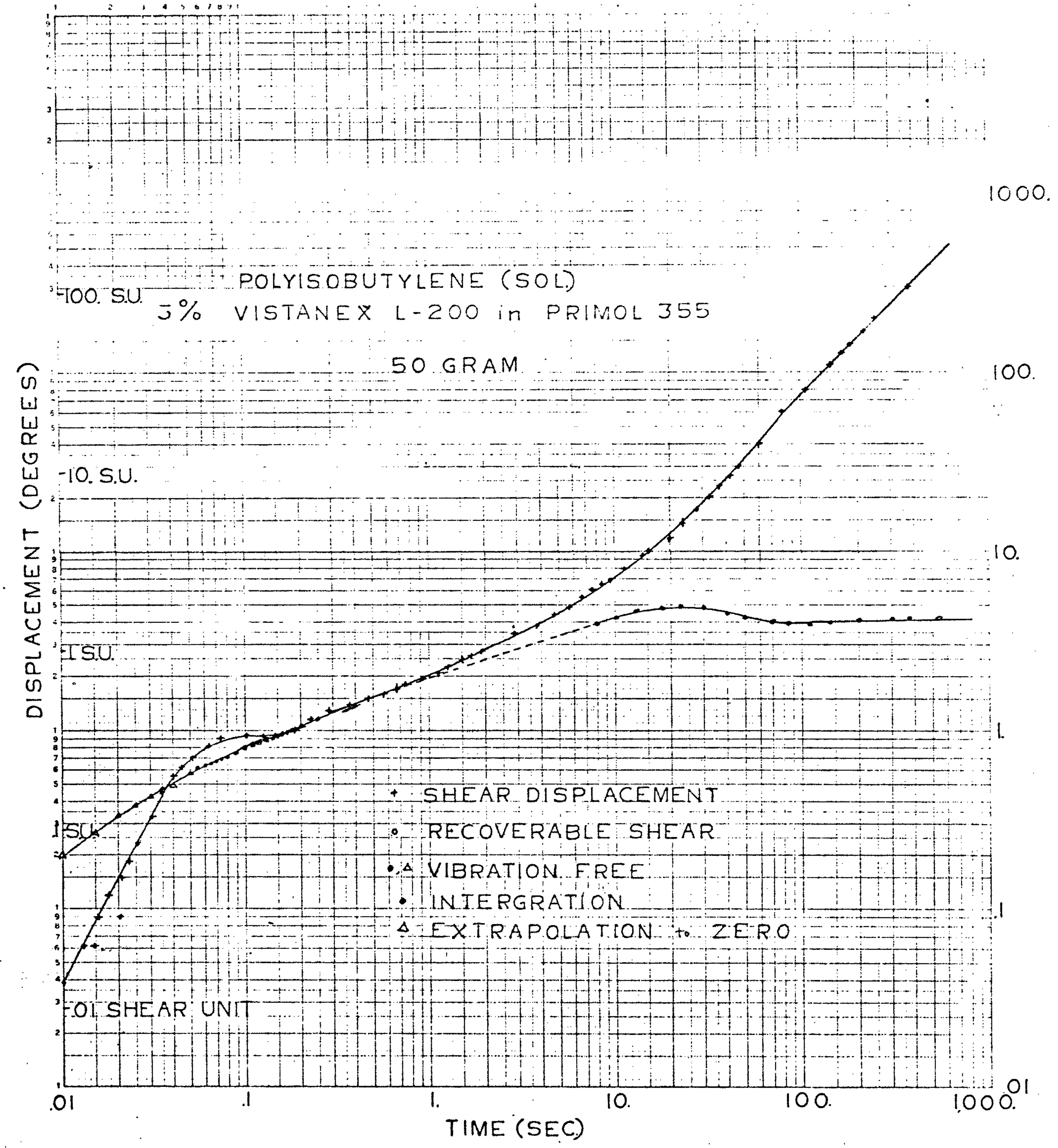
(20)W. Philippoff, Personal Communication, Meeting of Society of Rheology, Amherst, Mass., Oct. 21-24, 1974.

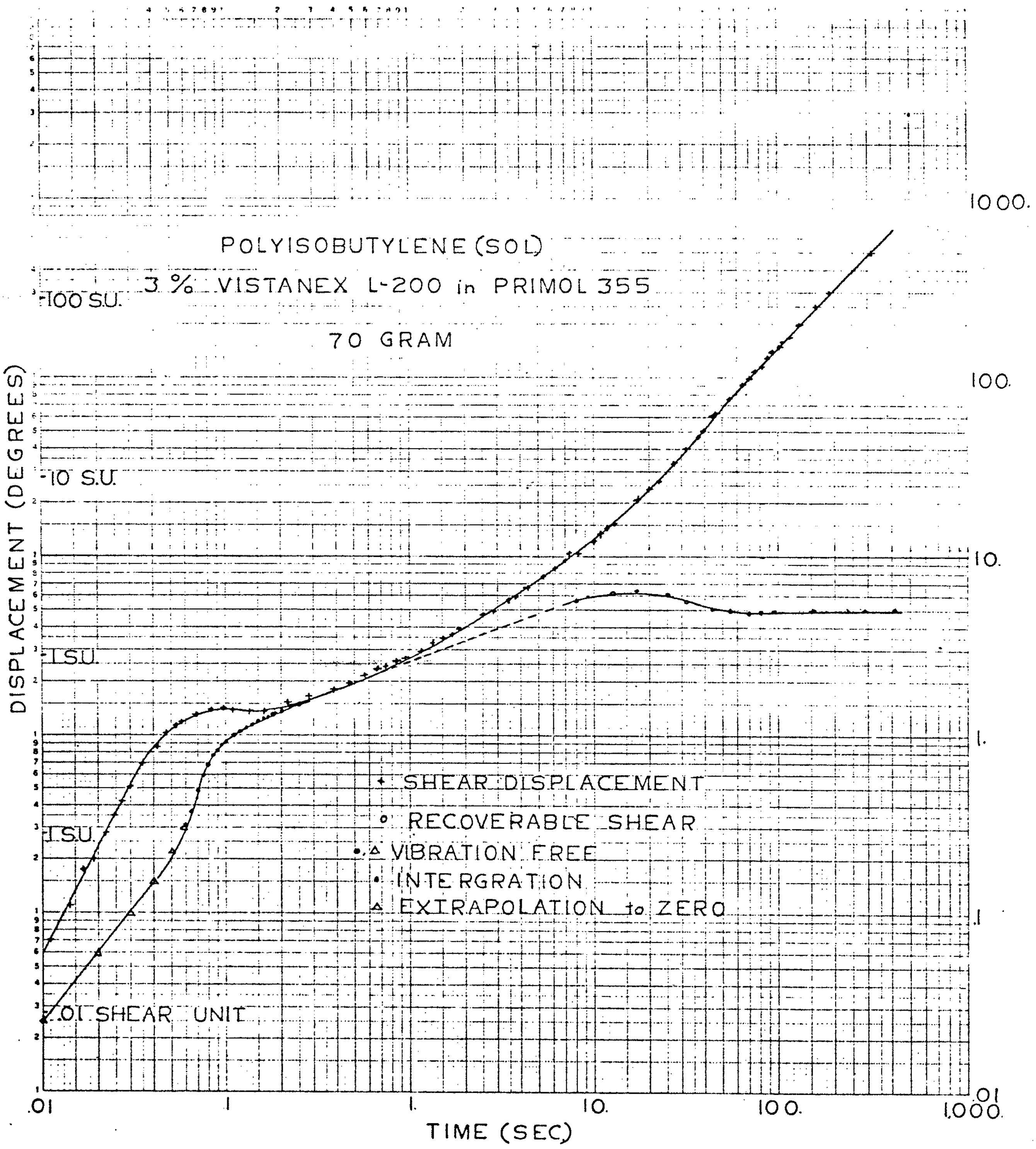

POLYISOBUTYLENE (SOL)
3% VISTANEX L-200 in PRIMOL 355
5 GRAM
1 S.U.
.1 SHEAR UNIT
.01 S.U.
+ SHEAR DISPLACEMENT
○ RECOVERABLE SHEAR
DISPLACEMENT (DEGREES)
TIME (SEC.)
10.
1.
.1
.01
.01
.1
1.
10.
100.
1000.

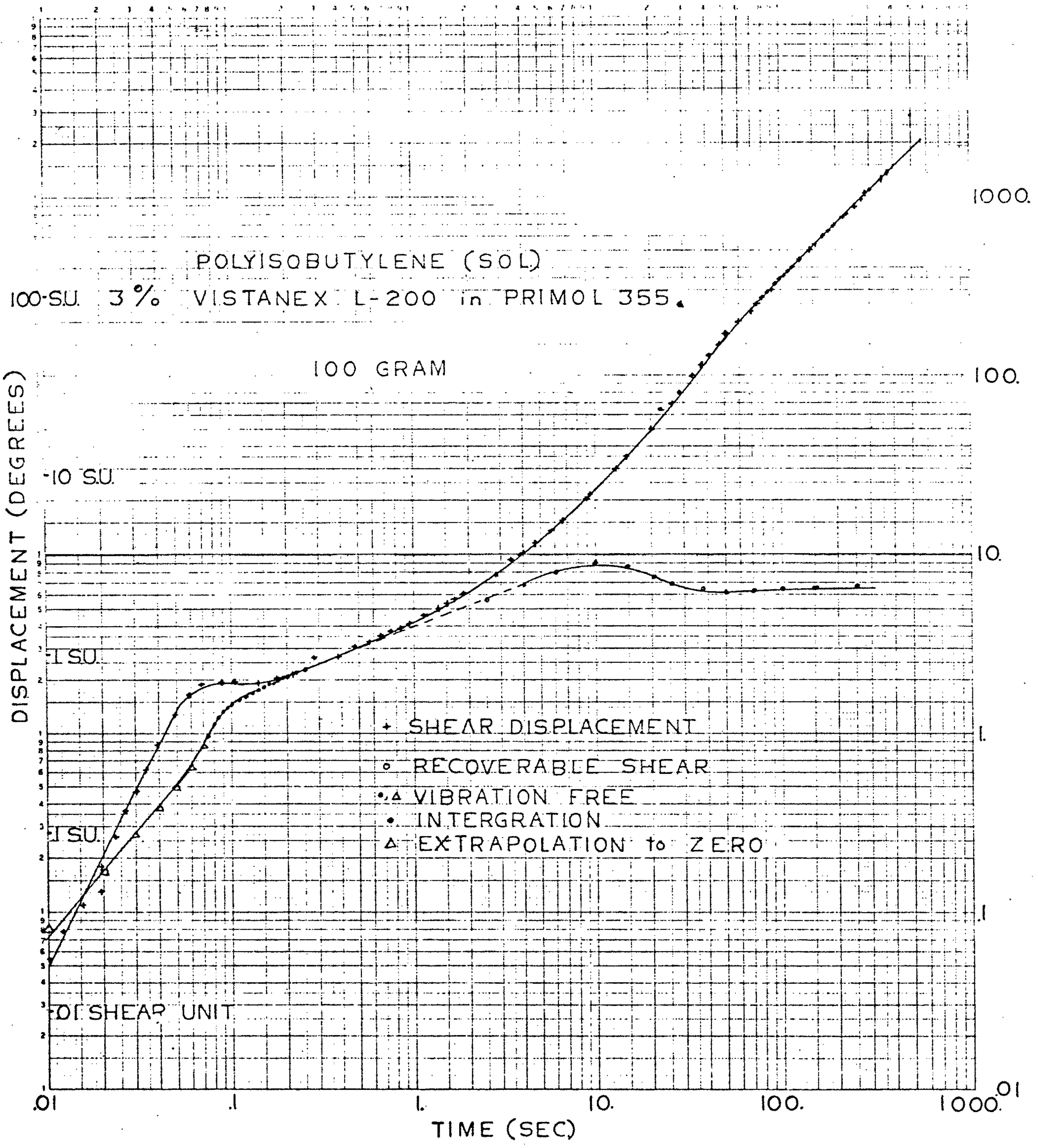

POLYISOBUTYLENE (SOL)
3% VISTANEX L-200 in PRIMOL 355
10 GRAM
100 S.U.
10. S.U.
1 S.U.
1 SHEAR UNIT
.01 S.U.
+ SHEAR DISPLACEMENT
∘ RECOVERABLE SHEAR
•,△ VIBRATION FREE
• INTERGRATION
△ EXTRAPOLATION to ZERO
DISPLACEMENT (DEGREES)
1000.
100.
10.
1.
.1
.01
.01
.1
1.
10.
100.
1000.
TIME (SEC)

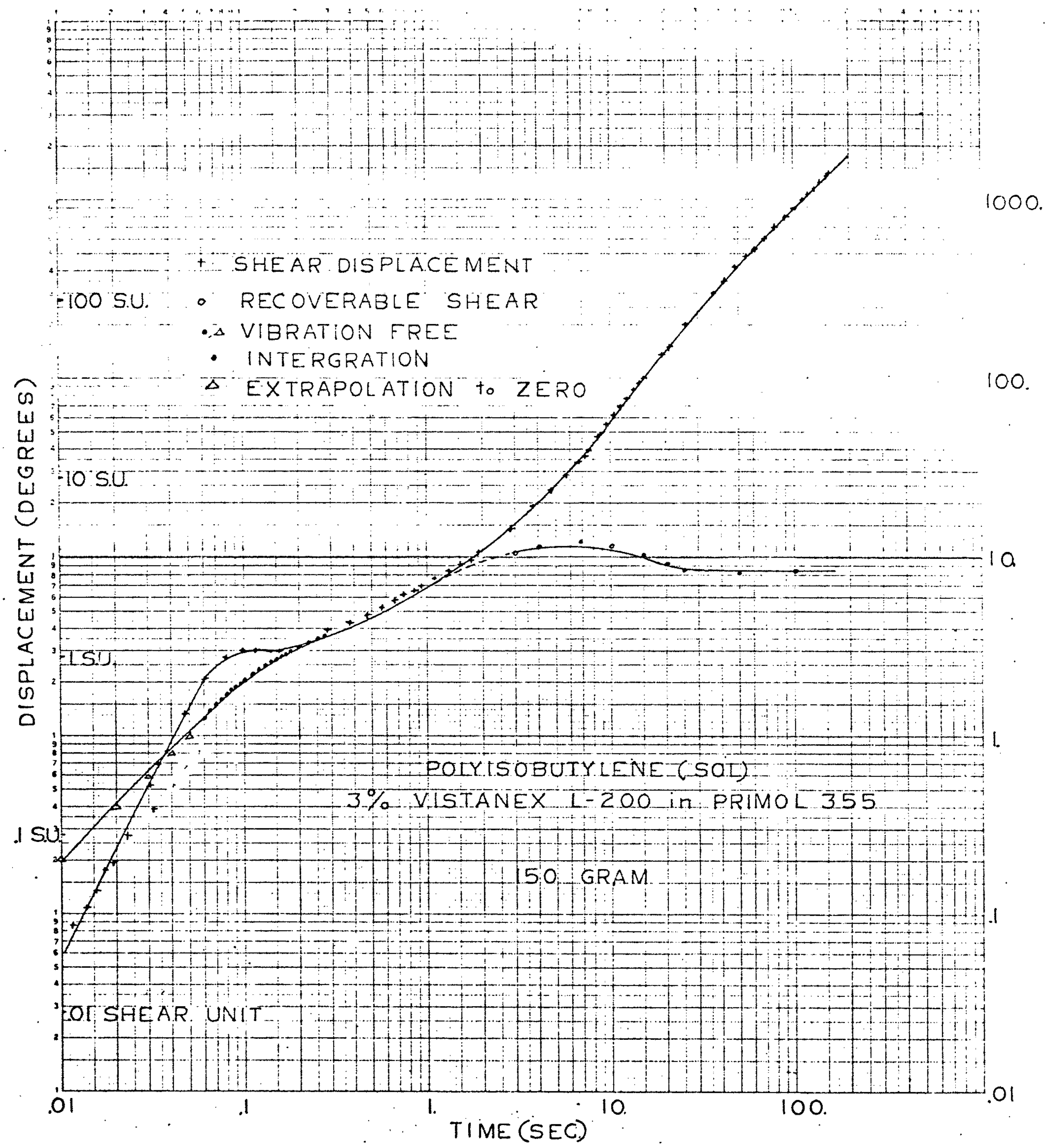

POLYISOBUTYLENE (SOL)
3% VISTANEX L-200 in PRIMOL 355
20 GRAM
10 S.U.
1 S.U.
.1 S.U.
.01 SHEAR UNIT
+ SHEAR DISPLACEMENT
○ RECOVERABLE SHEAR
∴ VIBRATION FREE
• INTERGRATION
△ EXTRAPOLATION to ZERO
DISPLACEMENT (DEGREES)
100.
10.
1.
.1
.01
TIME (SEC)
.01
.1
1.
10.
100.
1,000.

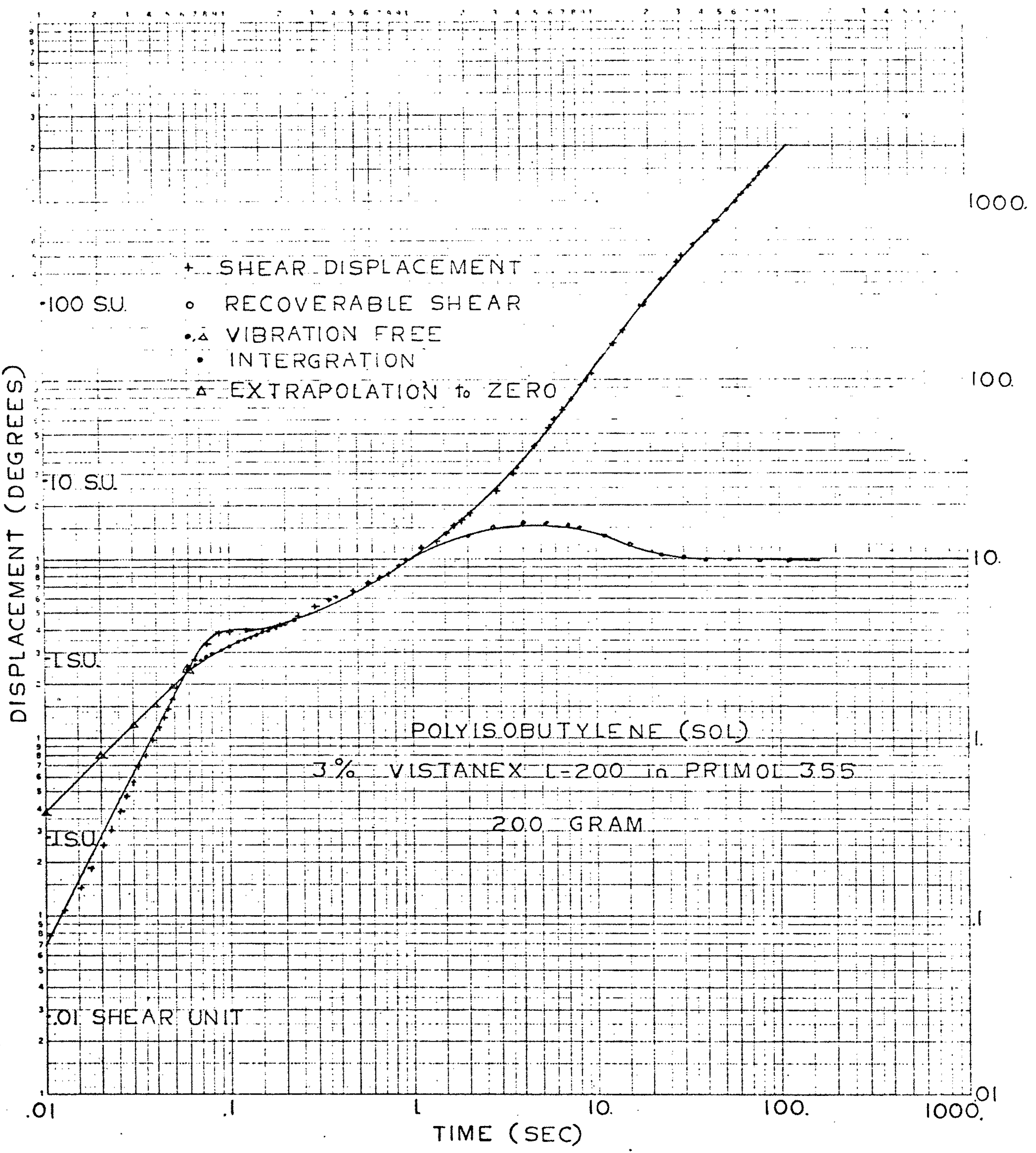

POLYISOBUTYLENE (SOL)
3% VISTANEX L-200 in PRIMOL 355
30 GRAM
100 S.U.
10 S.U.
1 S.U.
.1 S.U.
.01 SHEAR UNIT
+ SHEAR DISPLACEMENT
○ RECOVERABLE SHEAR
●,△ VIBRATION FREE
● INTERGRATION
△ EXTRAPOLATION to ZERO
DISPLACEMENT (DEGREES)
1,000
100.
10.
1.
.1
.01
.01
.1
1.
10.
100.
1000.
TIME (SEC.)

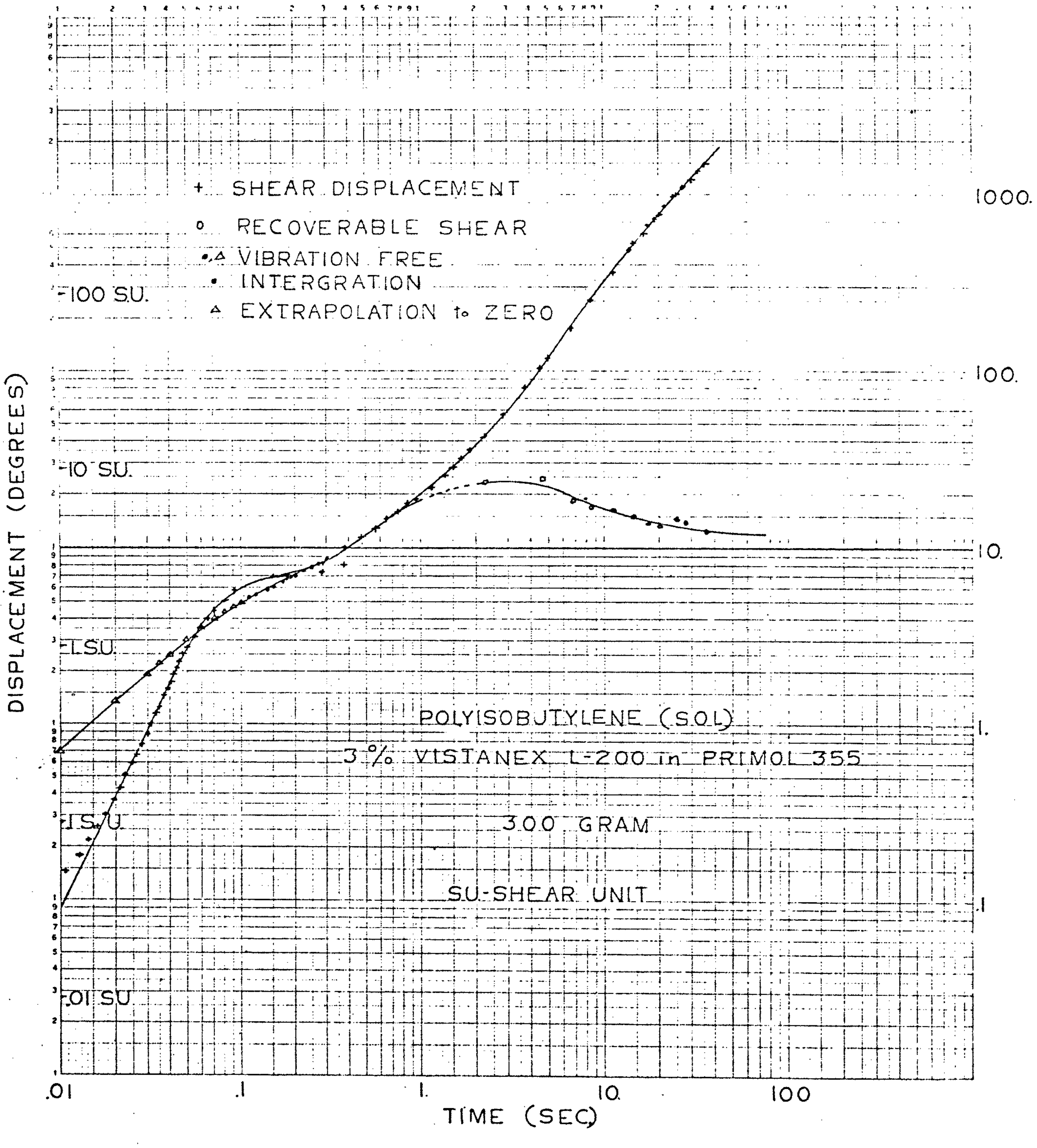

POLYISOBUTYLENE (SOL)
3% VISTANEX L-200 in PRIMOL 355
50 GRAM
100. S.U.
10. S.U.
1 S.U.
.1 S.U.
.01 SHEAR UNIT
1000.
100.
10.
1.
.1
.01
+ SHEAR DISPLACEMENT
∘ RECOVERABLE SHEAR
•,△ VIBRATION FREE
• INTERGRATION
△ EXTRAPOLATION to ZERO
DISPLACEMENT (DEGREES)
.01
.1
1.
10.
100.
1000.
TIME (SEC)

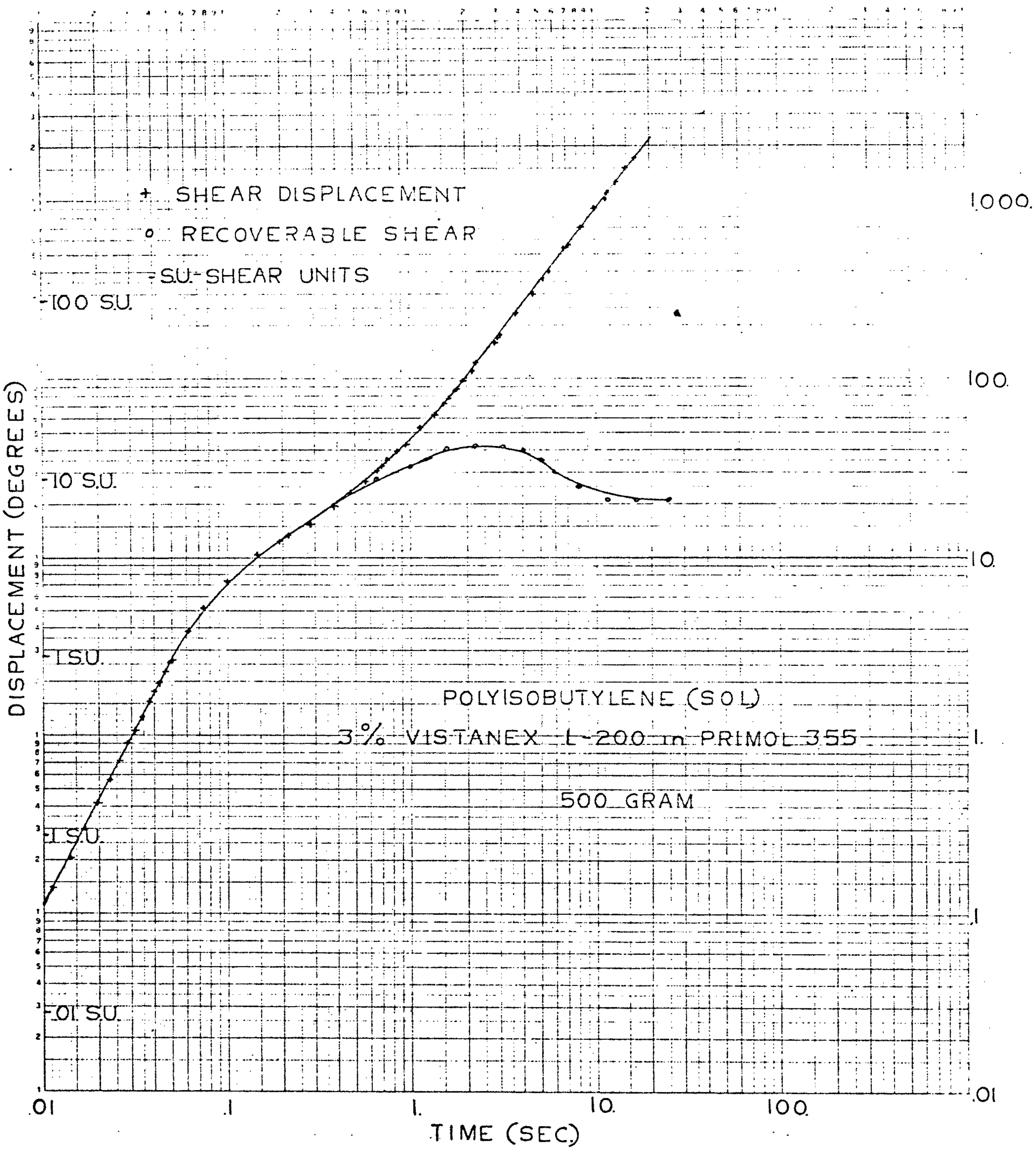

POLYISOBUTYLENE (SOL)
3 % VISTANEX L-200 in PRIMOL 355
70 GRAM
100 S.U.
10 S.U.
1 S.U.
.1 S.U.
.01 SHEAR UNIT
DISPLACEMENT (DEGREES)
1000.
100.
10.
1.
.1
.01
.01
.1
1.
10.
100.
1,000.
TIME (SEC)
+ SHEAR DISPLACEMENT
∘ RECOVERABLE SHEAR
•,△ VIBRATION FREE
• INTERGRATION
△ EXTRAPOLATION to ZERO

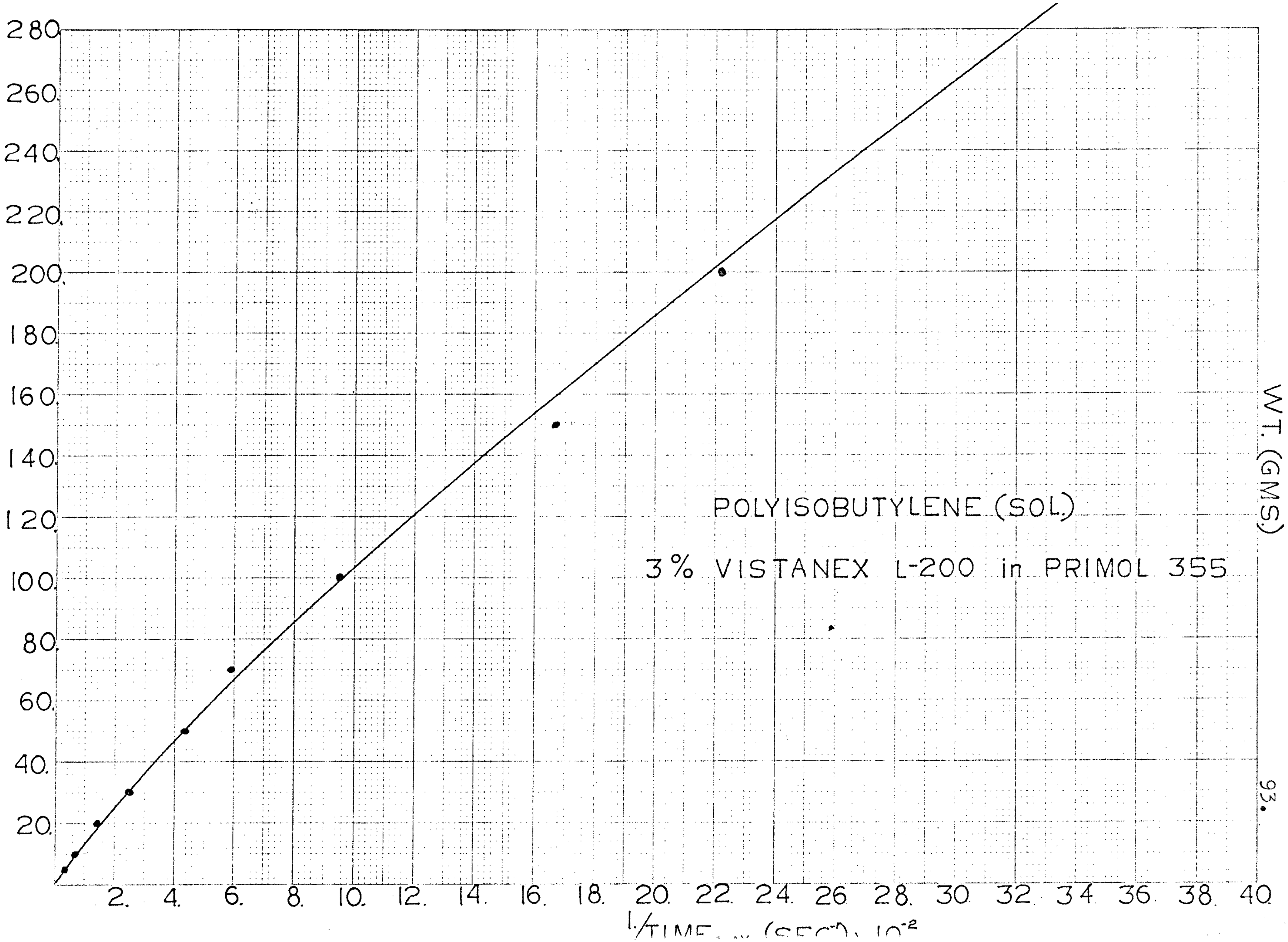

POLYISOBUTYLENE (SOL)
100-S.U. 3% VISTANEX L-200 in PRIMOL 355.
100 GRAM
DISPLACEMENT (DEGREES)
10 S.U.
1 S.U.
.1 S.U.
.01 SHEAR UNIT
1000.
100.
10.
1.
.1
.01
.01
.1
1.
10.
100.
1000.
TIME (SEC)
+ SHEAR DISPLACEMENT
○ RECOVERABLE SHEAR
•,△ VIBRATION FREE
• INTERGRATION
△ EXTRAPOLATION to ZERO

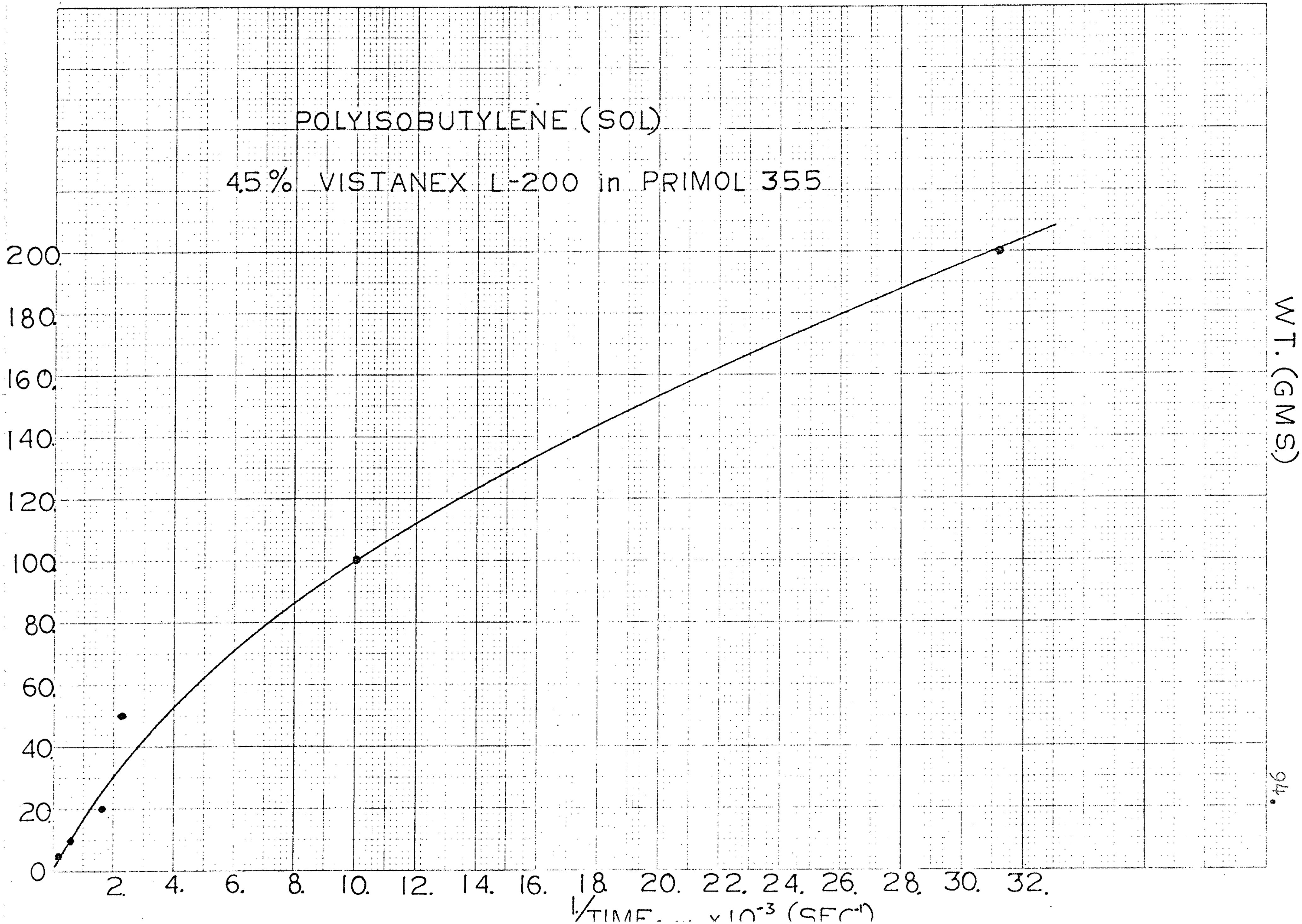

+ SHEAR DISPLACEMENT
○ RECOVERABLE SHEAR
•△ VIBRATION FREE
• INTERGRATION
△ EXTRAPOLATION to ZERO
POLYISOBUTYLENE (SOL)
3% VISTANEX L-200 in PRIMOL 355
150 GRAM
100 S.U.
10 S.U.
1 S.U.
.1 S.U.
.01 SHEAR UNIT
DISPLACEMENT (DEGREES)
1000.
100.
10.
1.
.1
.01
.01
.1
1.
10.
100.
TIME (SEC)

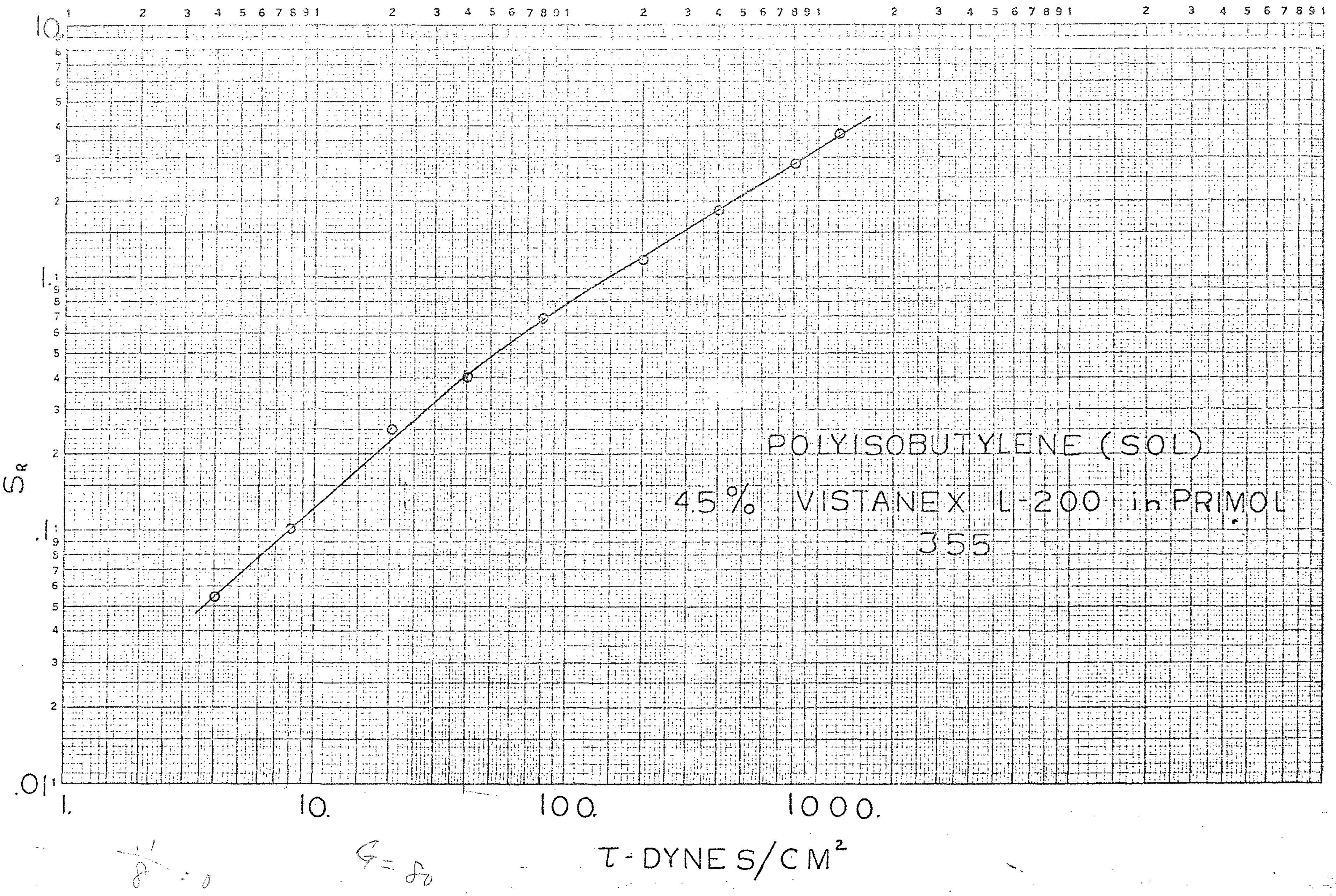

+ SHEAR DISPLACEMENT
○ RECOVERABLE SHEAR
•,△ VIBRATION FREE
• INTERGRATION
△ EXTRAPOLATION to ZERO
100 S.U.
10 S.U.
1 S.U.
.1 S.U.
.01 SHEAR UNIT
POLYISOBUTYLENE (SOL)
3% VISTANEX L=200 in PRIMOL 355
200 GRAM
DISPLACEMENT (DEGREES)
TIME (SEC)
.01
.1
1
10.
100.
1000.
1000.
100.
10.
1.
.1
.01

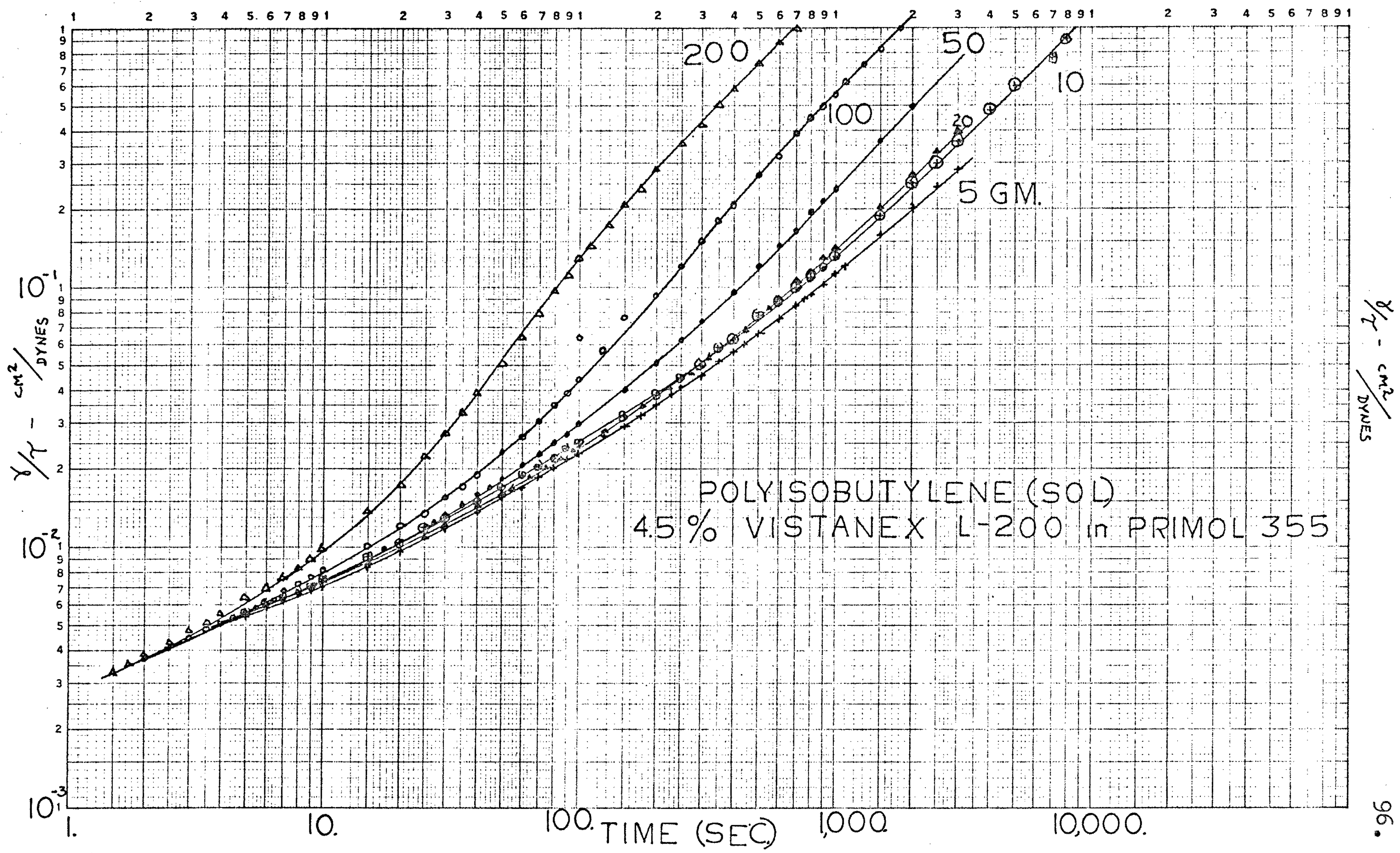

+ SHEAR DISPLACEMENT
○ RECOVERABLE SHEAR
•,△ VIBRATION FREE
• INTERGRATION
△ EXTRAPOLATION to ZERO
100 S.U.
10 S.U.
1 S.U.
.1 S.U.
.01 S.U.
1000.
100.
10.
1.
.1
DISPLACEMENT (DEGREES)
.01
.1
1.
10.
100
TIME (SEC)
POLYISOBUTYLENE (SOL)
3 % VISTANEX L-200 in PRIMOL 355
300 GRAM
SU-SHEAR UNIT


+ SHEAR DISPLACEMENT
o RECOVERABLE SHEAR
S.U. SHEAR UNITS
100 S.U.
10 S.U.
1 S.U.
.1 S.U.
.01 S.U.
POLYISOBUTYLENE (SOL)
3% VISTANEX L-200 in PRIMOL 355
500 GRAM
DISPLACEMENT (DEGREES)
TIME (SEC)
.01
.1
1.
10.
100.
1000.
100.
10.
1.
.1
.01

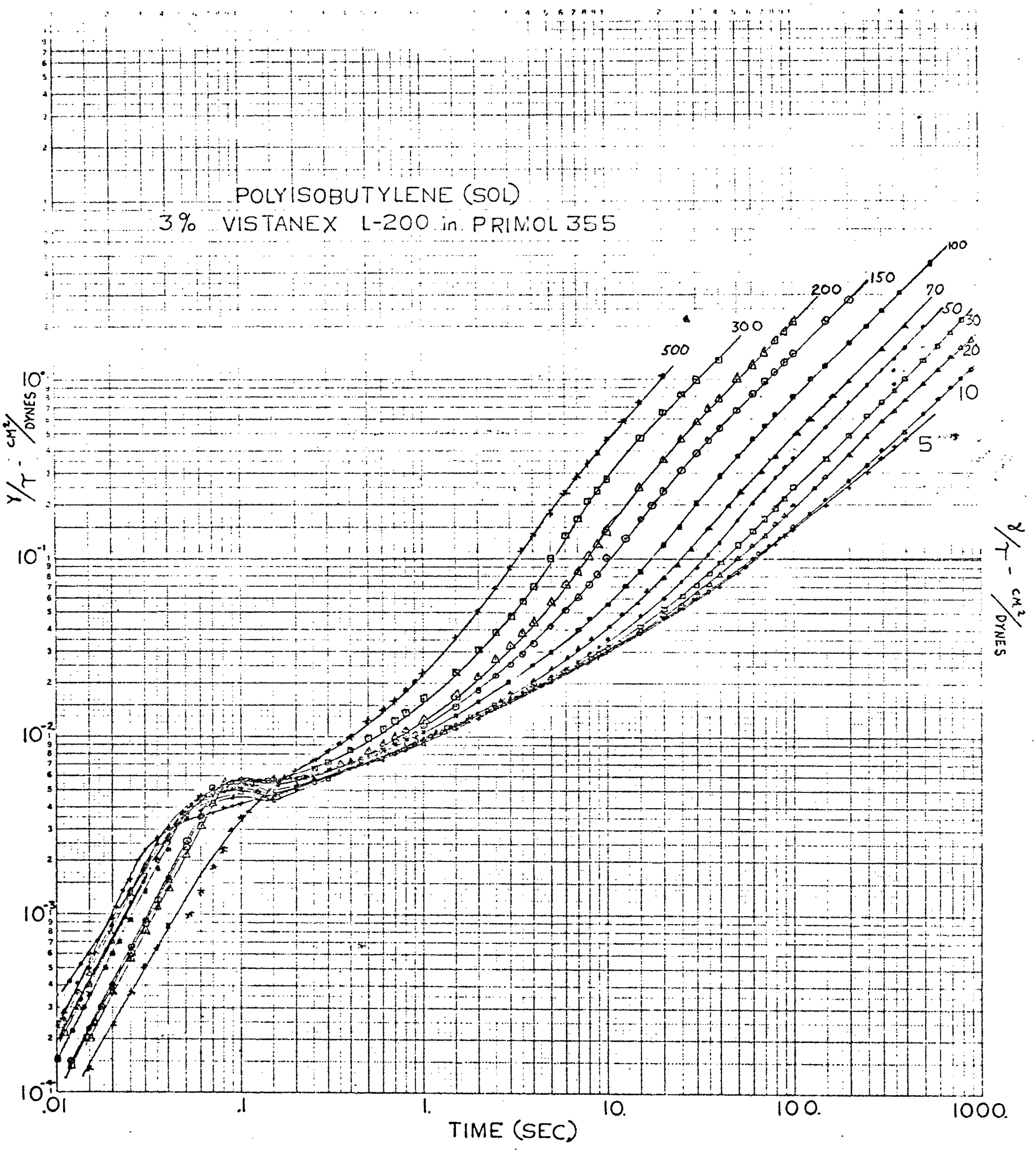

POLYISOBUTYLENE (SOL.)
3% VISTANEX L-200 in PRIMOL 355
W.T. (GMS.)
280.
260.
240.
220.
200.
180.
160.
140.
120.
100.
80.
60.
40.
20.
2.
4.
6.
8.
10.
12.
14.
16.
18.
20.
22.
24.
26
28.
30
32.
34
36.
38.
40
1/TIME (SEC⁻¹) 10⁻²


POLYISOBUTYLENE (SOL)
45% VISTANEX L-200 in PRIMOL 355
200.
180.
160.
140.
120.
100.
80.
60.
40.
20.
0
2.
4.
6.
8.
10.
12.
14.
16.
18.
20.
22.
24.
26.
28.
30.
32.
1/TIME x10^{-3} (SEC^{-1})
WT. (GMS)


POLYISOBUTYLENE (SOL)
45% VISTANEX L-200 in PRIMOL
355
S_R
10.
1.
.1
.01
1.
10.
100.
1000.
τ - DYNES/CM^2
$\gamma = 0$
G = 80



POLYISOBUTYLENE (SOL)
4.5% VISTANEX L-200 in PRIMOL 355

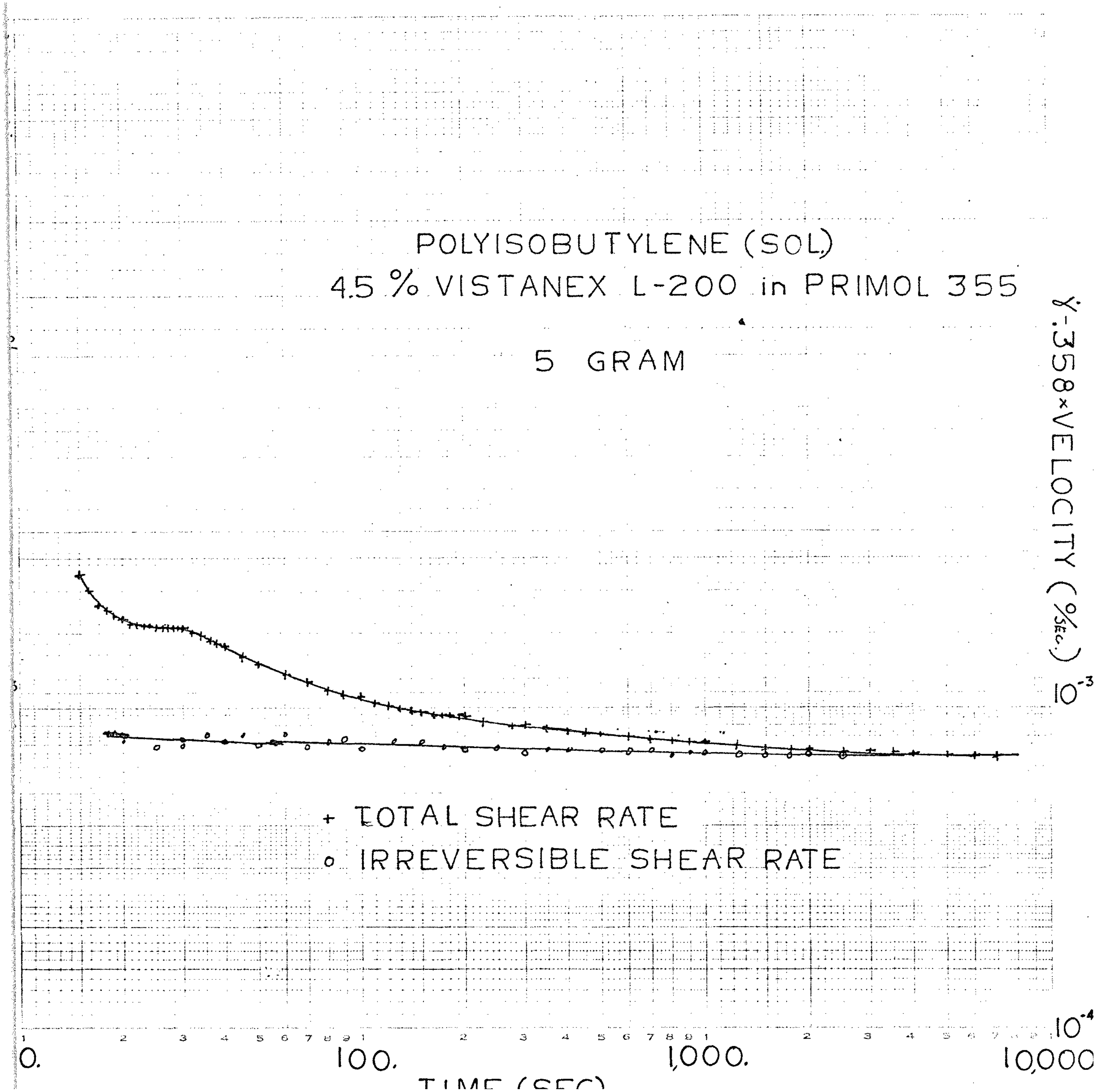

POLYISOBUTYLENE (SOL)
3% VISTANEX L-200 in PRIMOL 355
γ/τ - CM²/DYNES
γ/τ - CM²/DYNES
10⁰
10⁻¹
10⁻²
10⁻³
10⁻⁴
.01
.1
1.
10.
100.
1000.
TIME (SEC)
500
300
200
150
100
70
50
30
20
10
5

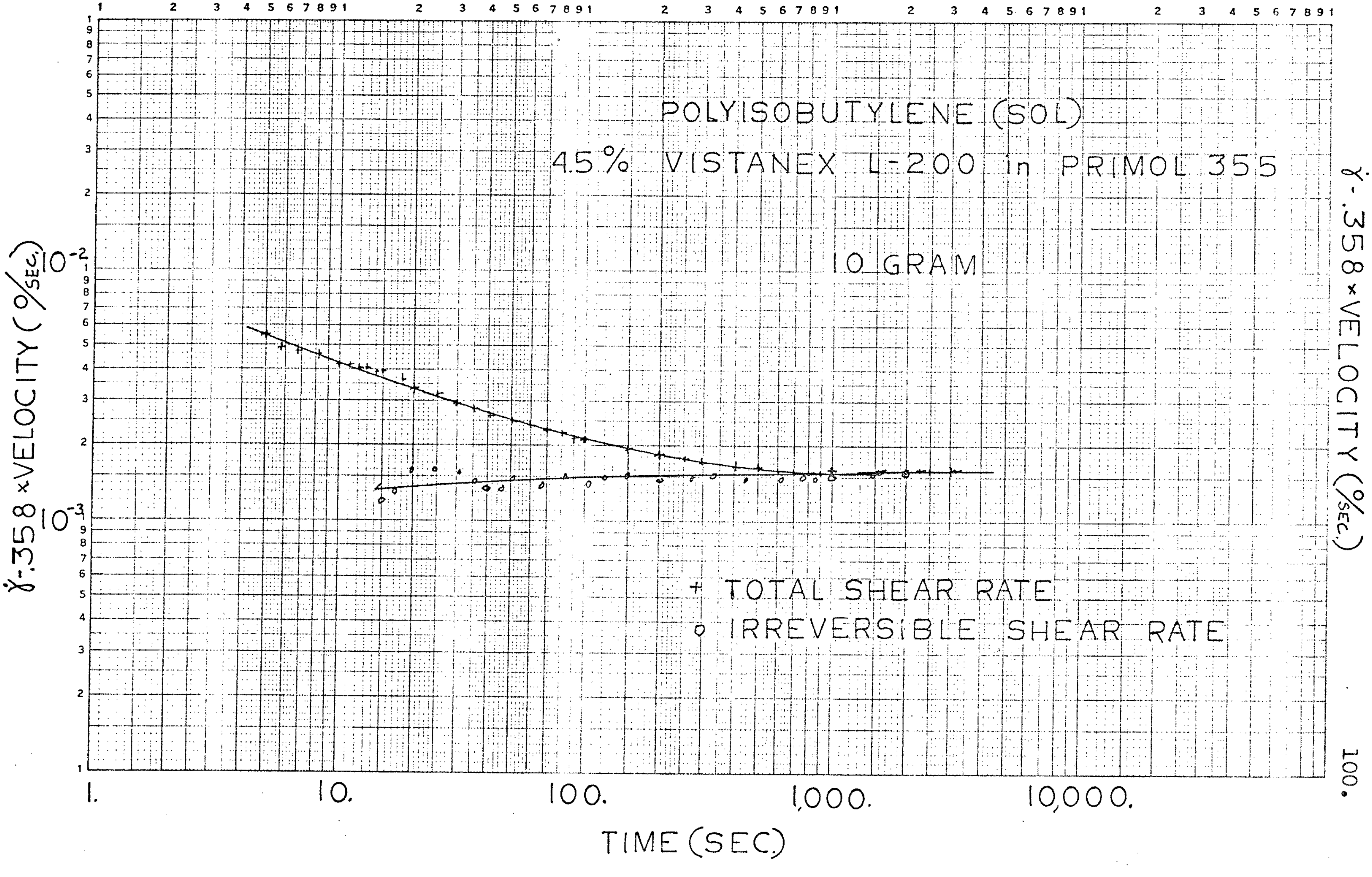
results indicate that this phenomena does occur.

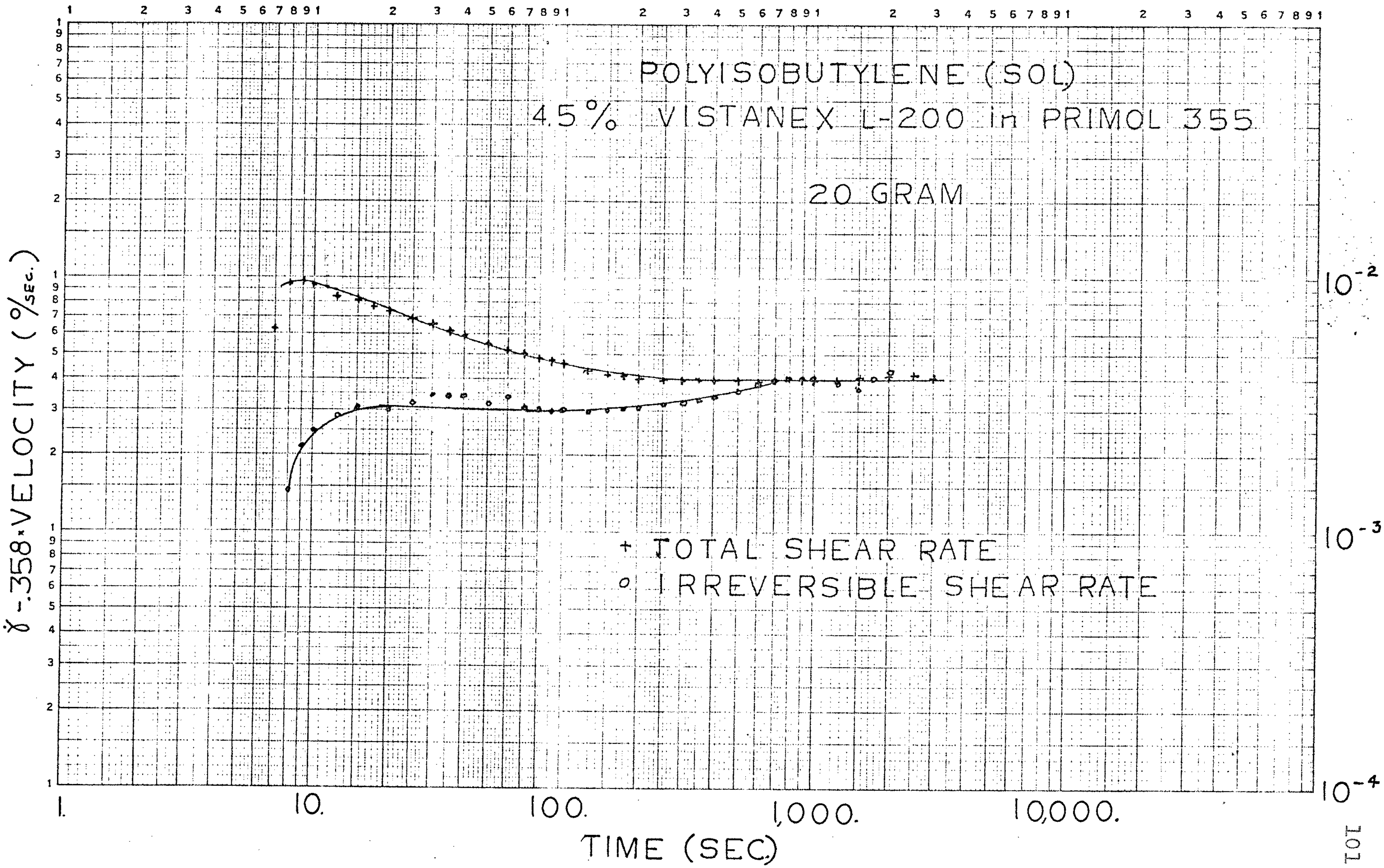
Shear Rate Profiles From Angular Displacement

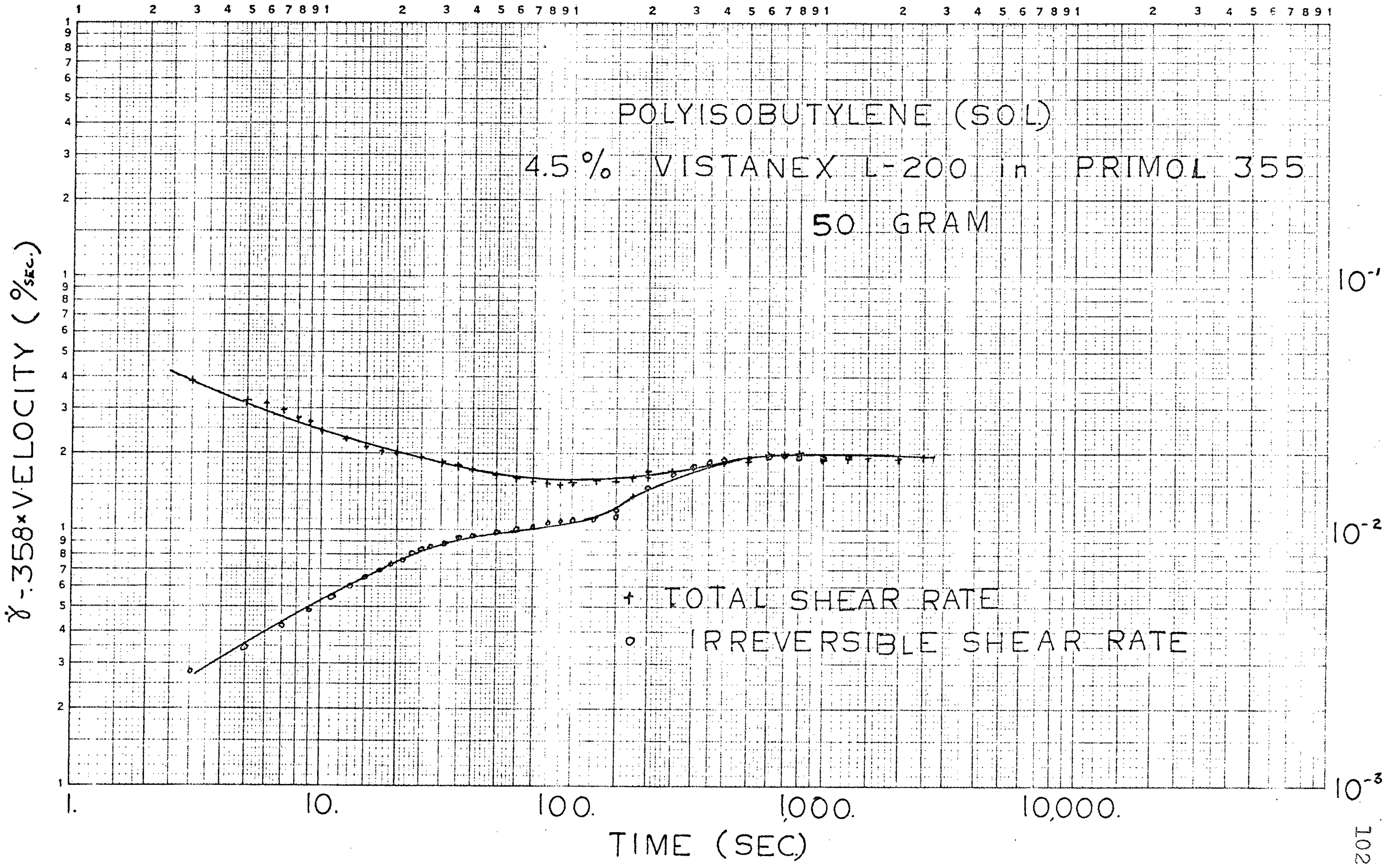
4½% PIB Solution. The shear rate of the 4.5% PIB solution as a function of loads and time are listed in the following graphs. It is evident from the graphs that the irreversible shear rate will merge with the total shear rate to some equilibrium constant value. The time required for constant shear rate is a function of the amount of loading used. This can be seen quite readily by comparing the 5 GM. load with the 200 GM load. For the 5 GM load it takes approximately 5,000 Sec, to attain constant shear rate, while for the 200 GM. load it takes only about 90 secs. For small loads, the irreversible shear seems to remain quite constant, but increases in slope as the amount of loading increases. The rate of shear ($\dot{\gamma}$) is expressed in sec^{-1} which is the product of shear velocity (o/Sec.) multiplied by conversion factor of one degree equal to .358 shear units.

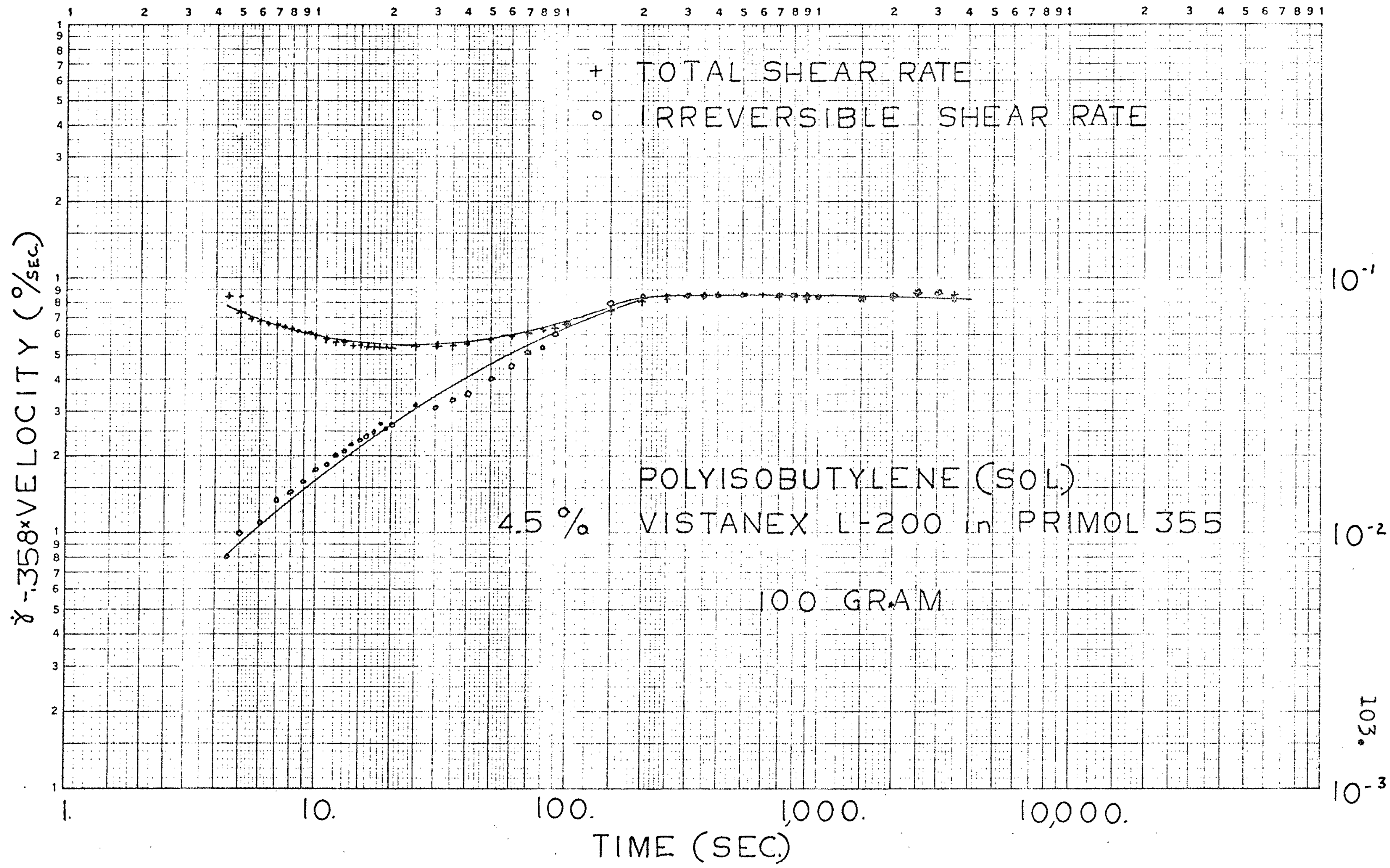
3% PIB Solution. For the 3% PIB solution we have the advantage of observing the shear rate for low times. The time needed for constant shear rate also decreased as the amount of loading is increased as it did with the 4.5% PIB solution. One obvious difference with the 3% PIB solution is that small increases in load does not reduce the time for constant equilibrium. It may not have any effect at all. Noticeable decreases in equilibrium time occurs when

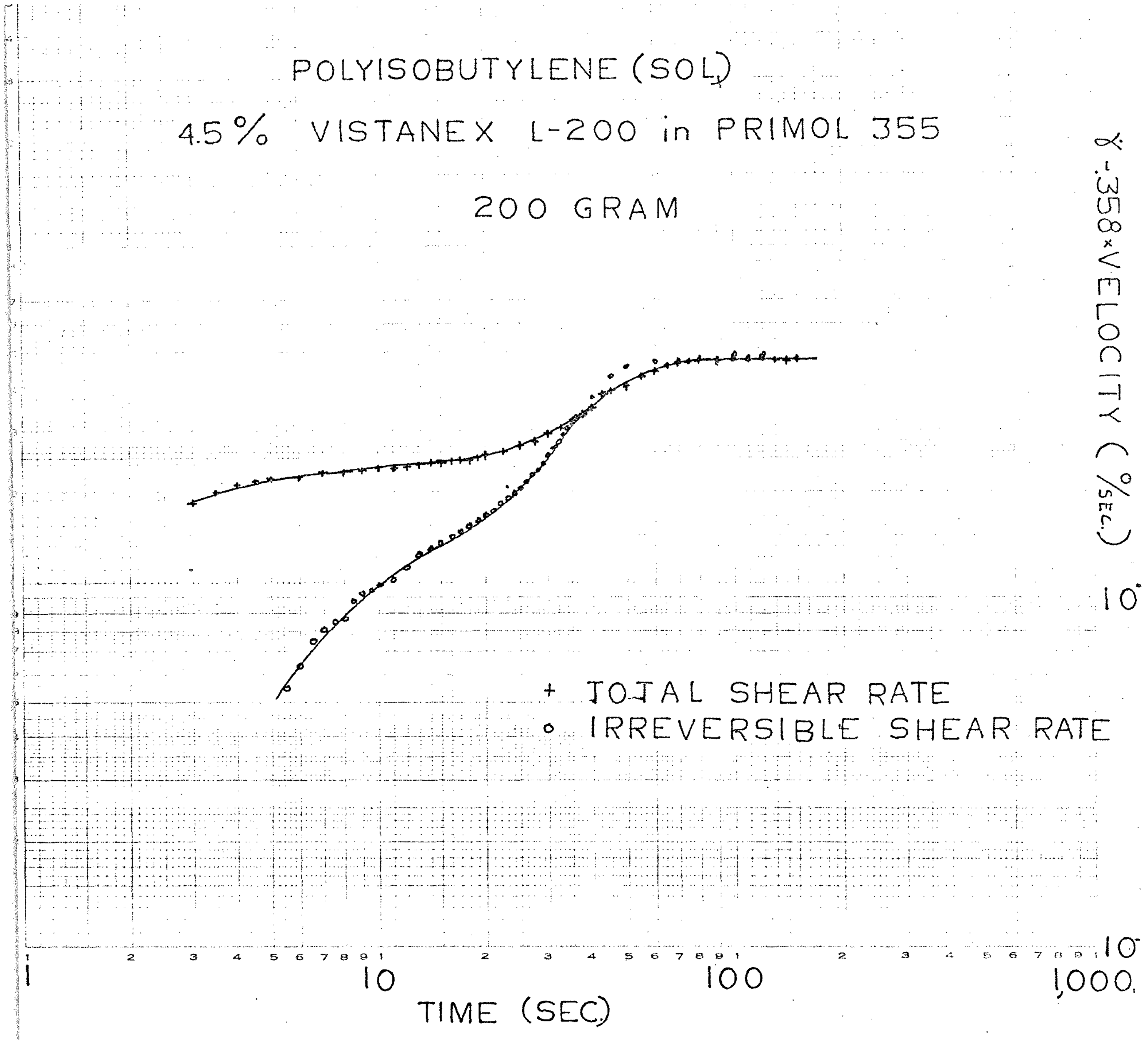

POLYISOBUTYLENE (SOL)
4.5 % VISTANEX L-200 in PRIMOL 355
5 GRAM
+ TOTAL SHEAR RATE
o IRREVERSIBLE SHEAR RATE
γ̇-.358×VELOCITY (%/SEC.)
10^-3
10^-4
0.
100.
1,000.
10,000
TIME (SEC)

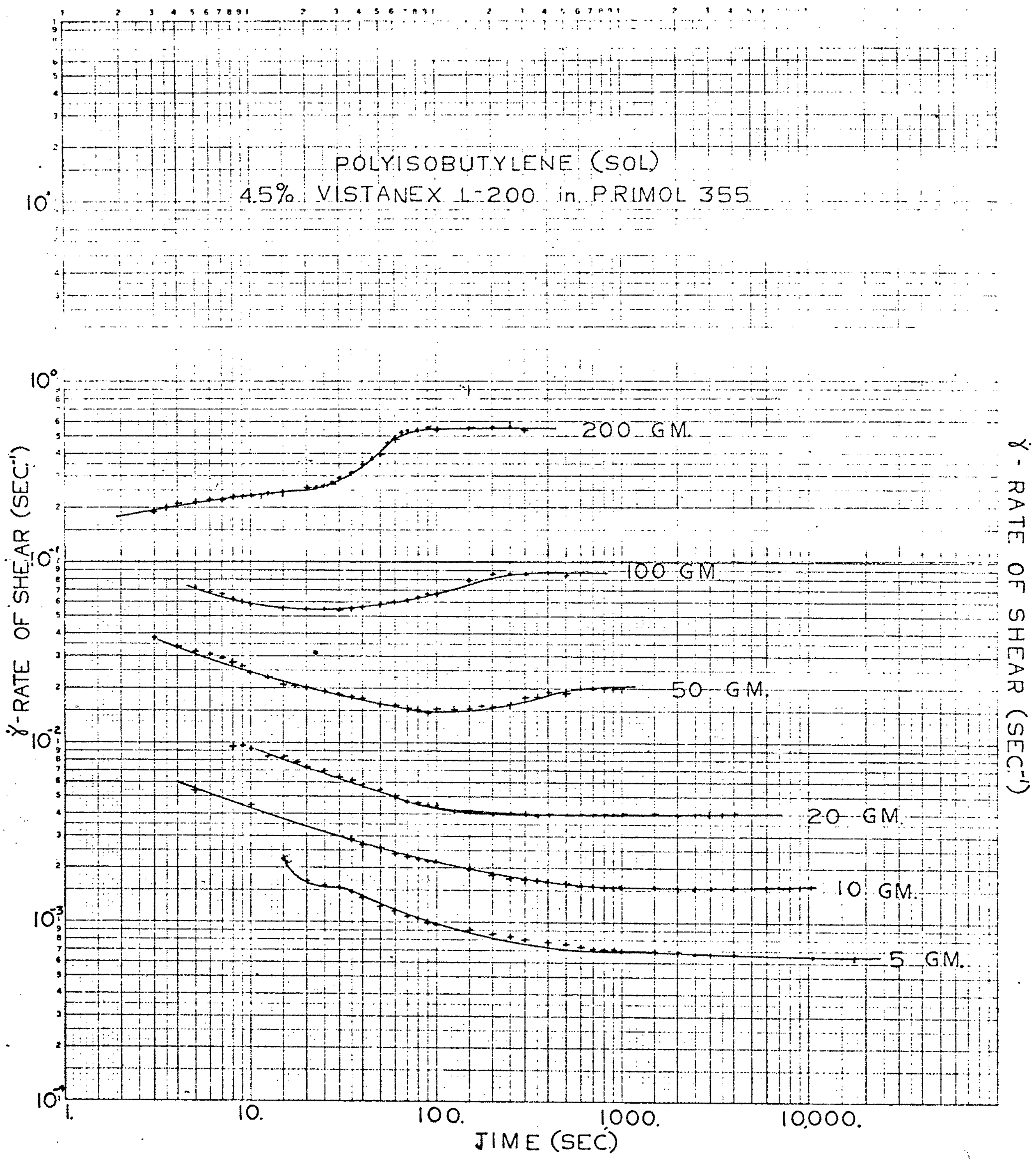

POLYISOBUTYLENE (SOL)
45% VISTANEX L-200 in PRIMOL 355
10 GRAM
+ TOTAL SHEAR RATE
o IRREVERSIBLE SHEAR RATE
$\dot{\gamma}$.358 × VELOCITY (%/SEC.)
10^{-2}
10^{-3}
1.
10.
100.
1,000.
10,000.
100.
TIME (SEC.)

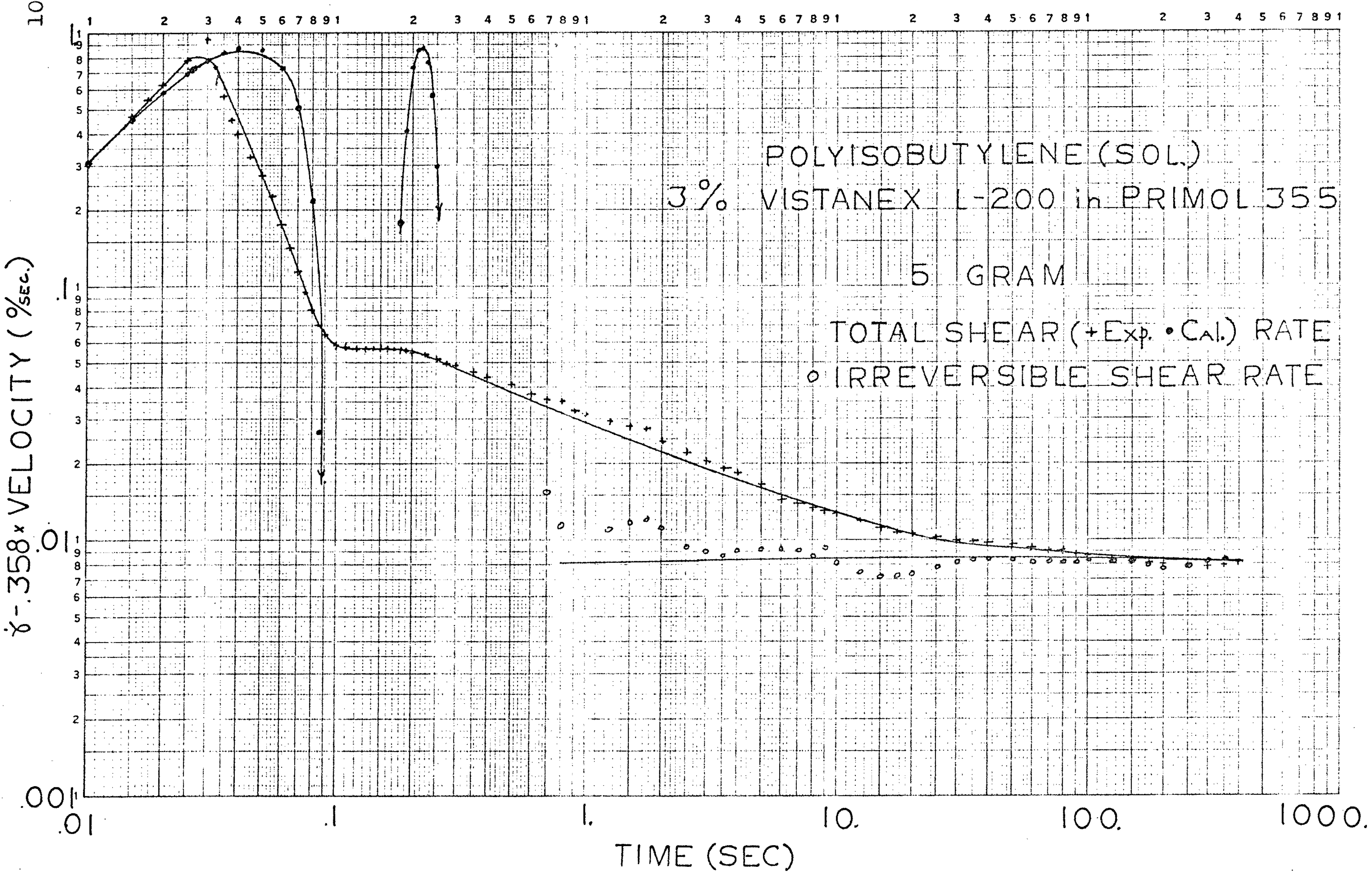

POLYISOBUTYLENE (SOL)
4.5% VISTANEX L-200 in PRIMOL 355
20 GRAM
+ TOTAL SHEAR RATE
o IRREVERSIBLE SHEAR RATE
$\dot{\gamma}$ - .358 × VELOCITY (%/sec.)
TIME (SEC)
1.
10.
100.
1,000.
10,000.
10^{-2}
10^{-3}
10^{-4}

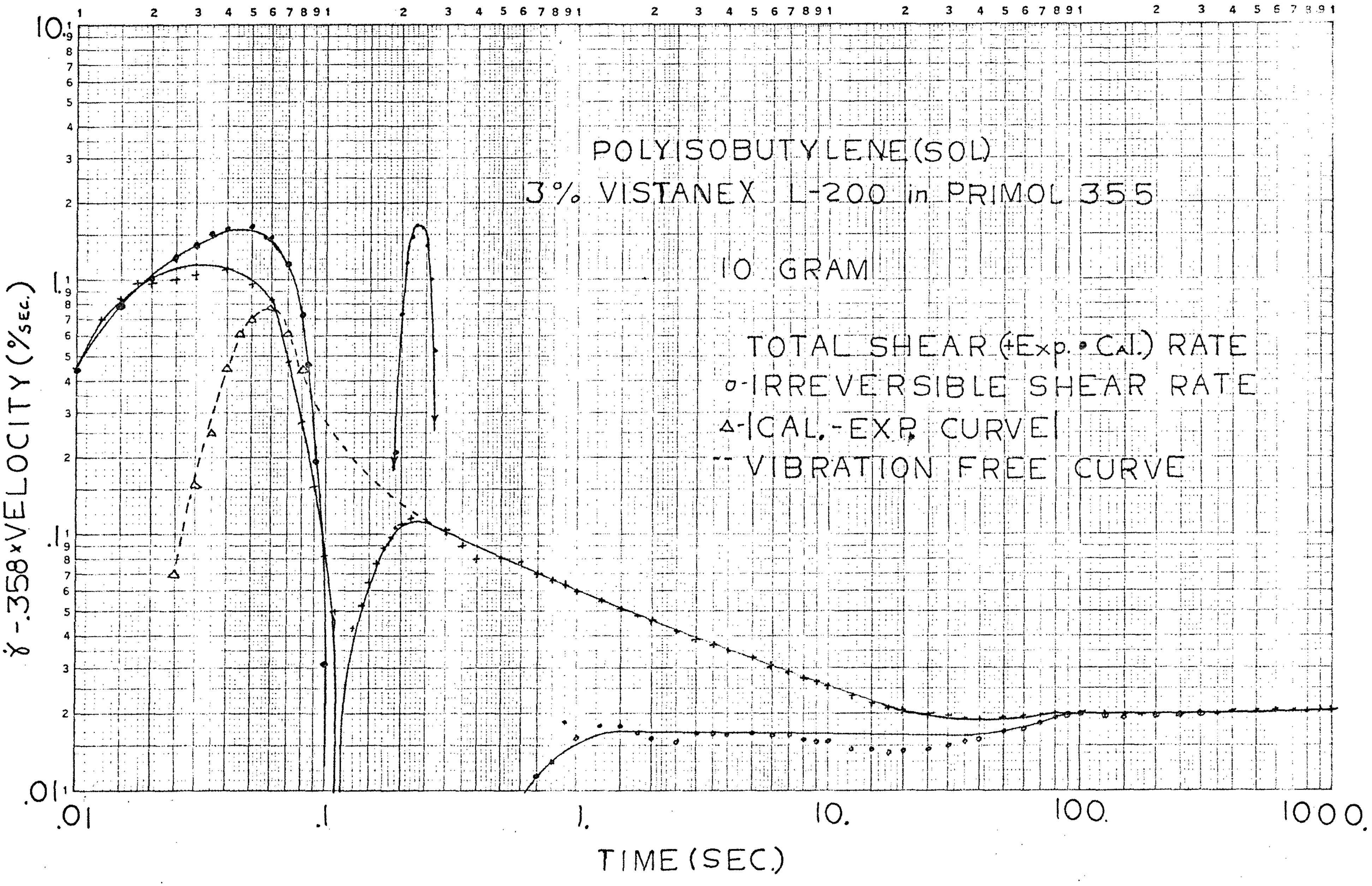

POLYISOBUTYLENE (SOL)
4.5% VISTANEX L-200 in PRIMOL 355
50 GRAM
+ TOTAL SHEAR RATE
o IRREVERSIBLE SHEAR RATE
γ̇ -.358 × VELOCITY (%/SEC.)
TIME (SEC)
1.
10.
100.
1000.
10,000.
10⁻¹
10⁻²
10⁻³

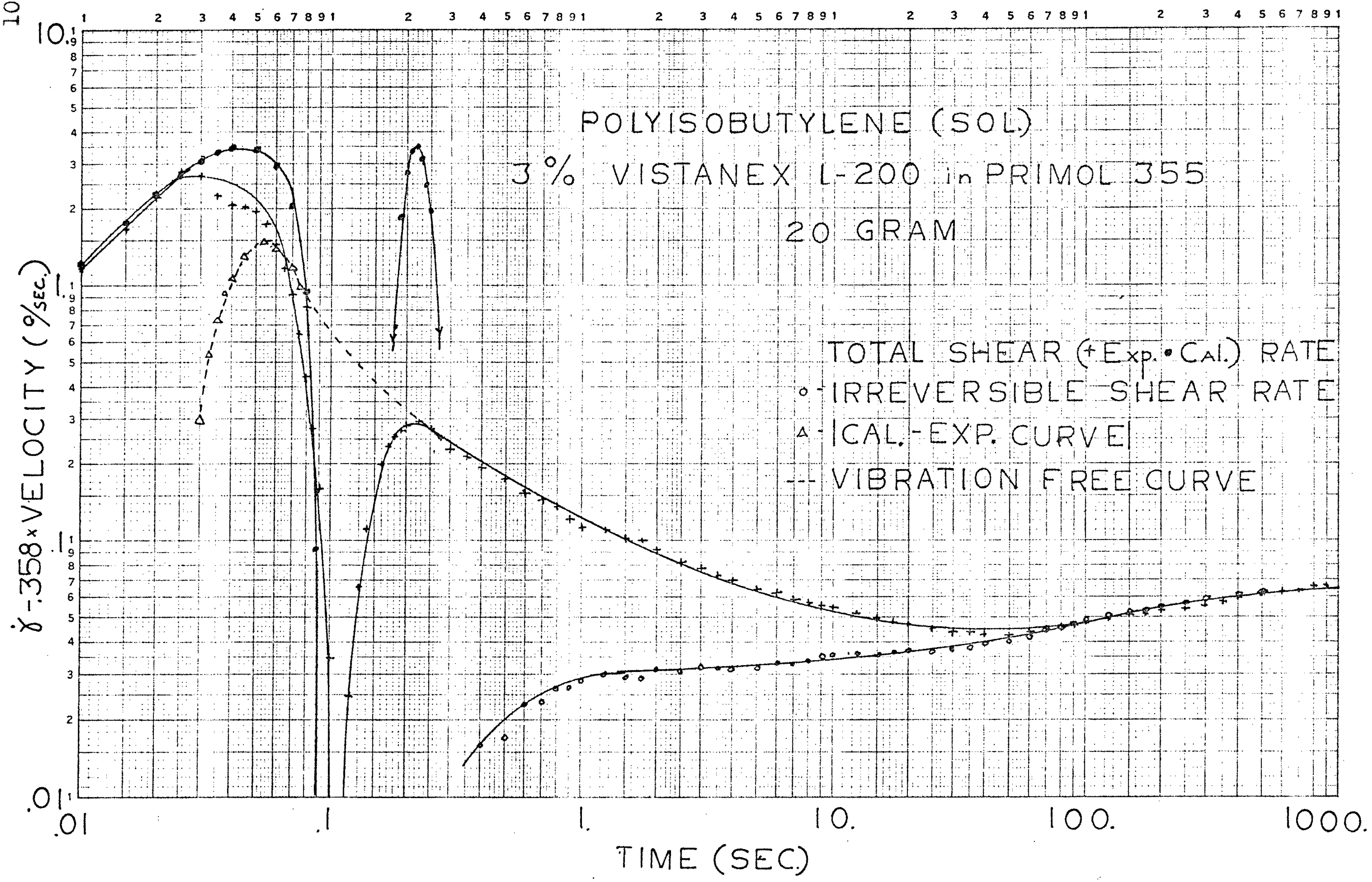

+ TOTAL SHEAR RATE
○ IRREVERSIBLE SHEAR RATE
POLYISOBUTYLENE (SOL)
4.5 % VISTANEX L-200 in PRIMOL 355
100 GRAM
$\dot{\gamma}$ -.358 × VELOCITY (%/SEC.)
TIME (SEC.)
1.
10.
100.
1,000.
10,000.
10^{-1}
10^{-2}
10^{-3}

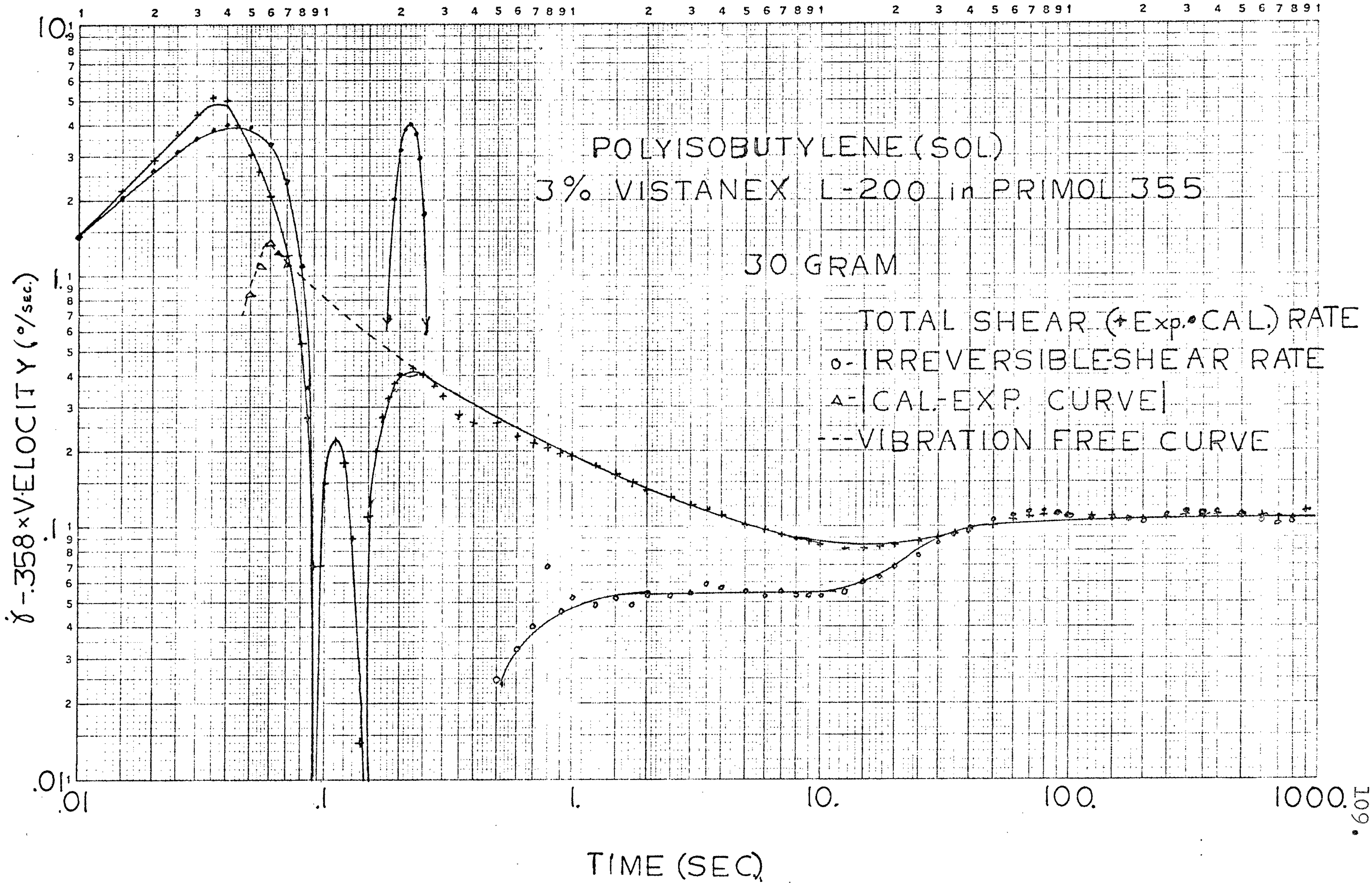

POLYISOBUTYLENE (SOL)
4.5% VISTANEX L-200 in PRIMOL 355
200 GRAM
γ̇ -.358×VELOCITY (%/SEC.)
10
10
+ TOTAL SHEAR RATE
○ IRREVERSIBLE SHEAR RATE
1
10
100
1,000
TIME (SEC)

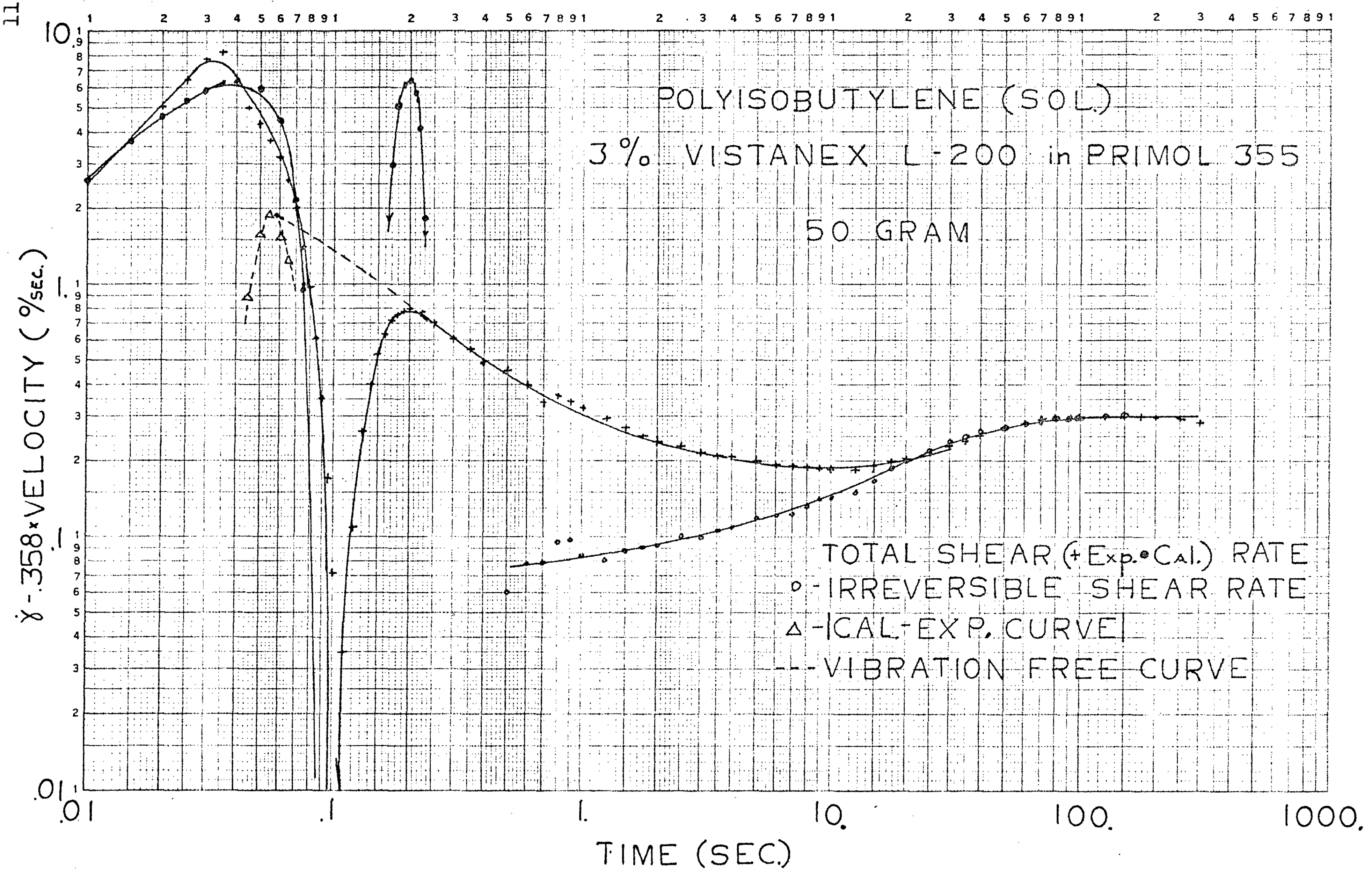

POLYISOBUTYLENE (SOL)
4.5% VISTANEX L-200 in PRIMOL 355
200 GM.
100 GM.
50 GM.
20 GM.
10 GM.
5 GM.
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
1.
10.
100.
1000.
10,000.
TIME (SEC)
$\dot{\gamma}$-RATE OF SHEAR (SEC^{-1})
$\dot{\gamma}$ - RATE OF SHEAR (SEC^{-1})

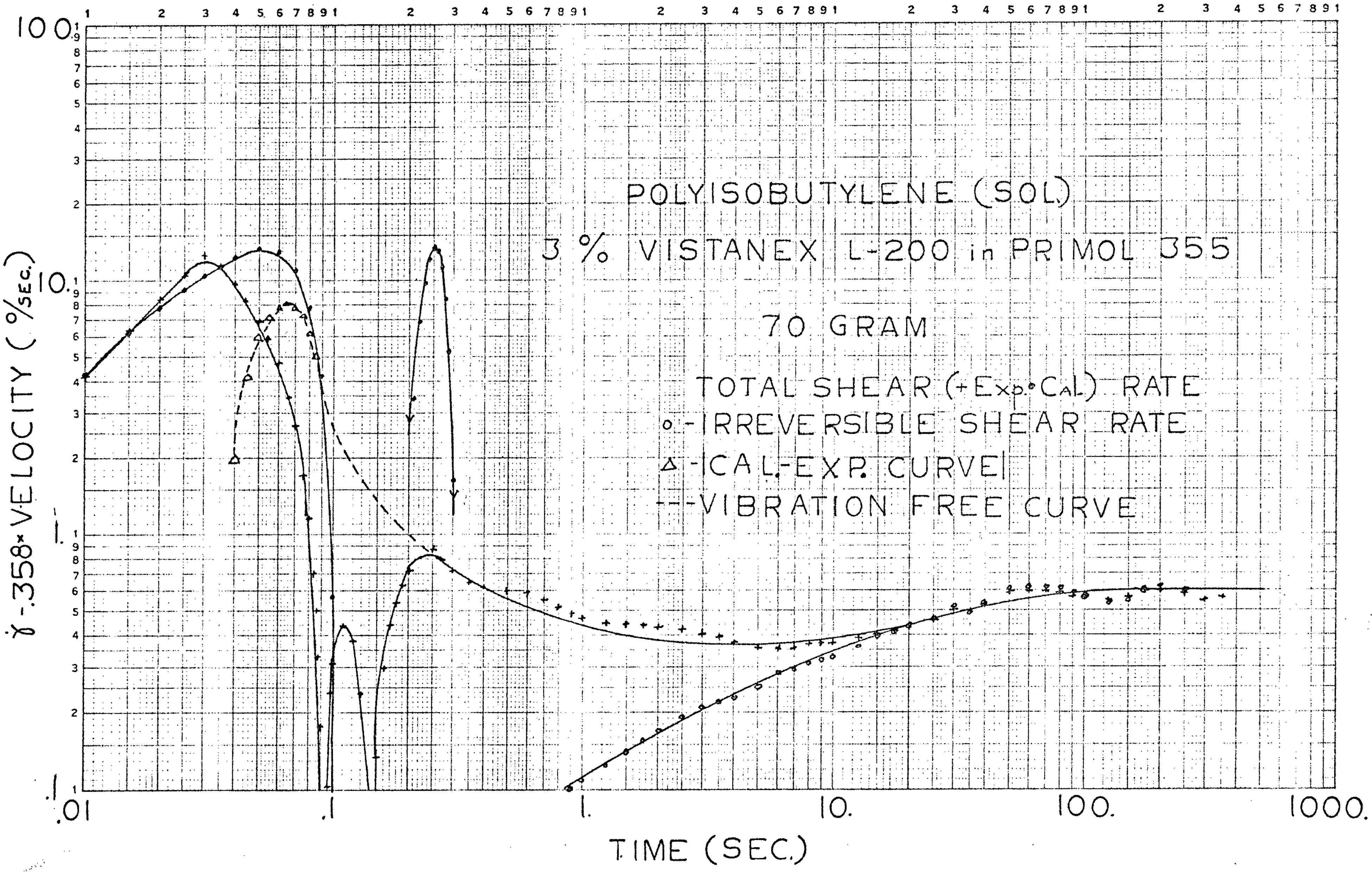

POLYISOBUTYLENE (SOL.)
3% VISTANEX L-200 in PRIMOL 355
5 GRAM
TOTAL SHEAR (+Exp. •Cal.) RATE
○ IRREVERSIBLE SHEAR RATE
γ̇-.358 × VELOCITY (%/sec.)
1
.1
.01
.001
.01
.1
1.
10.
100.
1000.
TIME (SEC)

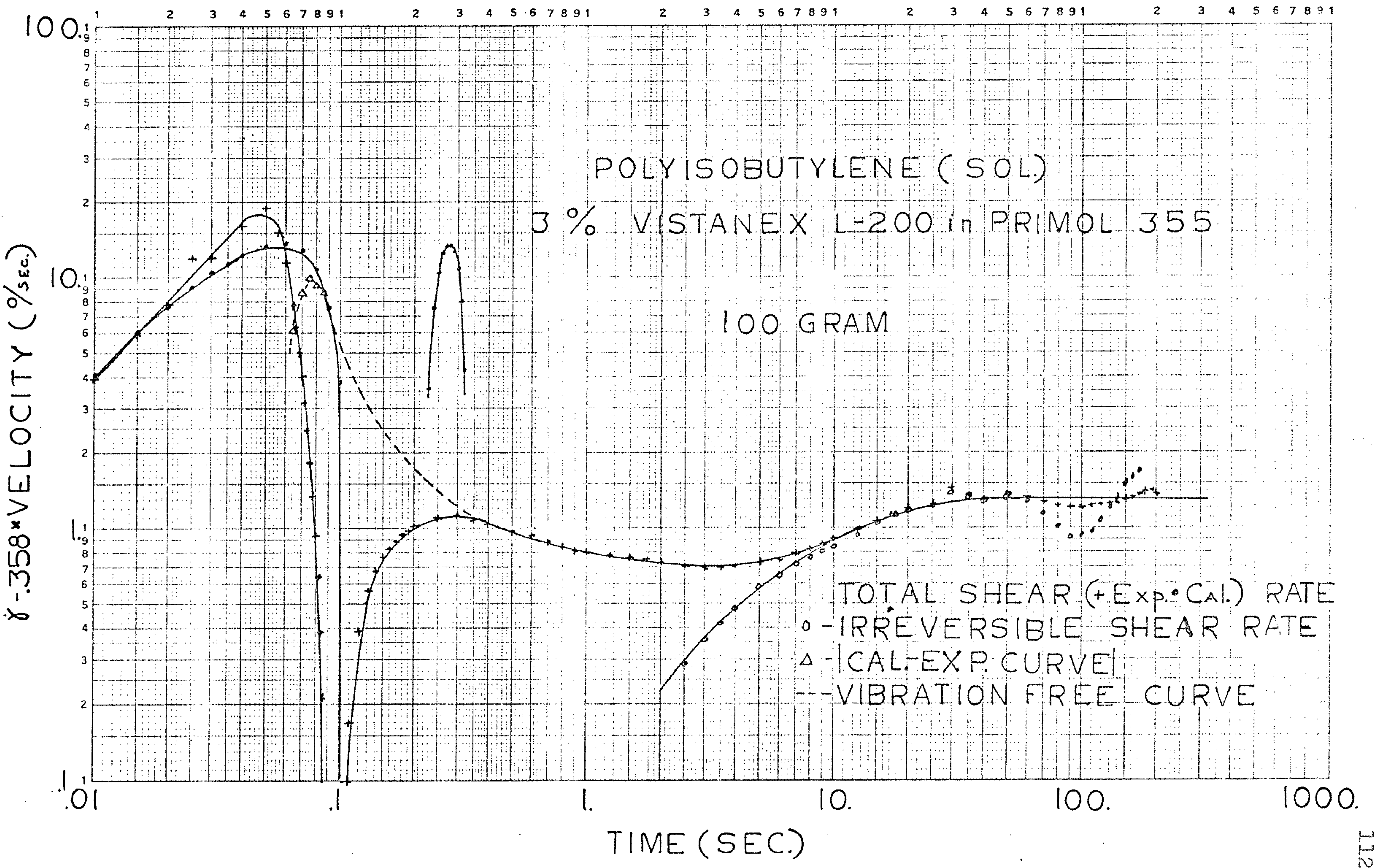

POLYISOBUTYLENE (SOL)
3% VISTANEX L-200 in PRIMOL 355
10 GRAM
TOTAL SHEAR (+Exp. • Cal.) RATE
o-IRREVERSIBLE SHEAR RATE
Δ-|CAL.-EXP. CURVE|
-- VIBRATION FREE CURVE
$\dot{\gamma}$ -.358 x VELOCITY (%/SEC.)
TIME (SEC.)
10.
1.
.1
.01
.01
.1
1.
10.
100.
1000.

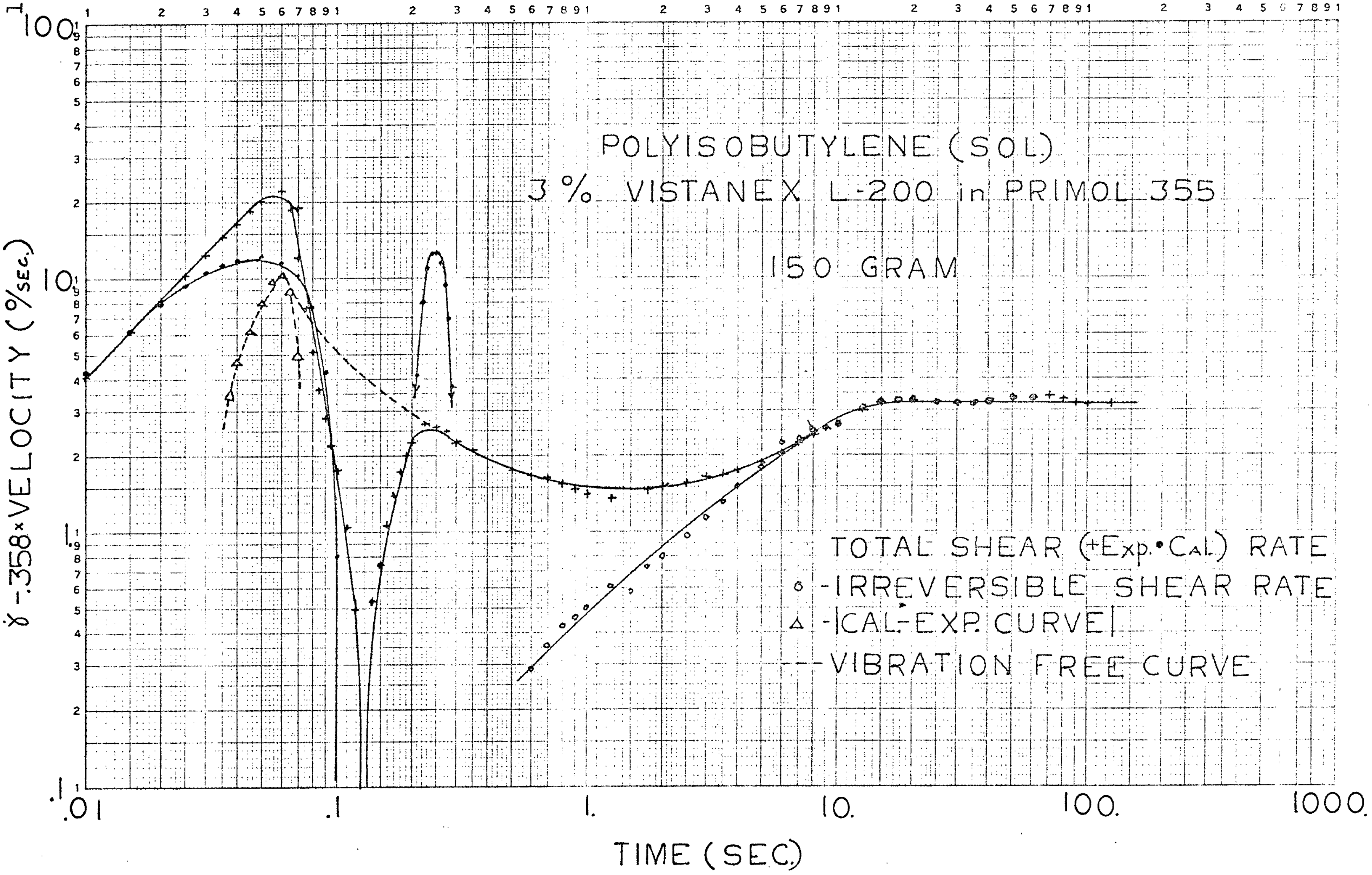

POLYISOBUTYLENE (SOL)
3% VISTANEX L-200 in PRIMOL 355
20 GRAM
TOTAL SHEAR (+ Exp. • Cal.) RATE
○ - IRREVERSIBLE SHEAR RATE
△ - |CAL.-EXP. CURVE|
--- VIBRATION FREE CURVE
γ̇ -.358 × VELOCITY (%/sec.)
10.
1.
.1
.01
.01
.1
1.
10.
100.
1000.
TIME (SEC)

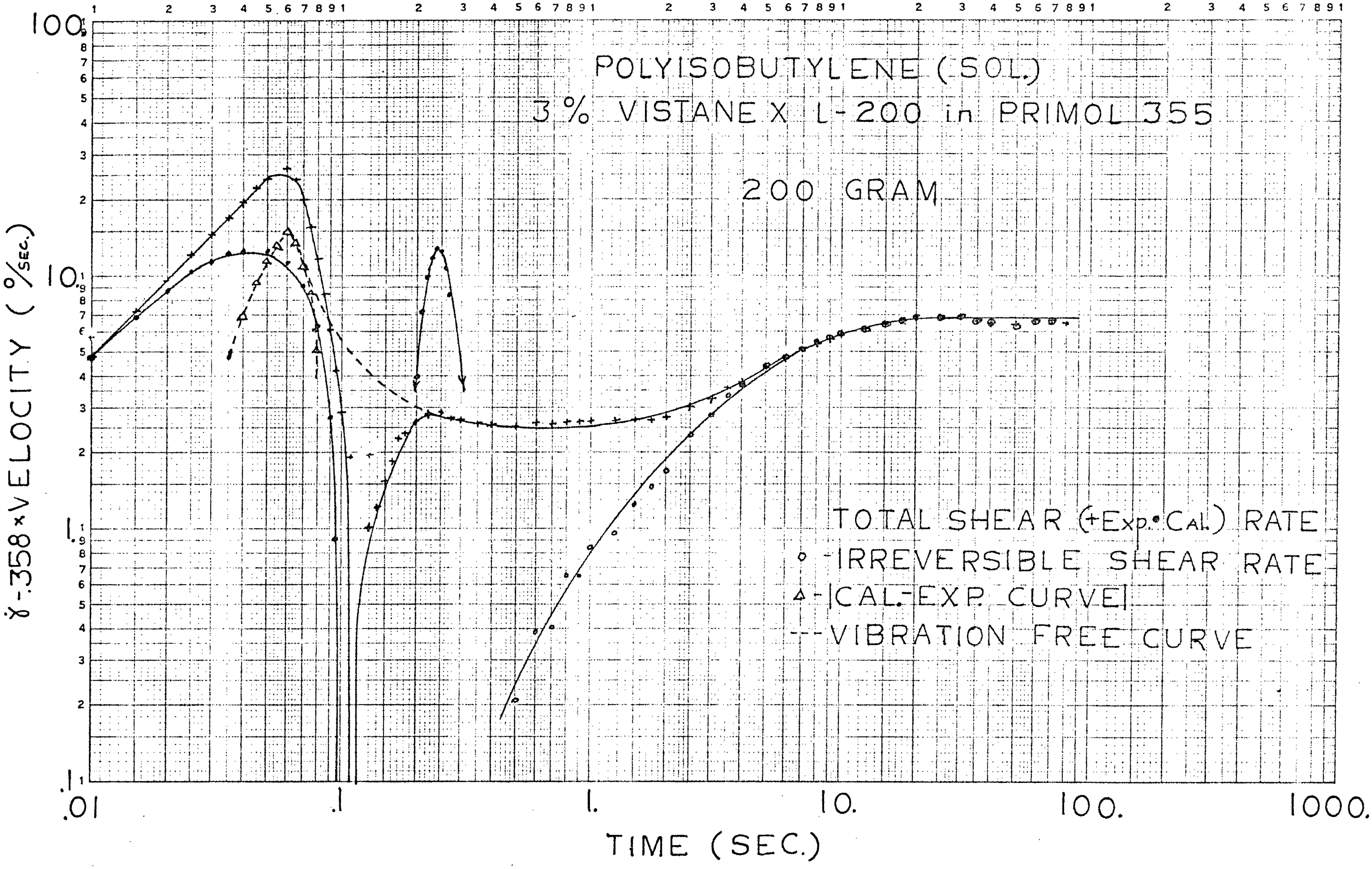

POLYISOBUTYLENE (SOL)
3% VISTANEX L-200 in PRIMOL 355
30 GRAM
TOTAL SHEAR (+ Exp. • CAL.) RATE
o- IRREVERSIBLE SHEAR RATE
Δ- |CAL.-EXP. CURVE|
--- VIBRATION FREE CURVE
$\dot{\gamma}$ -.358 × VELOCITY (°/sec.)
TIME (SEC)
10.
1.
.1
.01
.01
.1
1.
10.
100.
1000.

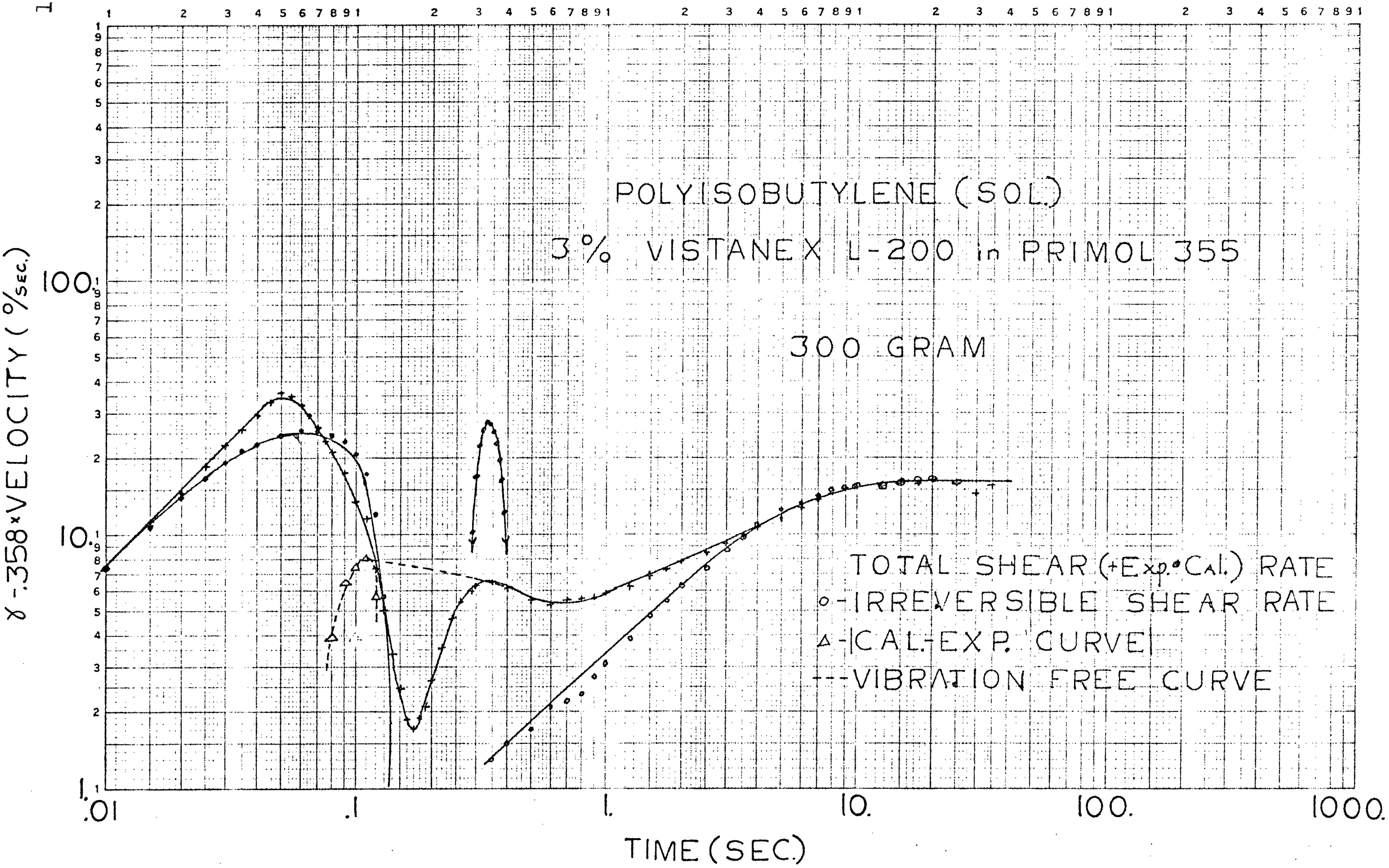

POLYISOBUTYLENE (SOL)
3% VISTANEX L-200 in PRIMOL 355
50 GRAM
TOTAL SHEAR (+Exp. ●Cal.) RATE
○-IRREVERSIBLE SHEAR RATE
△-|CAL.-EXP. CURVE|
---VIBRATION FREE CURVE
γ̇-.358×VELOCITY (%/sec.)
TIME (SEC.)
10.
1.
.1
.01
.01
.1
1.
10.
100.
1000.

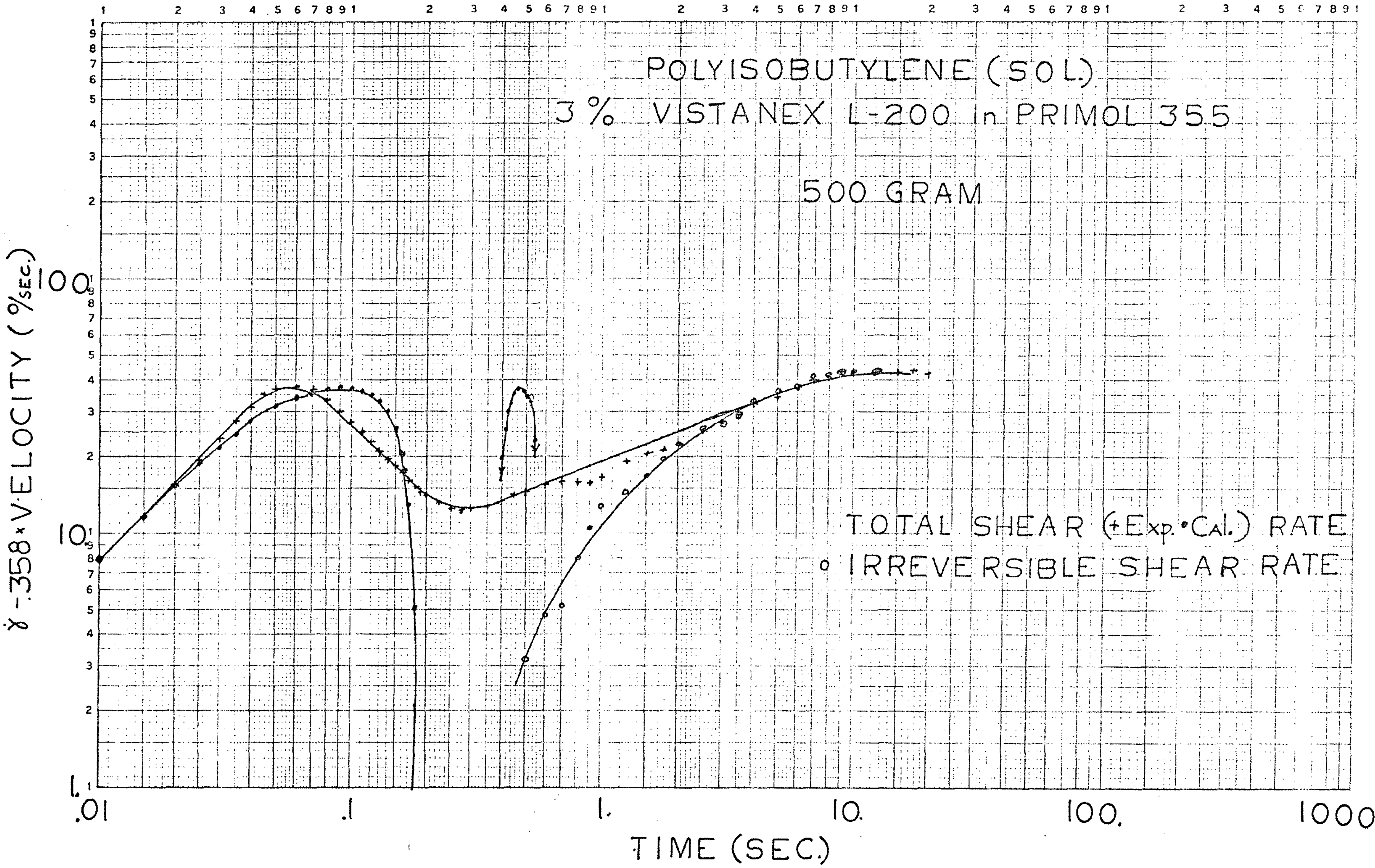

POLYISOBUTYLENE (SOL.)
3 % VISTANEX L-200 in PRIMOL 355
70 GRAM
TOTAL SHEAR (+Exp. ∘ CAL.) RATE
∘ - IRREVERSIBLE SHEAR RATE
△ - |CAL.-EXP. CURVE|
--- VIBRATION FREE CURVE
$\dot{\gamma}$ - .358 × VELOCITY (%/SEC.)
TIME (SEC.)
.01
.1
1.
10.
100.
1000.
100.
10.
1.
.1

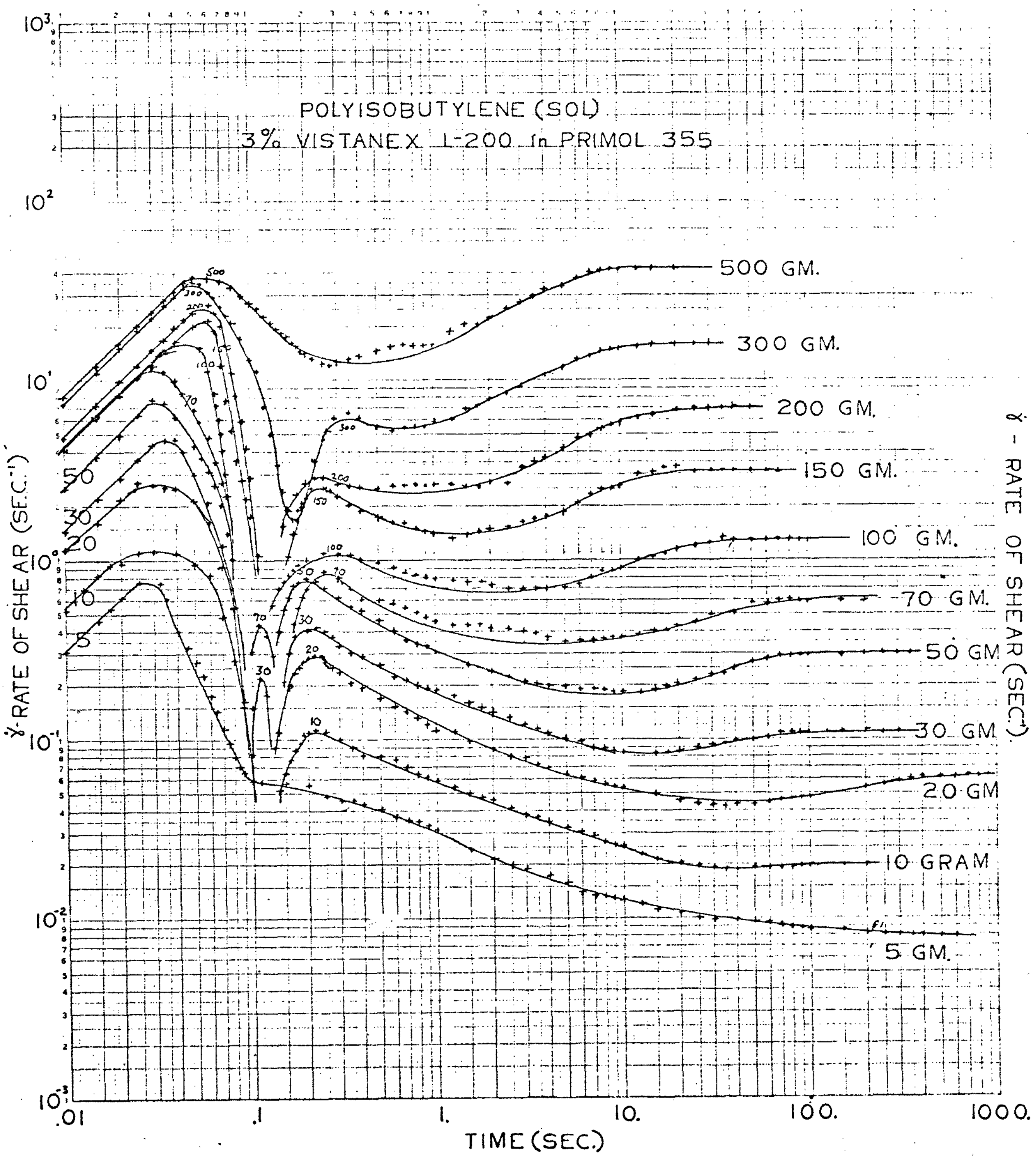

POLYISOBUTYLENE (SOL.)
3% VISTANEX L-200 in PRIMOL 355
100 GRAM
TOTAL SHEAR (+ Exp. • Cal.) RATE
o - IRREVERSIBLE SHEAR RATE
△ - |CAL.-EXP. CURVE|
--- VIBRATION FREE CURVE
γ̇ -.358 × VELOCITY (%/sec.)
100.
10.
1.
.1
.01
.1
1.
10.
100.
1000.
TIME (SEC.)


POLYISOBUTYLENE (SOL)
3% VISTANEX L-200 in PRIMOL 355
150 GRAM
TOTAL SHEAR (+Exp. •CAL.) RATE
o -IRREVERSIBLE SHEAR RATE
△ -|CAL-EXP. CURVE|
--- VIBRATION FREE CURVE
γ̇ -.358×VELOCITY (%/SEC.)
TIME (SEC.)
.01
.1
1.
10.
100.
1000.
.1
1.
10.
100.


POLYISOBUTYLENE (SOL.)
3% VISTANEX L-200 in PRIMOL 355
200 GRAM
TOTAL SHEAR (+Exp. • Cal.) RATE
○ - IRREVERSIBLE SHEAR RATE
△ - |CAL.-EXP. CURVE|
--- VIBRATION FREE CURVE
γ̇ -.358 × VELOCITY (%/sec.)
TIME (SEC.)
100.
10.
1.
.1
.01
.1
1.
10.
100.
1000.


POLYISOBUTYLENE (SOL)
3% VISTANEX L-200 in PRIMOL 355
300 GRAM
TOTAL SHEAR (+Exp. •Cal.) RATE
○-IRREVERSIBLE SHEAR RATE
△-|CAL.-EXP. CURVE|
---VIBRATION FREE CURVE
γ̇ -.358×VELOCITY (%/sec.)
1.
10.
100.
.01
.1
1.
10.
100.
1000.
TIME (SEC)


POLYISOBUTYLENE (SOL.)
3% VISTANEX L-200 in PRIMOL 355
500 GRAM
TOTAL SHEAR (+ Exp. • Cal.) RATE
o IRREVERSIBLE SHEAR RATE
$\dot{\gamma}$ - .358 × VELOCITY (%/SEC.)
1.
10.
100.
TIME (SEC.)
.01
.1
1.
10.
100.
1000.


POLYISOBUTYLENE (SOL)
3% VISTANEX L-200 in PRIMOL 355
500 GM.
300 GM.
200 GM.
150 GM.
100 GM.
70 GM.
50 GM
30 GM
20 GM
10 GRAM
5 GM.
50
30
20
10
5
$\dot{\gamma}$-RATE OF SHEAR (SEC.$^{-1}$)
$\dot{\gamma}$ - RATE OF SHEAR (SEC^{-1})
TIME (SEC.)
.01
.1
1.
10.
100.
1000.
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}

the increase in loading is larger. The rate of decrease in the time for constant shear rate to occur is much higher for the 4.5% PIB solution then for the 3% PIB solution. For the 3% solution, the time required for constant shear rate decreases from 500 secs. to 10 secs, for a load ranging from 5 GM to 500 GMS. In the 4.5% PIB solution, the time reauired for constant rate of shear decreases from 5000 secs to 90 secs, for a load ranging from 5 Gm to 200 GM. In other words, to decrease the time required for constant shear rate by fifty times starting with the 5 GM load, it would take a 200 Gm load to do it in the 4.5% PIB solution as opposed to a 500 GM load in the 3% PIB solution. From the above conclusions, it would imply that as the concentration of vistanex L-200 in Primol 355 increases, the time required for constant shear rate would also increase with each load used. The rate of decrease in the time required for constant shear rate would be much higher as the load is increased. For the 4.5% and 3% solutions, it is observed that for small loads, the shear rate decreases with time until equilibrium is reached. However, for high loads the shear rate decreases to a minimum and then increases to an equilibrium value.

As previously mentioned, the availability of the flow curves for the 3% Solution enables one the advantage of studying shear rates at low times. As can be observed from the graphs, that for loads ranging between 5 Gm and 500 GM, there appears the phenomena of zero shear rate. It is also evident that all the zero shear phenomena occurs in the time interval between .1 and .2 secs. The question arises whether the existance of the zero shear is a common phenomena inherent in the polymer solution or is it a factor influenced by outside disturbances. The results of this investigation leads to the following conclusion.

Flow Histories Free Of Angular Vibration

To determine a flow curve free from angular vibration, it was first surmised that the zero shear phenomena was the result of vibrations due to the string holding the load and to the polymer solution. The extent of the vibration due to either the string or the polymer solution was not understood. However, working on the premise that the zero shear rate is a result of vibration, a mathematical model, as outlined in the chapter before, was formulated in the area of complete elasticity. Substituting values of time into the equation, it was found that the calculated and experimental curves were manipulated to study their effect on the calculated curve, namely M_2, C_2 and C_1. The following conclusions were drawn. The rotational viscometer reacts with a higher inertial effect then was calculated. The spring constant for the polymer solution was much higher than previously calculated. The calculated curve is much more sensitive to changes in C_2 than C_1. Therefore the vibrations due to the polymer solution contribute largely to the vibrational effects of the viscometer. The spring constant for the polymer solution is a function of the amount of loading used. The following table shows the following conclusion based on coinciding the calculated curve with the experimental curve.

Wt. (GMS.)	ΔM_2(GMS)	M_2 Total (GMS)	C_2/C_1
5	0	0	1.
10	128.181	948.181	1.
20	0	0	1.
30	240.34	1060.345	1.3
50	153.3	973.301	1.5
70	0	0	.8
100	448.83	1268.83	1.1
150	958.049	1778.049	1.
200	1322.22	2142.22	2.4
300	1275.45	2095.45	1.2
500	2444.286	3264.286	-

One very important result of the calculated curve is that it does predict the zero shear rate, and that it is the direct result due to the vibration of the string and more significantly to the vibration of the polymer solution. There is initial vibration for the 5 GM load and 500 GM loads, but it is quickly eliminated before any significant effect to the curve can take place. Vibration does exist for very low times, but not long enough to obtain zero shear rate. For the 5 GM load, there is not enough of a load to cause prolonged vibrational effect. For the 500 GM load, the vibrational effect is quickly damped out before zero shear can occur.

The next step is to determine how the flow curves exist free of vibrational effects. The absolute difference between the experimental and calculated curve was determined and plotted before the zero shear rate. It is then extrapolated into the shear rate curve as indicated by the dash lines on the graphs. The dash lines up to the peak in the difference curve is than intergrated by the least square method using a computer program. The results are then plotted on linear graph paper to extrapolate it further to time zero. The results are then replotted on the 3% flow displacement curves. The solid dots represents that part of the curve done by intergration and the triangles represents the curve extrapolated to zero time on linear graph paper.

The increase in m_2 expressed as m_2 is not understood. It can only be explained as a property inherent with the PIB solution. The experimental m_2 when compared with Primol 355 and air agreed with calculated m_2.

CONCLUSIONS

The following conclusions were drawn from this investigation:

1. The rotational viscometer offers an invaluable too for determining the transient properties of polymer solutions. It can be used to measure viscosity at a variety of temperatures. Using the constant stress method, it can be used to study shear rate and irreversible shear rate growth as a function of time and shear stress. It can be used to measure the amount of elastic property as a function of time and shear stress in terms of recoil measurements. It can also separate the elastic property from the viscous property by its flow curves. The rotational viscometer also determines the time for attaining constant shear rate as a function of shear stress used.

2. For the 3% and 4 ½% PIB solution, it was shown that at short times the polymer solution was completely elastic, behaving as a hookean solid.

3. The attainment of steady state flow is characterized by an equilibrium in recoverable shear and an equilibrium of the total and irreversible shear

rate. However, all these do not occur at the same time. In most cases, shear rate equilibrium occurs first followed by constant recoverable shear equilibrium.

4. For the 4 ½% PIB solution, the time required for separation between elastic and viscous properties decreases as shear stress increases and to some extent for the 3% PIB solution.

5. For both the 3% and 4 ½% PIB solution, a maximum is observed in recoverable strain versus time at various shear stresses. The time required to attain these maxima decreases as the shear stress is increased and becomes more pronounced. The occurrence of these maxima is not completely understood. If one ventures to explain this phenomena, the following explanation is offered. The definition of a polymer is that it is a long chain consisting of many small units of monomers. The polymer chain can be made analogous to a long string. A polymer solution would be made up of millions of polymer chains. Since the polymer chains are always in motion, it is only conceivable that the polymer chains or strings tend to entangle with each other.

When a constant stress load is suddenly applied to the polymer solution, the individual molecule chain starts to stretch and disentangle with each other. During the beginning of the application of stress load, it is easy for the polymer chain to stretch and disentangle initially. After a short time elapses, it becomes more difficult for the polymer chain to stretch and disentangle from one another. The period is related to the maxima which occurs in the recoverable shear curve. Once the most difficult part of disentanglement is accomplished, the recoverable shear will then decrease to an equilibrium valve. This maxima does not exist for the 5 GM, because the process of disentanglement is slow and undetectable.

6. The zero shear phenomena is a by-product due to the vibrations of the string and polymer solution inherent with the operations of the viscometer. The vibration due to the polymer solution are more significant then the vibrations due to the string. The vibrational contribution of the polymer solution can be traced to the elastic property of the fluid. Further study of interest would be the possibility of a vibration-free rotational viscometer.

7. For the 3% and 4 ½% PIB solution, the maximum shear strain occurs within the area where total shear rate and irreversible shear rate converges together. This can be explained that in order for steady flow to occur, it must first pass the most difficult part of disentanglement or alignment of molecules. Once this has been accomplished steady viscous flow controls.

8. The rate of increase of irreversible shear rate increases with increase in shear stress for both solutions. As a result, the increase in shear stress has the tendency of damping out the elastic property of the solution.

9. The attainment of steady state is characterized by the merging of the constant total and irreversible shear rates. The time required for attainment of steady flow decreases with increase in shear stress.

10. The time lag occurring between total and irreversible shear rate can only be explained by the occurrance of complete elasticity at low times. From this time lag one can see that the maximum in total shear rate growth is completely due to the elastic property of the solution.

11. Shear rate growth as a function of time and shear stress occurs in the following manner. For low shear stresses, total shear rate growth approaches a maximum and then decreases to an equilibrium value converging with the irreversible shear rate. As shear stress increases, total shear rate growth undershoots as well as overshoots the equilibrium shear rate. The total shear rate growth reaches a maximum in the area of complete elasticity, then decreases due to the appearance of the irreversible shear rate. Total shear rate decreases to a minimum due to the appearance of the irreversible shear rate. The undershoot is accompanied by an increase in irreversible shear rate. This minimum can be classified as the "viscous strength" of the solution. A compromise between viscous and elastic property is attained, and the equilibrium total shear rate is thus situated between maximum and minimum total shear rate. The fact that the total shear rate is situated closer to the minimum total shear rate can be understood to mean that the viscous property of the polymer solution controls or predominates.

12. "Viscous Strength" minima in the total shear rate occurs before onset of maximum recoverable shear strain.

13. The amount of undershoot occurring in recoverable strain is very small and often negligible for both the 3% and 4 ½% PIB solution.

14. The result of this investigation also disproves L. J. Zapas' conclusion that the shear displacement corresponding to the maxima in recoverable shear is the same for different shear stresses.

15. For the 4 ½% PIB solution, it was noted that for small shear stresses equilibrium shear rate took over an hour to occur. Even when measuring recoverable shear, it sometimes took hours before reaching a finite value regardless of shear stress used.

16. The increase in the theoretical equivalent mass of the viscometer drum is up to now unexplainable. The increase in shear inertia can only be explained as a property inherent with the polyisobutylene solution. In experiments involving air or Primol 355, the values obtained complied with the theoretical equivalent mass. $\Delta m_2 >> m_2 >> m_1$

RECOMMENDATIONS

1. The flanges of the rotational viscometer which is submerged under a constant water bath should be covered with water insoluable putty to prevent water leakage.

2. A stronger stop-load clamp with a high frictional coating to prevent slippage when using higher loads and increase the accuracy of data measurements.

3. A device that would rigidly clamp the rotational viscometer in place that would prevent rotational slippage.

4. Insulated covering over the constant water temperature bath will prevent water loss, so that the equilibrium temperature will not be offset by replacing the water loss.

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