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A STUDY OF DEGRADATION IN THE PUMPING OF DILUTE POLYMER SOLUTIONS

BY

I-CHUNG CHANG, 1936

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A

THESIS

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I. INTRODUCTION

In the course of an investigation of the turbulent flow properties of dilute high polymer solutions in organic solvents, a number of supplementary investigations were required. These were:

1. Determination of the molecular weights of a number of polymers by intrinsic viscosity measurements.

2. Determination of the effect of pumping on the degradation of high polymers in dilute solutions. This included development of a method for estimating the concentration of dilute polymer solutions.

3. Determination of the effects of density, viscosity and non-Newtonian behavior on the calibration of turbine flow meters.

II. REVIEW OF LITERATURE

The review of literature will be confined to the following items: (1) intrinsic viscosity, (2) degradation, and (3) turbine flow meters.

1. Intrinsic Viscosity.

The determination of polymer molecular weights from intrinsic viscosity measurements of a number of dilute high polymer solutions constitutes a major portion of the experimental effort in this study. Therefore, a review of intrinsic viscosity-molecular weight relationships is necessary.

The following terms are used in describing the viscosity of dilute polymer systems:

η_{rel} = the relative viscosity $= \eta_{solution} / \eta_{solvent}$

η_{sp} = the specific viscosity = $\eta_{rel} - 1$

C = concentration, normally in grams/deciliter

η_{sp}/C = viscosity number or reduced viscosity.

By definition, the ratio η_{sp}/C at infinite dilution is termed the intrinsic viscosity or so-called limiting viscosity number and is designated by the symbol $[\eta]$. At infinite dilution, $(\ln \eta_{rel})/C$ is identical with the intrinsic viscosity:

$$[\eta] = (\eta_{sp}/C)_{C\to 0}$$

$$= \left(\frac{\ln \eta_{rel}}{C}\right)_{C\to 0}$$

Arrhenius (1) gave a simple equation for the viscosity of a polymer solution:

$$\frac{\ln \eta_{rel}}{C} = k_A \qquad (1)$$

where k_A is a specific constant for a particular sample of polymer solute dissolved in a particular solvent.

A much more recent equation proposed by Martin (2) is:

$$\ln \frac{\eta_{sp}}{C} = \ln [\eta] + k' [\eta] C \qquad (2)$$

Huggins (3) has shown that equations (1) and (2) reduce to the following in dilute solution:

$$\eta_{sp}/C = [\eta] + k' [\eta]^2 C \qquad (3)$$

where k' is a constant characteristic of the given solvent-polymer pair and independent of the molecular weight of the latter.

The Huggins equation is widely used at low concentrations. According to the equation, a plot of η_{sp}/C vs. C gives a straight line in dilute solution. The values of

η_{sp}/C are extrapolated to infinite dilution to obtain the intrinsic viscosity.

The alternate definition of the intrinsic viscosity leads to the equation: (4)

$$(\ln \eta_{rel})/C = [\eta] - k'' [\eta]^2 C \qquad (4)$$

where $k' + k'' = 1/2$.

At very low concentration, anomalous viscosity behavior of some polymer solutions has been found in the form of deviations from the linear η_{sp}/C vs. C relationship (5). Various explanations have been suggested, for example:

1. the disentanglement of polymer chains, that is, the achievement of complete solution at very low concentrations which is not attained at high concentration (6, 7).

2. an expansion of the polymer coils with dilution may play a significant role in the anomaly in the viscosity behavior of polymer solutions at very low concentrations (below 0.1 gm/dl) (8, 9, 10).

3. an anomalous density effect also occurs in very dilute solutions. This suggests that the anomalous viscosity behavior might be closely connected with the configuration of the polymer chain in very dilute solution (11, 12).

4. the adsorption of polymer on the walls of the viscometer capillary resulting in a reduction of the true concentration of solution and in the effective radius of the capillary (13, 14).

In estimating intrinsic viscosities, viscosity data extrapolated from concentrations above this anomalous region give consistent results.

Recently, several one-point methods of intrinsic viscosity from one viscosity measurement on a solution of known concentration have been reported (15, 16, 17).

The following equations have been proposed:

$$[\eta] = \frac{\eta_{sp} + \gamma \ln \eta_{rel}}{(1 + \gamma)\, C} \qquad (5)^{15}$$

$$[\eta] = \frac{\sqrt{2}}{C} \sqrt{\eta_{sp} - \ln \eta_{rel}} \qquad (6)^{16}$$

where $\gamma = k'/k''$.

Comparison of values of intrinsic viscosity estimated from these equations with extrapolated values showed deviations of only ± 4 per cent for polystyrene solutions in toluene (15, 16).

Staudinger (18, 19, 20, 21) working with linear polymers of relatively low molecular weight, developed the following empirical relationship:

$$\eta_{sp}/C = K_s M \qquad (7)$$

where K_s is a specific constant for a particular polymer and solvent.

Mark (22, 23) proposed the form

$$[\eta] = K_m M^a \tag{8}$$

where K_m and a are two characteristic constants.

Since most high polymers are not homogeneous, the nature of the "average" molecular weight yielded by the equation is of considerable importance. Flory (24) has shown that, more generally:

$$[\eta] = K_F \bar{M}_v^a \tag{9}$$

where $\bar{M}_v$ is the average molecular weight based upon viscosity measurement.

A double logarithmic plot of intrinsic viscosity vs. molecular weight for a given solvent and temperature is linear, in accordance with equations (8) and (9). The constants, K and a, are determined from this log-log plot. Measurement of the intrinsic viscosity of a linear polymer is widely used as the simplest means of characterizing its molecular weight.

2. Degradation.

It is well known that the unique long chain structures of polymer molecules suffer breakdown due to shear forces on grinding, milling, mastication, shaking, beating, high speed stirring, turbulent flow or ultrasonic irradiation.

Staudinger, Heuer, and Dreher (25, 26) milled polystyrene in a ball mill. They found that, given identical circumstances, polymer molecules of different initial chain lengths are degraded to very similar final chain lengths. Hess, Steurer and Fromm (27) reported that appreciable degradation took place by milling cellulose or polystyrene in a swing mill (Schwingmuhle) (the main effect is due to impact of the balls, friction being negligible). The primary process, under the conditions of their experiments, was a purely mechanical one.

Morris and Schnurmann (28) reported that with an apparatus giving rates of shear of the order of 10^5 $\sec^{-1}$ under laminar flow conditions, long-chain molecules of molecular weight above 100,000 (the nature of the polymer was not indicated by the author) were broken down.

Sonntag and Jenkel (29) found that when a polymethyl methacrylate solution in toluene, containing quartz powder as adsorbent, was shaken or stirred, an irreversible decrease in specific viscosity took place.

Goodman (30) studied the degradation of polyisobutylene (Vistanex B-100) having an $\overline{M}_v$ of 1,740,000 in cetane (n-hexadecane) solutions (3 - 20 weight per cent). Degradation was produced by mechanical shearing action in a McKee consistometer which is essentially a capillary viscometer in which a single sample can be repeatedly passed through the capillary at rates of shear of 50,400, 33,000, 25,100, and 14,300 sec^{-1}. Goodman describes degradation as resulting from focalization of mechanical energy by means of molecular entanglements present in concentrated solution. If sufficient energy is concentrated in this manner into a given bond, the bond breaks, resulting in a decrease in polymer molecular weight. His studies indicated that for a particular solution at constant temperature, the logarithm of the initial rate constant for the degradation is a linear function of the reciprocal rate of energy application. The 3 weight per cent solution had a much greater negative slope than for higher concentrations. This indicated a decreased efficiency for the focalizing of mechanical energy into breaking the polymer molecules in less concentrated solutions.

Bestul (31) observed the shear degradation of polyisobutylene solutions in cetane. The polymers investigated were six unfractioned commercial Vistanex polyisobutylene samples. (Vistanex B-40, 60, 80, 100, 120, and 140). The degradation was investigated as a function of concentration in the range of 5 to 20 weight per cent at nominal rates of shear from 9,000 to 66,000 sec^{-1}, of temperature in the range of 20 to 80°C, and of initial viscosity average molecular weights from 490,000 to 2,520,000. A decrease of shearing load with successive passes of the solution through the shearing capillary was taken as an indication of the occurrence of degradation. The extent of degradation decreased with increasing temperature and increased with increasing shear rate. The final molecular weights were lower for solutions of lower initial molecular weight.

Bestul and Belcher (32) also investigated the degradation of a wider range of molecular weights of polyisobutylene solutions in dichlorobenzene on shearing. Vistanex solutions (5, 10, and 15 weight per cent Vistanex of molecular weights ranging from 40,000 to 2,300,000 $\bar{M}_v$) in dichlorobenzene were forced through a capillary with a nominal shear rate of 65,000 sec^{-1} at 37.8°C. An appreciable decrease in molecular weight took place, when the molecular weight was greater than 500,000. Very little viscosity decrease was observed for polymers having molecular weights below 500,000.

Bestul (33) also sheared solutions of 9.4 weight per cent Vistanex B-100 polyisobutene (1,740,000 $\bar{M}_v$) in n-hexadecane in the McKee consistometer, initially at rates of shear of 66,000 and 33,000 sec^{-1}, respectively, and subsequently interchanging the rates. In the initial shearing each solution viscosity levelled off. Additional shear at 33,000 sec^{-1} of the solution sheared at 66,000 sec^{-1} had no effect. However, the solution which had been sheared at 33,000 $\sec^{-1}$ showed an additional viscosity decrease when it was sheared at 66,000 $\sec^{-1}$ before ultimately levelling off.

Thus, a critical molecular weight existed, dependent on the severity of shearing, above which individual molecules in sufficient concentration suffered degradation and below which shear degradation did not occur. For fractions of previously degraded polymer, the reported molecular weight was just under two million. This limit previously was found to be somewhat below one million for unfractionated, undegraded polymer. The concentrations of very high molecular weight polymer may be the same in both these cases. Similarly shaped degradation curves were also observed for 10 weight per cent solution of polystyrene (an unfractionated sample about 5 million $\bar{M}_v$) and 5 weight per cent solution of polymethyl methacrylate (a top fraction of about 5 million $\bar{M}_v$) both in α-methylnaphthalene (33). From these results, Bestul suggested that the degradation observed for the three different chemical compositions occurs by the same common general mechanism described earlier.

Literature reports of polyisobutene shear degradation (32, 33, 34, 35, 36) have been quite generally limited to bulk polymer and solution conditions of MV greater than about 15,000 to 17,000, where M is $\bar{M}_v$ and V is the polymer volume fraction. For higher polymer molecular weight and concentration, that is, above the critical condition $(MV)_c$, a 3.4 power dependence of viscosity on molecular weight has been found (34, 35, 36, 37, 38, 39). In this region, substances show both pronounced non-Newtonian flow characteristics and flow shear degradation (34). Nearly all the reported data are for concentrations above 3 per cent and most of it above 10 per cent where polymer molecules are entangled. Little data are available at low concentrations where most polymer molecules are effectively separated.

Merrill, Mickley, and Ram (40) studied the degradation of several high polymers in solution in two different types of experiments.

In the first experiment a variety of polymer solutions were splashed vigorously against the walls of a flask by a reciprocating motion. Concentrations ranged from 0.05 to 0.21 gm/dl (except for one solution) and most viscosities were in the low viscosity range, 1 to 2 centipoise, to promote splashing. In the second experiment, more viscous solutions of several polyisobutylene polymers in decalin were passed through a coaxial cylinder viscometer in laminar flow at a shear rate in the annulus of 96,000 $\sec^{-1}$. Here concentrations ranged from 0.1 to 2.0 gm/dl and viscosities from 4 to 27 centipoises.

Based on the results of the splashing experiment, they claimed that for polyisobutylene in toluene and cyclohexane, polystyrene in toluene and polymethyl methacrylate in ethylene dichloride no significant degradation occurred if the degree of polymerization was 40,000 or less. This is equivalent to molecular weights of about 2.2×10^6 for polyisobutylene and about 4 million for the other two polymers. For polymers with higher degrees of polymerization, the fraction of residual molecular weight remaining after comparable periods of agitation decreased with increase in molecular weight.

From the second experiment they concluded that one pass of the more viscous decalin solutions through the viscometer was equivalent to 33 hours of splashing of toluene solutions of about the same concentrations.

3. Turbine Flow Meters.

Turbine flow transducers are in-line, volumetric fluid metering instruments used commonly for the precise measurements of flow rates of liquids and gases over a wide range of flow rates. Various turbine flow meters have been designed commercially for these purposes.

Generally, the turbine-type flow transducer consists of only four basic components: (i) transducer housing, (ii) low-mass rotor, (iii) support assembly, and (iv) magnetic pick-up.

The bladed rotor, supported by a single journal bearing, revolves at a rate proportional to the velocity of the fluid passing through the transducer housing (41, 42). A magnetic pick-up, mounted on the housing, generates an electrical pulse each time a blade tip passes it. The transducer pick-up generates a low voltage sine wave at a frequency which is exactly proportional to fluid flow rate. These pulses can be amplified and shaped to make them compatible with the requirements of all types of digital and analog readout devices. The advantages of the turbine type flow meter are simplicity, small size, accuracy, fast response, adaptability to remote indication and telemetering (41).

Hochreiter (43) applied the principles of dimensional analysis to a kinetic flow meter of the turbine type and found a dimensionless correlation of coefficients for the turbine type flow meters. He gave the result as:

$$Q/n\ D^3 = \Phi\ (n\ D^3/\nu) \tag{10}$$

where Q = volumetric flow rate,

n = rotor angular velocity,

D = meter bore diameter,

ν = fluid kinematic viscosity.

Shafer (41) commented that the relation, equation (10), is useful for evaluating the general characteristics of a given meter, especially for a determination of viscosity sensitivity.

For constant diameter, from equation (10), he gave:

$$f/Q = \Phi_1 (f/\nu) \tag{11}$$

where f = frequency,

f/Q = calibration factor or pulses per unit volume.

A plot of f/Q vs. f/ν would give a smooth curve.

For consideration of the performance characteristics of turbine flow meters, Shafer mentioned that one of the characteristics of interest is the calibration factor, which is expressed in electrical pulses generated per unit volume of throughput and is a function of flow rate and viscosity, in accordance with equation (11). In so-called linear operation the calibration factor remains constant within stated limits. The range of linear operation, hence constant calibration factor, depends upon the design and size of meter, and the liquid viscosity. Rotational flow or swirls upstream of the meter will change the angle of attack between the fluid and the turbine blades, with a resultant effect upon turbine speed at a constant flow rate. Some swirls are nearly always present in conventional flow systems. The influence of swirl increases with decrease in flow rate. This will cause variations in the calibration factor in this flow range. Straightening vanes or a form of honeycomb are required for effective swirl elimination.

Shafer shows precise calibration data in which the calibration factor of a 1/2-inch meter is constant to ± 0.5 per cent through an f/ν range of 5 : 1 and in a 2-inch meter is constant through a range of 50 : 1. The actual extent of viscosity influence and of linearity for any particular turbine meter can be determined only by calibration using liquids of different viscosities within the range of interest. Shafer stated that lower rates, small meter sizes, and higher viscosities all tend to decrease the range of linear operation.

III. EXPERIMENTAL

There were three objectives for this investigation. The first objective was to measure accurately the intrinsic viscosities of some linear high polymers. From published intrinsic viscosity-molecular weight relationships, the molecular weights of these polymers were estimated. Based on their molecular weights, some of the polymers were then selected to prepare dilute solutions for the drag reduction investigation. The second objective was to find the effects of degradation in the pumping system. By measuring the intrinsic viscosities of polymer solutions, after different periods of turbulent flow, the effect of pumping on polymer degradation was found. The third objective was to calibrate the turbine-type flow meters used in the pumping system and to study the effect of flow rate and viscosity on the calibration factor.

A. Materials

The list of the materials used in this investigation and their specifications are given in Appendix A.

B. Apparatus

1. Viscosity Measurements.

a. Viscometer. All viscosity measurements were made using a Ubbelohde suspended-level viscometer (44, 45, 46, 47, 48, 49). This viscometer had 0.4 mm diameter capillary tube and an efflux time for pure distilled water at 30°C of 610 seconds. It was calibrated for the kinetic energy correction term (50, 51, 52).

Since the flow time obtained with a Ubbelohde suspended-level viscometer does not depend on the volume of liquid in the instrument, the viscometer can be modified by introducing a large bulb for diluting the solution. This enables the operator to perform intrinsic viscosity determinations without cleaning the viscometer after each concentration. The reservoir of the viscometer used held approximately 100 ml of liquid without disturbing the suspended level. A schematic diagram of the Ubbelohde suspended-level viscometer is shown in Figure 1, page 18.

b. Viscometer Mounting. The viscometer was mounted parallel to a brass tube (1/2-inch O.D.) by means of two plexiglass holders one just above the dilution bulb and the other near the top of the wide entrance Ubbelohde tube. Each plexiglass holder consisted of a square horizontal bar three inches long with two parallel vertical holes which just fitted the viscometer tube and the brass tube. Each bar was slit vertically in half. Each set of the slit bars was screwed tightly together by means of a horizontal screw at the center of the side faces to hold the brass tube and the

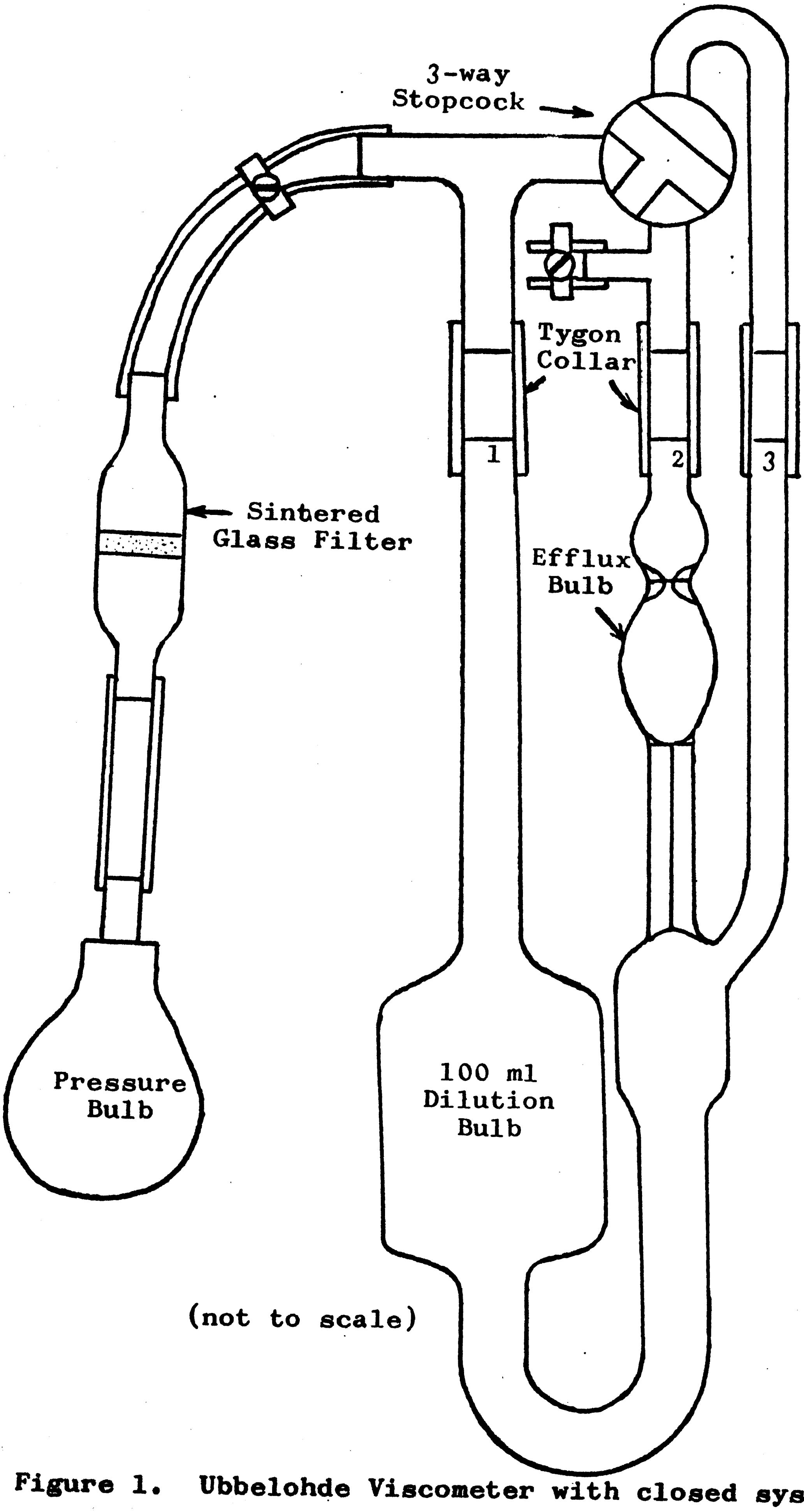


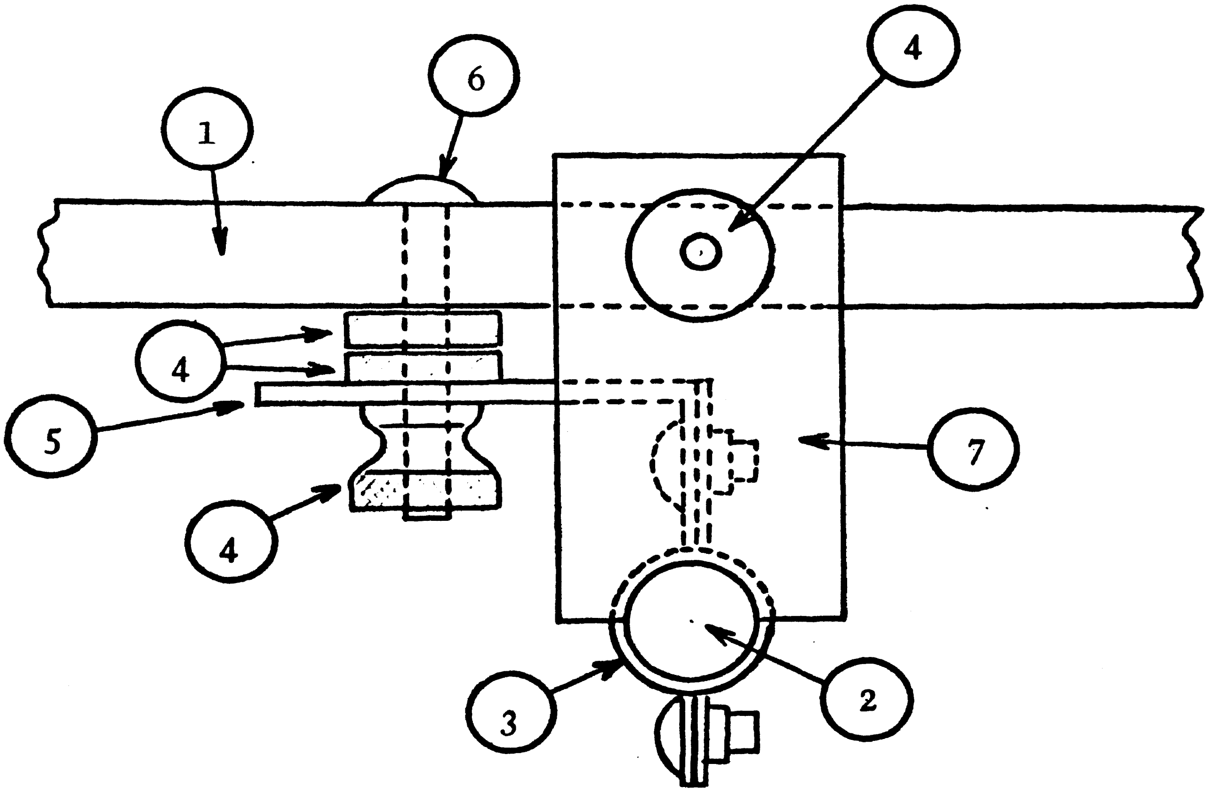
Figure 1. Ubbelohde Viscometer with closed system.

viscometer. An additional screw was used for each holder to fix the plexiglass bar firmly to the brass tube. The brass tube extended about one foot above the viscometer. This allowed the viscometer to be mounted and immersed to a sufficient level in the constant temperature water bath. For mixing after dilution and for cleaning, the viscometer had to be removed from the water bath quite often.

To ensure that the calibration of the viscometer would be accurate at all the times the position of the viscometer had to be reproducible. For this reason it was mounted in the following manner (see Figure 2, page 20): Two pairs of metal plates 1/2-inch wide and 1 1/2-inch long were screwed tightly together to fit over the brass tube. The end of one plate was bent at 90° and connected to a 1 1/2-inch extension. A small hole 3/16-inch in diameter was drilled in the center of this extension. One set was fixed on the brass tube one inch above the upper plexiglass holder and the other one was fixed seven inches above.

A framework was built up around the constant temperature water bath for holding the viscometer and the thermometers. Two 5/8-inch O.D. horizontal support bars each two feet long were clamped seven inches apart on the frame work. A male screw (3/16-inch in diameter) two inches long was screwed horizontally through the middle of each support bar.

Top View



1-horizontal support bar (5/8" O.D.)
2-vertical brass tube (1/2" O.D.)
3-metal plate (1/2" x 1 1/2")
4-circular nuts
5-extension plate (1/2" x 1 1/2")
6-male screw (3/16" O.D., 2" long)
7-vertical positioning plate (1" x 3")

Figure 2. Viscometer Mounting and Positioning Units.

These two screws just fit the holes in the extension plates and were tightened by a circular nut.

For holding the viscometer in a vertical position, two metal plates one inch wide and three inches long were mounted horizontally on each of the two horizontal support bars (see Figure 2, page 20). A half circle was cut out which just fitted the outside diameter of the extended part of the vertical brass tube and positioned the viscometer. The positions of these two plates could be varied horizontally until the capillary tube was perfectly vertical and then they were permanently tightened into place.

In order to ensure that the viscometer was in a vertical position, a small plumb bob consisting of a one centimeter length of solder wire and a piece of silk thread was used. The thread with the plumb bob was moved close to the capillary tube of the viscometer and the perpendicularity of the capillary tube was checked by visual examination.

c. Closed System. In using a viscometer of the Ubbelohde type it is necessary to apply either suction or pressure to transfer the test liquid to the upper reservoir before making a measurement. For precise work, especially with concentration-sensitive systems, such as solutions of high polymers in liquids of high volatility, it is essential to avoid a change of concentration by loss of solvent vapor. A closed system was used in this work, which was similar to that suggested by McElwain (53). The arrangement can be seen in Figure 1, page 18.

A three-way stopcock was held five inches above the viscometer by means of an extension clamp with an angular clamp to the framework. Two small size glass tees and one glass tube were connected to the three-way stopcock and the viscometer by fitting them with suitable short lengths of tygon tubing. These connections gave an entirely closed system which could be quickly and easily connected to the viscometer.

A rubber pump bulb was used to force the liquid into the efflux bulb. The exit air was filtered through a medium-porosity sintered glass filter which was connected between the rubber bulb and the viscometer through tygon tubing.

d. Constant Temperature Water Bath. The viscosity of polymer solutions is very sensitive to change in temperature. Therefore, for precise viscosity measurements, temperature should be maintained within plus or minus 0.01°C of the desired test temperature.

For this investigation, the temperature of a water bath was held constant within plus or minus 0.01°C by means of a thermo-regulator, an electronic relay, and mercury control switches. The bath consisted of a pyrex glass cylindrical jar 15 inches high and 16 inches in diameter which was suitable for immersion of the viscometer to within 5 cm of its top. In order to prevent the formation of scale on the walls of the bath, distilled water was used. According to ASTM method 445-46T (54), the water surface should always be above the higher reservoir bulb of the viscometer. A pump was used to circulate the water for keeping uniform temperature in the bath. The motor of the pump was mounted on a separate frame to reduce the vibration.

Two flexible immersion heaters about 50 inches and 20 inches long, of 750 and 200 watts respectively, were bent to a desired contour around the walls of the cylinder and submerged in this bath. The heater voltages were controlled by two variable transformers. The variable transformer for the larger heater was controlled manually to hold the bath a few degrees below the desired temperature. The small heater was the fine temperature controller. It was turned on and off by a relay-controlled circuit connected to a thermo-regulator in the bath. The thermo-regulator was held in a vertical position near the viscometer. Temperature settings were made by simply turning a magnetic ring knob on the regulator, which turned a screw attached to the contact wire. This wire could be raised and lowered inside a fine capillary tube. It made a contact with mercury in the tube, which activated the H-B electronic relay.

The load circuit was controlled by a hermetically sealed mercury-plunge relay. When the bath reached the desired temperature, the mercury in the regulator rose in the capillary, completed the circuit with the contact wire and activated the relay, which shut off the heater. A cooling water coil of 1/8-inch copper tubing was connected to tap water for lowering the temperature in the bath, if it were to be run just above or below room temperature. Temperature control was checked by observing fluctuations in a Beckmann thermometer. Temperature variations were less than plus or minus 0.01°C from the set temperature. A thermometer with the range of 18 to 30°C which could be read to plus or minus 0.01°C, or one with a range of 0 to 100°C which also can be read to plus or minus 0.01°C was used for obtaining temperature settings.

e. Timer. Efflux was measured in seconds with an accurate electric timer. The Standard Electric Model S-10 Timer was used for all measurements. This clock has graduations of 1/10 second and adds up to 1,000 seconds and then starts again. The average error in the timing operation was probably of the order of 0.05 to 0.10 seconds.

f. Weighing Buret. Concentration errors were generally caused by evaporation of the solvent during the handling and diluting of the various solutions. However, these errors were minimized by diluting in the viscometer. To assure accurate results, dilution was done by weight.

Weight dilution is more accurate than volume dilution in the viscometer, but is not justified because of the other errors also inherent in the viscosity determination. However, weight dilution makes it possible to assume that the concentration of the various solutions is exact, thereby permitting a least-squares determination of the intrinsic viscosity.

The amount of solvent added in a dilution can be determined from differences in weight, using a weighing buret. This is a short buret of large diameter. It has approximate graduations and a volume of 60 ml. From a practical point of view, the advantages of a weighing buret over a volume pipet are that the buret does not need calibration and changes in temperature have no effect. The instrument can be suspended from the stirrup hook of the left-hand balance pan and thus weighed before and after a given dilution. All weighings were done on an analytical balance to plus or minus 0.0001 gram.

g. <u>Filter</u>. The most serious problem in these viscosity measurements was the presence of suspended foreign matter in some of the polymer solutions. This problem is particularly accute in small diameter capillary tubes, such as the 0.4 mm tube used here. The presence of any particle or trace of dust leads to erratic results. The problem of erroneous flow times caused by partial plugging of the capillary by the particles was minimized by filtration immediately preceding the measurement. The top of a medium sintered glass filter 1 1/2-inches in diameter and 50-inches long was connected to a male adapter 1-inch in diameter and 6-inches long. The bottom was connected to another male adapter 1/2-inch in diameter and 3-inches long. This filter, which was clamped vertically on a stand, was connected through the top adapter to a stopcock which was connected to a rubber pressure pump by tygon tubing about one foot long. All solutions, including solvent, were filtered through this medium sintered glass filter into the weighing buret to exclude dust to as great an extent as possible.

h. Pycnometer. All density measurements were made accurately in a 5 ml pycnometer for the volatile liquids. This pycnometer was purchased from Scientific Glass Apparatus Company Inc., Bloomfield, N.J. (Catalog No. JB-2616). It consists of a horseshoe-shaped capillary tube with two small reservoir bulbs in one of the two legs. The longer leg has a 5 ml reservoir bulb near the base of the U and a 1 ml reservoir bulb near the top. The two legs are graduated into 7 and 6 units, respectively, each unit having 10 divisions.

The middle of the shorter leg has a small hook for hanging the pycnometer on the analytical balance or in the water bath.

2. Pumping System.

The pipeline flow used for the polymer degradation study was carried out in a recirculating system which was designed and constructed by Hershey and Patterson (55). This pumping system had three smooth-bore test sections of 1/2, 1, and 2 inches I.D. in parallel. From a 100 gallon capacity reservoir the process fluid was pumped by either or both of two Viking positive displacement pumps (described below) through the particular size test section desired and back into the reservoir. Positive displacement pumps cause less turbulence in the pump than centrifugal pumps. The flow rate could be varied continuously up to 85 gpm by changing the setting on the variable-speed drives attached to the pumps.

The Viking Model Q-124 heavy duty pump with teflon packing rated at 200 gpm at 380 rpm in water, was driven by a 10 hp hydraulic transmission whose output speed could be infinitely varied between 0 per cent and 150 per cent of the input speed. The transmission was in turn driven by a 10 hp, 220-440 volt motor which was totally enclosed and kept under positive air pressure. The other pump was a Viking K-135 heavy duty pump, rated at 35 gpm at 400 rpm. This pump was driven by a 3 hp Reeves Varidrive unit which was donated by the Humble Co. The pump speed was controlled by an air regulator located near the frequency meter. At 355 rpm the Viking K-135 pump delivered 29 gpm at about 75 psig. An elaborate temperature control system was designed to maintain plus or minus 0.1°C. Further details of this apparatus and the procedures used are available in Hershey's Ph.D. thesis (55). A schematic diagram of this pumping system is shown in Figure 3, page 29.

3. Turbine Meter Equipment.

a. Turbine Flow Meters. The flow rate was measured by one of the two turbine meters located in parallel in the discharge line between the pumps and the test sections. Hydropoise 3/4-inch and 1 1/2-inch turbine flow transducers manufactured by Brooks Instrument Co., Inc., were used for the flow rate measurements in this investigation. The turbine meter specifications are listed in Table I, page 30.

The details of the mounting of the meters are shown in Figure 4, page 31. In order to reduce the amount of swirl at the meters, calming sections of straight-run pipe were inserted upstream from the meters. Table I, page 30, presents the recommendations of Brooks Instrument Co. (42) for upstream and downstream calming sections compared to those

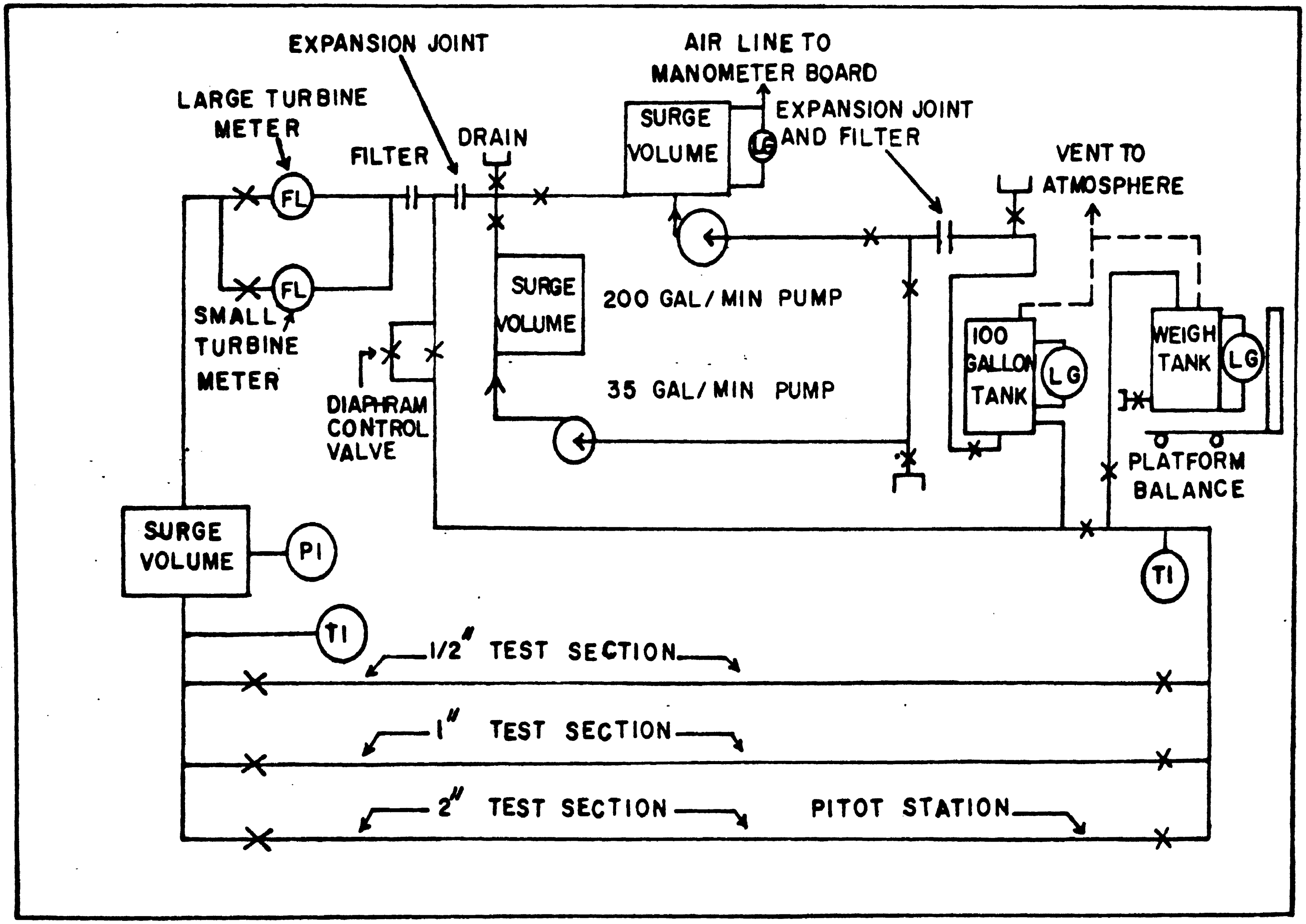


Figure 3. Schematic Diagram of Pumping System.

TABLE I

Turbine Meter Specifications

Specification	Meter	
	HP-12N	HP-24N
Nominal Size (inch)	3/4	1 1/2
Flow Range (gpm)	1.5/15	6/140
Pressure Rating (psi-ASA)	150	1500
Maximum Operation Rate (cps)	1250	1050
Diameters Upstream		
Experimental Equipment	70	22
Manufacturer's Recommendation (42)	15	15
Diameters Downstream		
Experimental Equipment	10	6
Manufacturer's Recommendation (42)	6	6

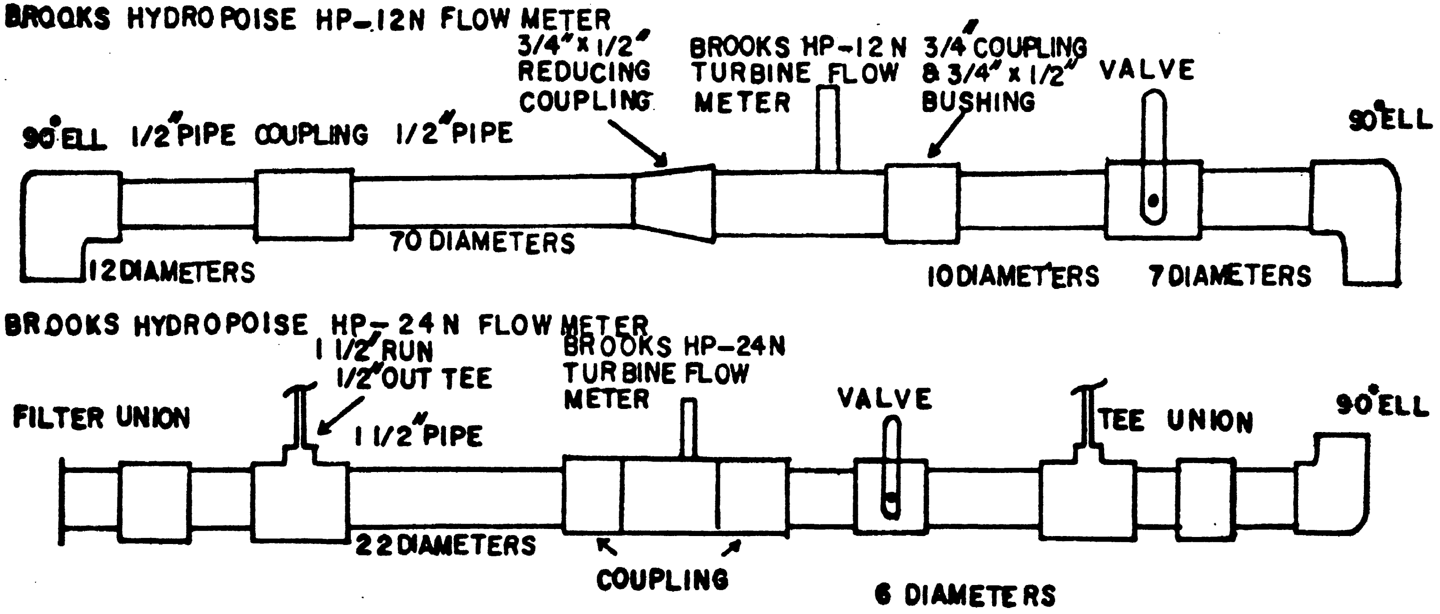


Figure 4. Details of the Mounting of the Turbine Flow Meters.

used here. It can be seen that this installation met or exceeded the manufacturer's recommendations.

The frequency output signal from the meters was read by a Heathkit Audio Frequency Meter Model af-1 (as modified by the McDonnell Co., St. Louis). Although the frequency meter was carefully warmed up and calibrated with a Heathkit Audio Generator Model IG-72 before each day's experimentation (55), it proved to be the principle source of inaccuracy in friction factor determinations because of its poor response and readability.

b. Flow Rate Calibration. A flow meter calibration may be considered accurate only for the conditions existing at the time the calibration data are taken. Thus, those quantities which can influence the performance of the turbine meter must be known, measured, and controlled during precise calibration work. Extreme accuracy is possible in the measurement of mass and time. For the gravimetric-type calibrator a scale of conventional design, equipped with weighbeam and counterpoise is recommended by Shafer (56). Volatility of the liquid is a consideration because of loss by evaporation, but no measureable evaporation was detected by Shafer who worked with water.

The turbine flow meters were calibrated by weighing the process fluid into a drum for a measured time interval. The apparatus used for calibration is shown in Figure 5, page 33.

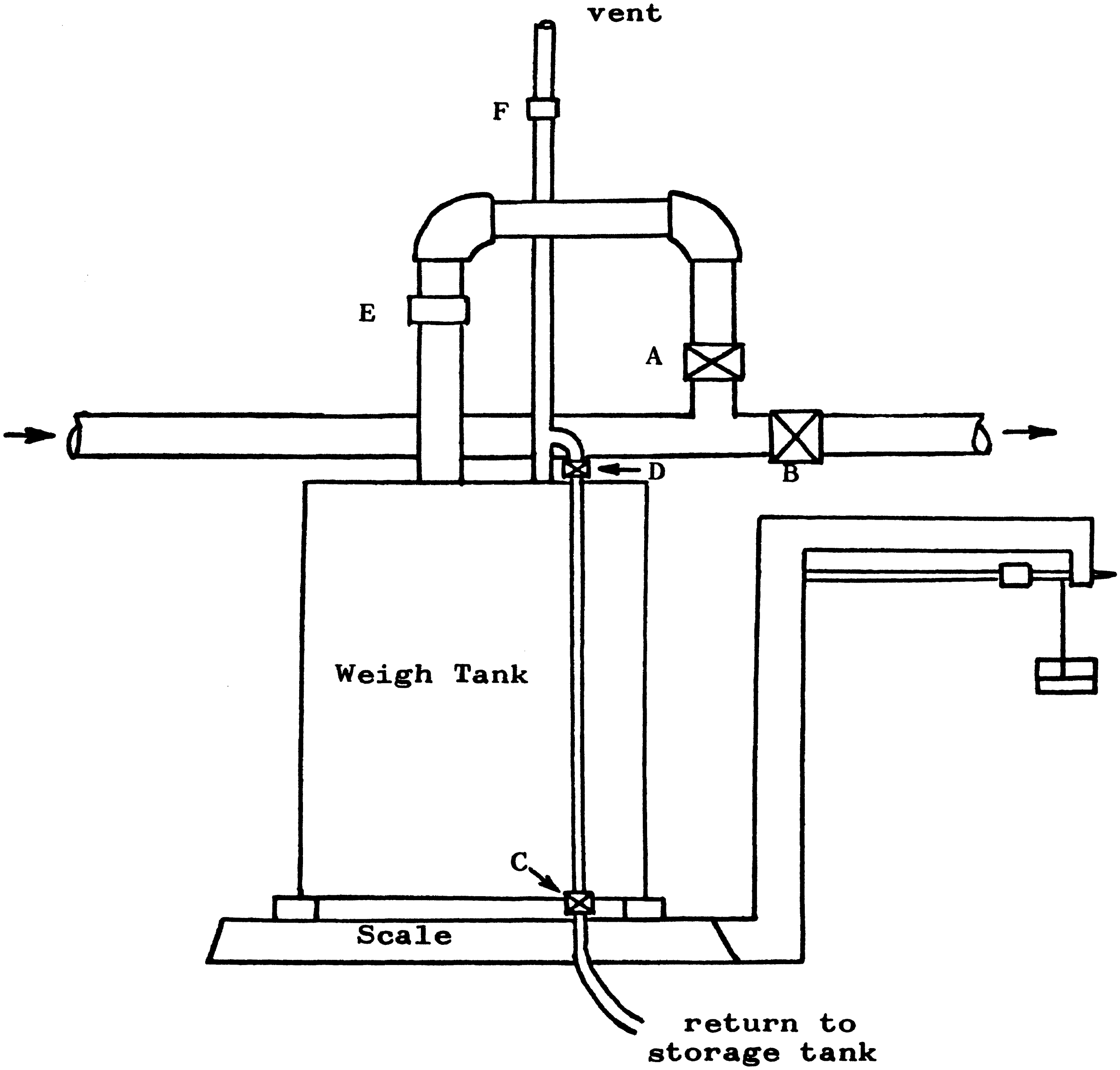


Figure 5. A Schematic Diagram of the Static Weighing Calibration System.

It is similar to the NBS static weighing calibrator recommended by Shafer (56). Essential components are the flow rate supply and control, the meter under calibration, flow diverter valves, a stop watch, a platform scale, and a weigh tank. The weigh tank was built from a 55 gallon shipping drum. A vent line was connected to the discharge line of this weigh tank. The platform scale was a self-contained, straight-level type, equipped with suspended main load-bearing assemblies and a simple bar weighbeam graduated to 50 lbs in 0.25 lb divisions. A complement of counterpoise weights provided a total capacity of 600 lbs.

C. Procedure

1. Intrinsic Viscosity Measurements.

a. Solution Preparation. The solutions were prepared volumetrically by weighing the appropriate amount of dried polymer into a 50 or 100 ml volumetric measuring flask. Solvent was added to the flask to just below the mark and the solution was shaken and allowed to stand overnight in the water bath. The volumetric flask was clamped inside the constant temperature water bath. Additional solvent was added to the volumetric flask until the solvent level was right on the mark. Before use, the solution was shaken vigorously. Sufficient polymer solution was poured off for the viscosity and density measurements. For all calculations and plotting, the concentration of the solution was expressed in terms of the number of grams of polymer in 100 ml of solution (grams per deciliter). All polymer samples were put in reagent bottles and stored in a desiccator inside a dark closet to keep them free from moisture and dust and the degrading effect of light. Calcium chloride ($CaCl_2$) was used as the desiccant for this purpose.

b. Intrinsic Viscosity Measurements. A trace of dust or dirt in the polymer solution will cause erratic results in viscosity measurements. Therefore, before charging the solution to the viscometer, it was passed through a medium-porosity sintered glass filter to remove any dust in the solution. All diluting solvent added to the viscometer was also filtered through the filter. The amount of solvent for each dilution was determined from differences in weight using the weighing buret. Dilutions were made directly into the dilution bulb of the Ubbelohde viscometer; consequently, the danger of dust contamination was minimized.

After each dilution, the viscometer was removed from the bath and shaken to mix the solution thoroughly. The time required for adequate mixing of diluted solutions and equilibration to the bath temperature was about 5 minutes. The dilutions were repeated several times until the solution reached the capacity of the dilution bulb (about 100 ml). About 15 ml were required to obtain the first reading.

When the three-way stopcock was closed, the liquid in the dilution bulb was forced into the efflux bulb and tube 3 by pressing the rubber bulb. In order to avoid applying vacuum, the tube above the efflux bulb was opened to the atmosphere until the liquid had filled the efflux bulb. As soon as the efflux bulb was filled by the test liquid, the three-way stopcock was opened so that all three tubes were connected, and the opening above the efflux bulb was clamped shut until the run was complete. This maintained the three viscometer tubes at the same pressure. During these operations, the liquid in tube 3 quickly dropped back into the dilution bulb and a thin fluid layer with a flat surface was at once formed at the lower end of the capillary. The free surface of this layer faces downward forming the "suspended level". For all liquids which wet glass, it occurs in the same place. The downward traction of the layer flowing over this surface is supposed to overcome and balance the upward pull of the surface in the higher reservoir bulb, hence eliminating the surface tension effect (48).

Flow times for the meniscus of the liquid to fall from the upper mark to the lower mark were measured by observing the time with a Standard Electric Timer clock. Determinations were repeated two or more times until the two lowest efflux times agreed within plus or minus 0.05 per cent, the average of these determinations being used for calculation of the kinematic viscosity. Generally, a third reading was also obtained. Reduced viscosities were calculated from these results together with density and concentration data. The intrinsic viscosity was obtained by plotting η_{sp}/C vs. C and extrapolating to zero concentration. The intercept at zero concentration was actually found by calculating the coefficients of the least-squares line through the linear portion of the data.

c. Viscometer Calibration. The kinetic energy correction was determined by calibrating the viscometer with standardized oil samples and purified solvents. Ubbelohde (43, 44) pointed out the necessity for the kinetic energy corrections and recommended an equation of the type:

$$\nu = A\,t - B/t \qquad (12)$$

where ν = fluid kinematic viscosity, centistokes
A = instrument constant
B = constant factor in kinetic energy correction term
t = time for liquid to flow from or into the fiducial bulb, seconds.

Equation (12) may be written in the form:

$$\nu/t = A - B/t^2$$

Hence, from a plot of ν/t vs. $1/t^2$, A is obtained as an intercept and B as a slope (57).

Toluene, benzene, oil A, oil γ were used for the calibration of this viscometer (A-1) by Zakin (58). The calibration constants and other characteristics of this viscometer are listed in Table II.

TABLE II

Viscometer Characteristics$^{(58)}$

Viscometer	Capillary		Upper-Bulb Volume	Viscometer Constants	
	Length	Diameter			
	cm	mm	ml	A	B
A-1	10.0	0.40	5.0	0.001315	1.34

For minimizing the kinetic energy correction term, the efflux times of the viscosity measurements in the suspended-level viscometer should be greater than 200 seconds (59). All viscosity measurements in this work exceed 460 seconds.

Viscosities of polymer solutions are sensitive to shear rate at high molecular weight. At a given temperature the shear effects are greater the higher the molecular weight and the more expanded the configuration of the polymer molecules in solution (57). When the solutions are shear dependent, it is necessary to carry out suitable extrapolations to zero rate of shear to obtain an accurate value of intrinsic viscosity (60).

Fox and Flory (61) stated that the effect of rate of shear was small for values of intrinsic viscosities of polystyrene under 3, and that corrections to zero rate of shear are therefore not necessary. For polystyrene, Sharman, Sones, and Cragg (57) also found that the threshold value of intrinsic viscosity seems to be somewhat higher in a good solvent, where the molecules are expanded, compared to a poor solvent, where they are not (approximate value being 2.0 in toluene and 1.3 in cyclohexane). Weissberg, Simha, and Rothman (62) were also unable to detect any appreciable shear rate effect in their studies of the polystyrene-toluene system with intrinsic viscosities up to 2.0. For this viscometer the maximum average shear rate (63) in the capillary tube for toluene is about 1,120 sec^{-1}, which is relatively low. All polymer solutions had lower average shear rates. Significant non-Newtonian effects would not ordinarily be expected, even for the higher molecular weight polymers in a good solvent at these low shear rates, and thus, no shear rate corrections were made.

d. Density Measurements. The pycnometer used for the density measurements was calibrated with distilled water at 30°C and 20°C. Densities of water at these temperatures are 0.99823 and 0.99567 gram/milliliter, respectively.(64). A correction for the bouyant effect of air must be applied to all weights used in this pycnometer. The formula can be written as:

$$W^o = W + W\,(a/d - a/d') \qquad (13)$$

where W = the weight of the substance in air, grams,

W^o = the weight of the substance in vacuo, grams,

a = the weight of a unit volume of air, gram/milliliter,

d = the density of the substance, gram/milliliter,

d' = the density of the brass weights (= 10.76 grams/milliliter) (64).

Although the value of a varies slightly with the temperature and barometric pressure, the approximate value of 0.0012 grams for the weight of 1 ml of air may be used. From equation (13), the weight of distilled water in vacuo was determined and then divided by the density at a specific temperature to get the volume of water at that temperature. The sum of the readings on the two pycnometer legs was plotted against the calculated volume of the weighed liquid of known density (i.e. water). A first degree least-squares polynomial line fitted the experimental calibration data very well, as shown in Figure 6, page 41. The calibration data are listed in Appendix B. The calibration result at 30°C is:

$$\text{Volume} = 4.9995 + 0.01182 \times \text{Pycnometer Reading}\;.$$

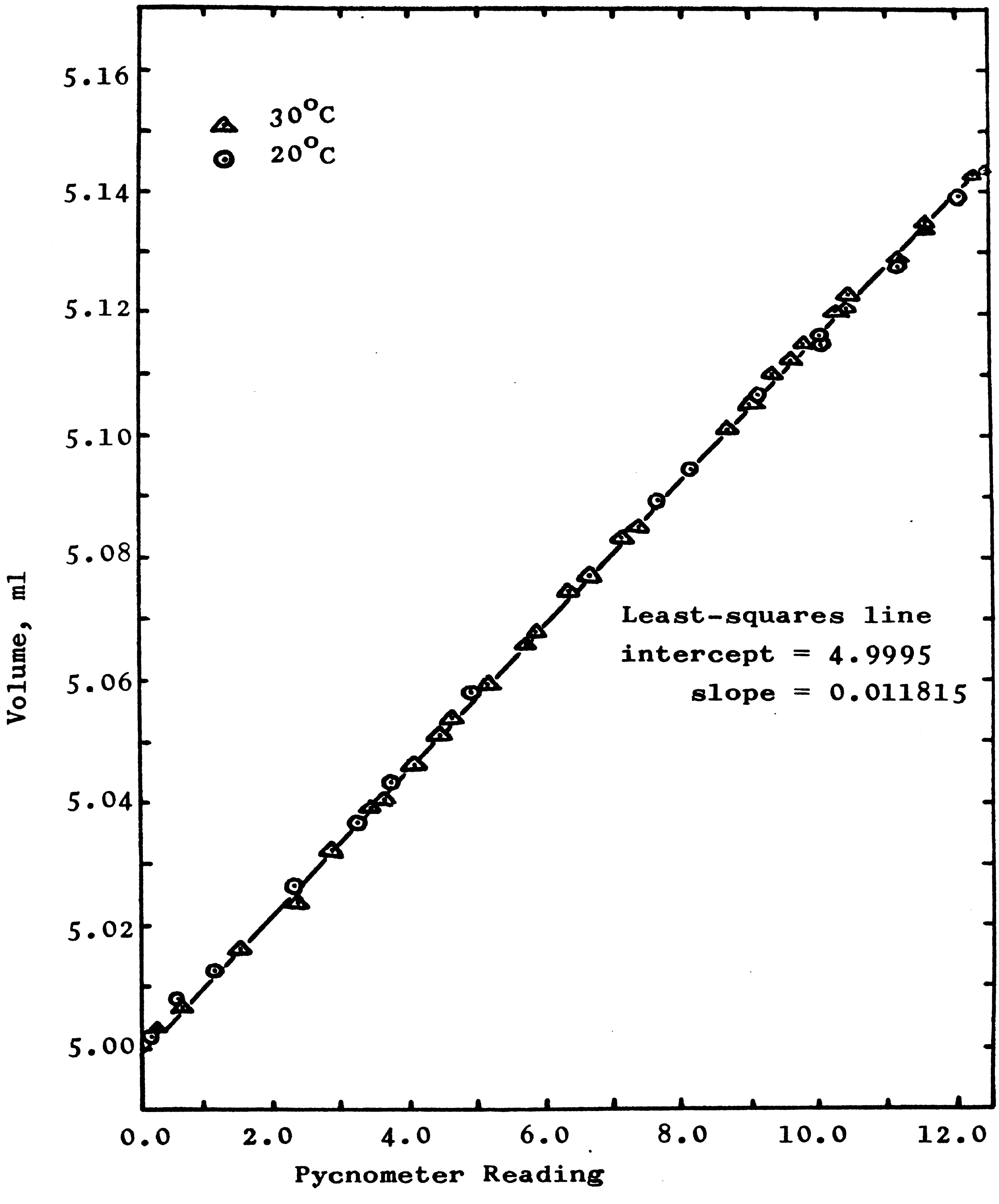


Figure 6. Calibration of Pycnometer with Distilled Water.

A calibration was also made at 20°C, but the measured volumes were within 0.04 per cent of those at 30°C. Therefore, the effect of temperature on calibration was insignificant and the calibration result at 30°C was used throughout this investigation.

For the density measurements, the dry, clean pycnometer was first weighed using a looped wire to hang the pycnometer on the analytical balance stirrup. The filtered test liquid was introduced into the pycnometer by capillary action and then siphoned to a convenient level. The liquid and pycnometer could be weighed at any convenient temperature such as room temperature. In order to get an accurate volume, the reading had to be measured at the test temperature in a constant temperature water bath. For each test liquid, two or three measurements were made and an average value was used for the density of this liquid.

e. Cleaning and Drying. Between successive determinations, the viscometer was rinsed thoroughly several times with an appropriate solvent completely miscible with the sample, followed by a completely volatile solvent. Distilled acetone was used for this purpose. The viscometer was then dried by passing filtered dry air through it until the last trace of solvent was removed. After the cleaning procedure, or whenever no measurement was made, the viscometer was clamped upside down on the framework and its tubes were capped with aluminium foil to prevent any contamination.

Periodically, it was necessary to clean the instrument with cleaning solution to remove organic deposits. This was followed by rinsing thoroughly with distilled water and then distilled acetone, and drying with clean dry air. Cleaning solution was made by dissolving about 10 grams of technical grade potassium dichromate in 20 ml of hot water in a 500 ml flask. When cooled, 175 ml of concentrated sulfuric acid were added to it slowly, with constant stirring. The cleaning solution was stored in a glass-stoppered bottle. The filter and pycnometer were cleaned in similar ways.

2. Degradation.

Degradation of a polymer took place when the polymer solution was pumped for a long period of time in the piping system.

Samples of each dilute polymer solution were taken from the pumping system at various times in the pumping experiments. Intrinsic viscosities were determined for these samples. From their intrinsic viscosities, the molecular weights of these samples were estimated.

However, the determination of intrinsic viscosity depends on knowledge of the concentration of the test solution. Therefore, a method for finding the concentration of polymer solutions was needed. The method chosen is a simple gravimetric analysis which gives sufficient accuracy at the low concentrations found in most of these polymer solutions.

About 15 grams of test solution were filtered through the medium-sintered glass filter, weighed by means of a weighing buret, and charged into an open aluminium weighing dish of known weight. From the measurements taken, the density of this solution was determined and its volume calculated. The weighing dish was placed on a hot plate and heated to about 40 to 60°C. When the dish and residue reached a constant weight the weight of polymer per volume was calculated.

In order to check the accuracy of the method of concentration analysis, three polymer solutions, that is, polystyrene in toluene, polyisobutylene L-80 in benzene, and polyisobutylene LMMH in cyclohexane, were prepared. Several concentration analyses were made for these solutions. The results are listed in Table III, page 45. The results for polystyrene show the method to give fairly accurate results. The consistently low results for the high molecular weight polyisobutylene L-80 in benzene are believed due to thermal degradation and volatilization of the polymer. This was due to the high temperatures required to evaporate all of the solvent for this relatively concentrated high molecular weight sample.

TABLE III

Concentration Analysis Results

Test No.	Density	Wt. of Solution	Wt. of Sample	Concentration		% Error
				Actual	Measured	
	gm/ml	gm	gm	gm/dl	gm/dl	
a. Polystyrene-E in Toluene						
1.	0.8594	19.4416	0.2193	0.9784	0.9693	-0.92
2.	"	6.3997	0.0703	"	0.9453	-3.37
3.	"	9.2556	0.1043	"	0.9684	-1.02
4.	0.8612	12.8925	0.0698	0.4664	0.4661	-0.02
5.	"	12.6034	0.0671	"	0.4585	-1.68
b. Polyisobutylene L-80 in Benzene						
1.	0.8746	20.3806	0.2523	1.4024	1.0820	-22.80
2.	"	23.3782	0.2922	"	1.0930	-22.60
3.	"	10.4130	0.1196	"	1.0040	-28.40
c. Polyisobutylene LMMH in Cyclohexane						
1.	0.7784	19.2507	0.1657	0.6713	0.5586	-16.80
2.	"	19.2514	0.1676	"	0.7096	+5.70
3.	"	23.0855	0.1983	"	0.6683	-0.40

When this method was used, at least two measurements were made to check the concentrations for each sample and an average value of these calculated concentrations was used.

3. Flow Meter Calibration.

One of the two turbine meters was connected to the frequency meter. The desired reading on the frequency meter was adjusted either by controlling the speed of the pump or with the by-pass valve. As soon as the reading was constant, the flow rate was measured with the equipment described in Section 3a, page 28 and shown in Figure 5, page 33. Valve A was opened and valve B was closed simultaneously sending the fluid stream into the weigh tank. After collection of an appropriate amount of fluid, valve A then was closed and valve B was opened again. The time interval was measured by means of a regular stop watch. The tare weight of the weigh tank was determined beforehand. After loosening the connection screws E and F, the gross weight was measured and the net weight determined for the indicated time interval. The frequency meter readings were calibrated by means of a standard sine wave generator (55).

IV. RESULTS AND DISCUSSION

A. Estimated Molecular Weight for a Number of Polymers from Intrinsic Viscosity Measurements

Commercial solvents to be used in the pumping experiments were used for the intrinsic viscosity measurements. Density and viscosity data for each solvent are listed in Table IV, page 48. Comparisons of the measured values with published values for highly refined materials indicate that the solvents were fairly pure.

Intrinsic viscosities of five polystyrene and one polymethyl methacrylate samples were measured in good solvent. Three polyisobutylene samples were measured in both good and in poor (theta) solvents (67). The viscosity, density, and concentration data for intrinsic viscosity measurements are listed in Appendix C.

Values of intrinsic viscosity were calculated by least-squares analyses of the linear portions of plots of η_{sp}/C vs. C, which are shown in Figures 7 to 10, pages 49 to 52, respectively. From the intercepts and slopes of these plots, intrinsic viscosities and Huggins constants were found, and are listed in Table V, page 53.

The constants, K and a, for equation (9) relating intrinsic viscosity and molecular weight were obtained from published literature (67, 68, 69, 70). Values of K and a

TABLE IV

Physical Properties of Solvents

Solvent	Temperature	Density		Absolute Viscosity	
		Measured	Literature*	Measured	Literature*
	°C	gm/ml		Centipoise	
Toluene (A)	30	0.8556	0.8577	0.5177	0.5187
Toluene (B)	30	0.8573	0.8577	0.5202	0.5187
Cyclohexane	25	0.7736	0.7749	0.8892	0.8892
Benzene	24	0.8736	0.8745	0.6053	0.6105

* Ref. (65,66)

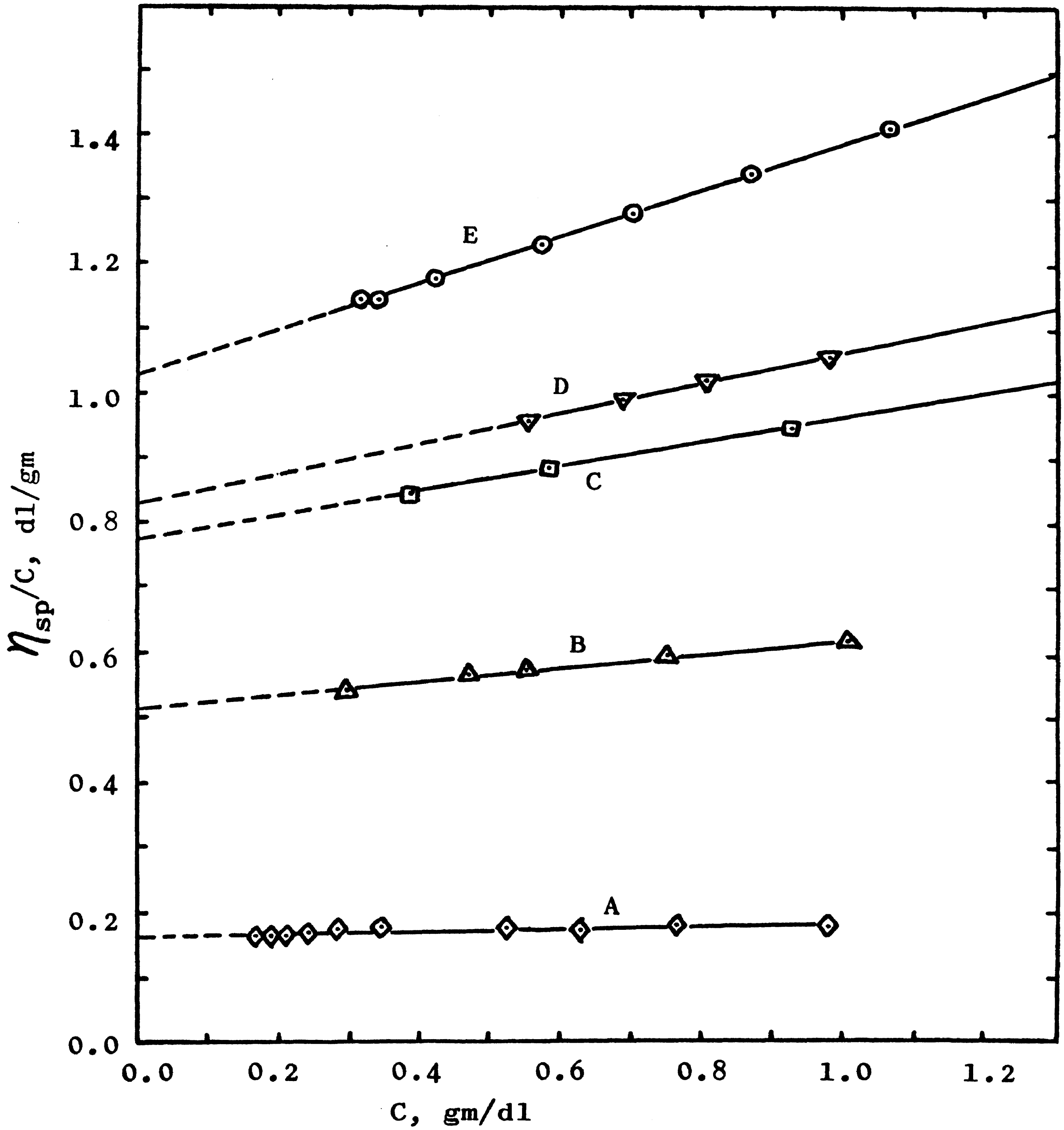


Figure 7. Reduced Viscosity vs. Concentration for Polystyrene in Toluene at 30°C.

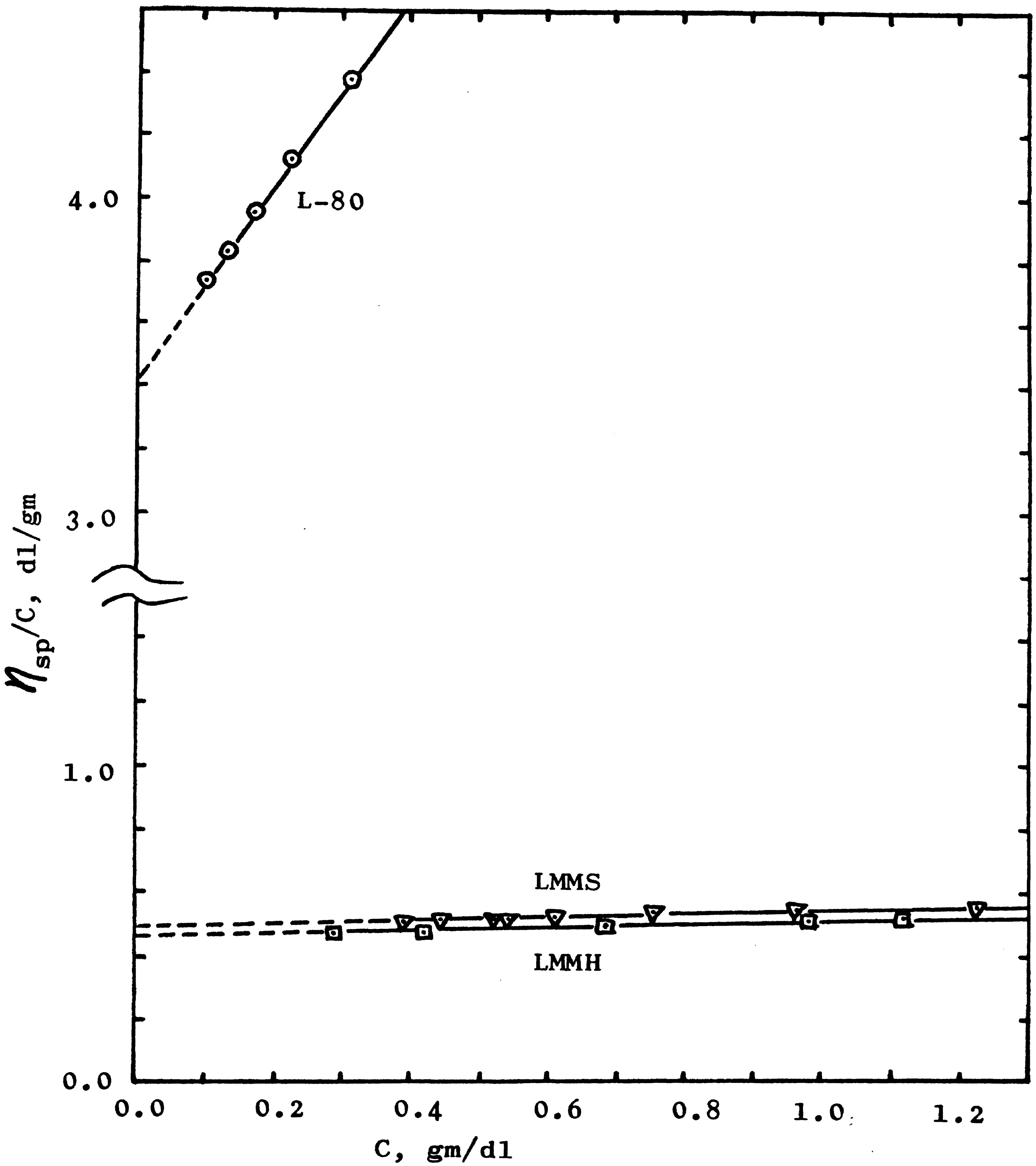


Figure 8. Reduced Viscosity vs. Concentration for Polyisobutylene in Cyclohexane at 25°C.

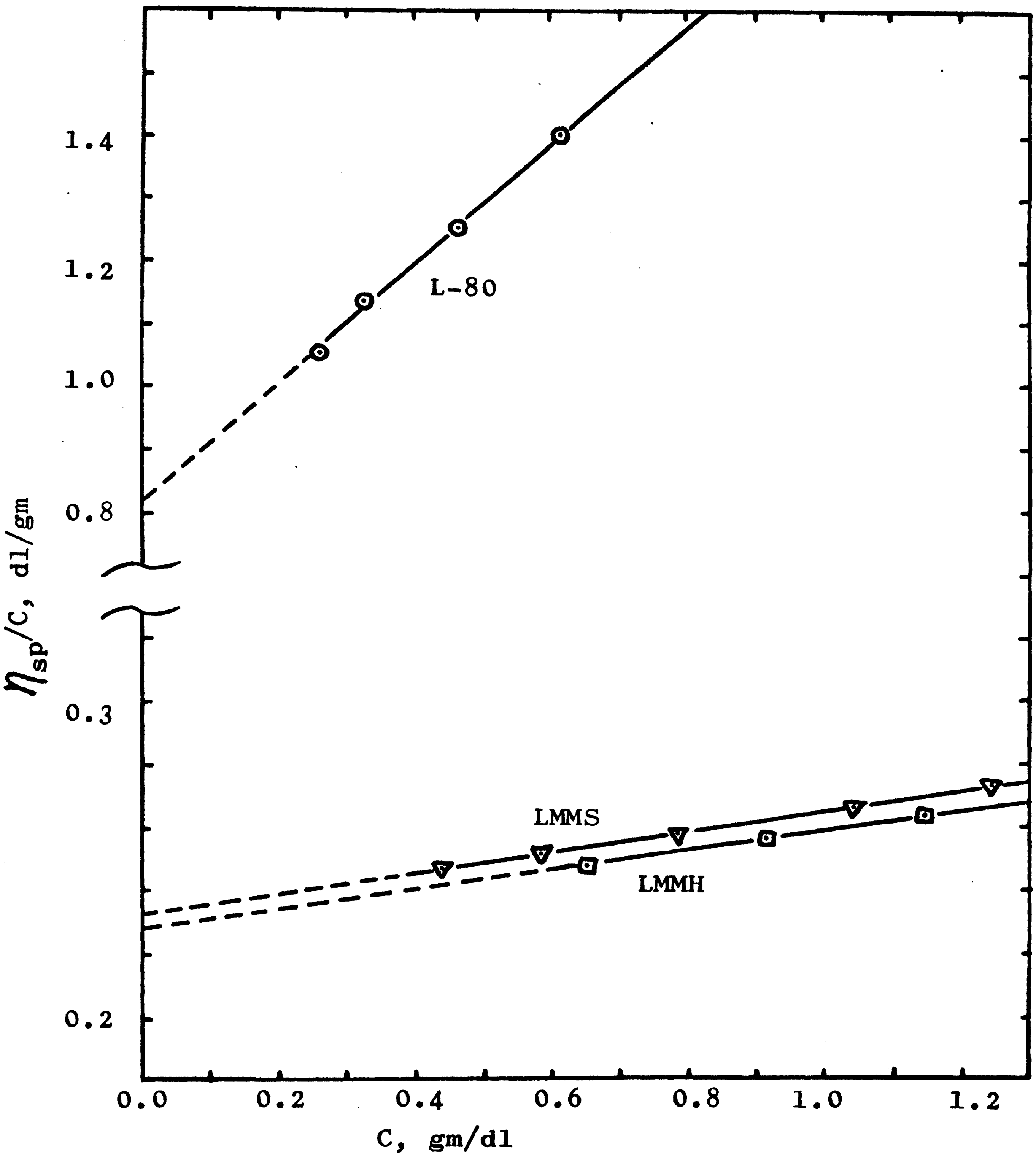


Figure 9. **Reduced Viscosity vs. Concentration for Polyisobutylene in Benzene at 24°C.**

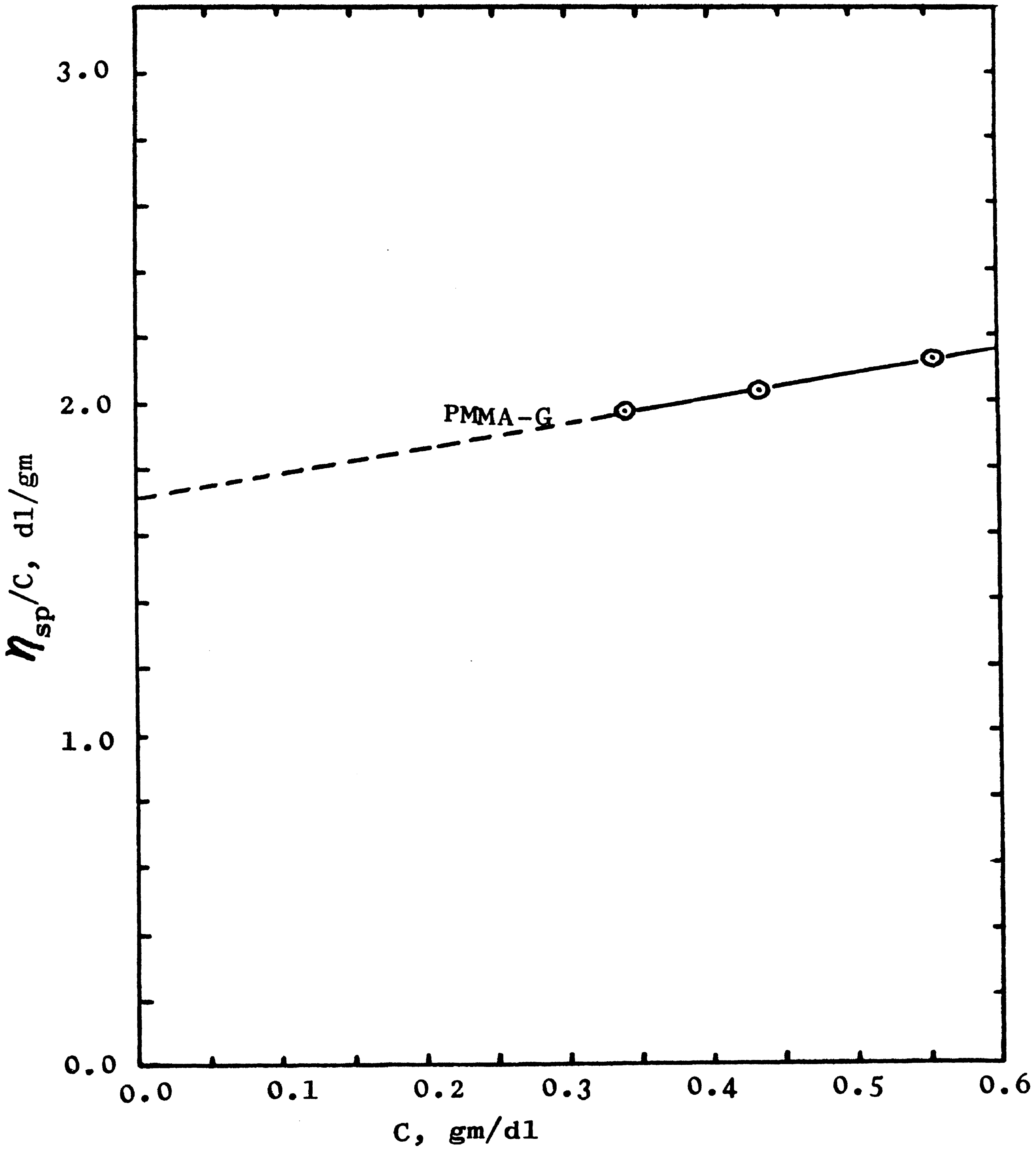


Figure 10. Reduced Viscosity vs. Concentration for Polymethyl Methacrylate in Toluene at 30°C.

TABLE V

Intrinsic Viscosities of Polymer Solutions and Estimated Molecular Weights of the Polymers

Test No.	Polymer	Solvent	Temp. °C	$[\eta]$	$k'[\eta]^2$	k'	$\bar{M}_v$
1	Polystyrene-A	Toluene	30	0.166	0.012	0.44	19,000
2	Polystyrene-B	Toluene	30	0.523	0.087	0.32	97,000
3	Polystyrene-C	Toluene	30	0.773	0.184	0.31	164,000
4	Polystyrene-D	Toluene	30	0.832	0.224	0.32	182,000
5	Polystyrene-E	Toluene	30	1.026	0.356	0.34	242,000
6	Polyisobutylene LMMH	Cyclohexane	25	0.469	0.062	0.28	48,000
7	Polyisobutylene LMMS	Cyclohexane	25	0.489	0.059	0.25	51,000
8	Polyisobutylene L-80	Cyclohexane	25	3.436	3.099	0.26	865,000
9	Polyisobutylene LMMH	Benzene	24	0.228	0.032	0.61	45,000
10	Polyisobutylene LMMS	Benzene	24	0.232	0.330	0.61	47,000
11	Polyisobutylene L-80	Benzene	24	0.819	0.951	1.42	586,000
12	Polymethyl Methaerylate-G	Toluene	30	1.703	0.745	0.26	1,500,000

for all polymer-solvent systems used in this work are listed in Table VI.

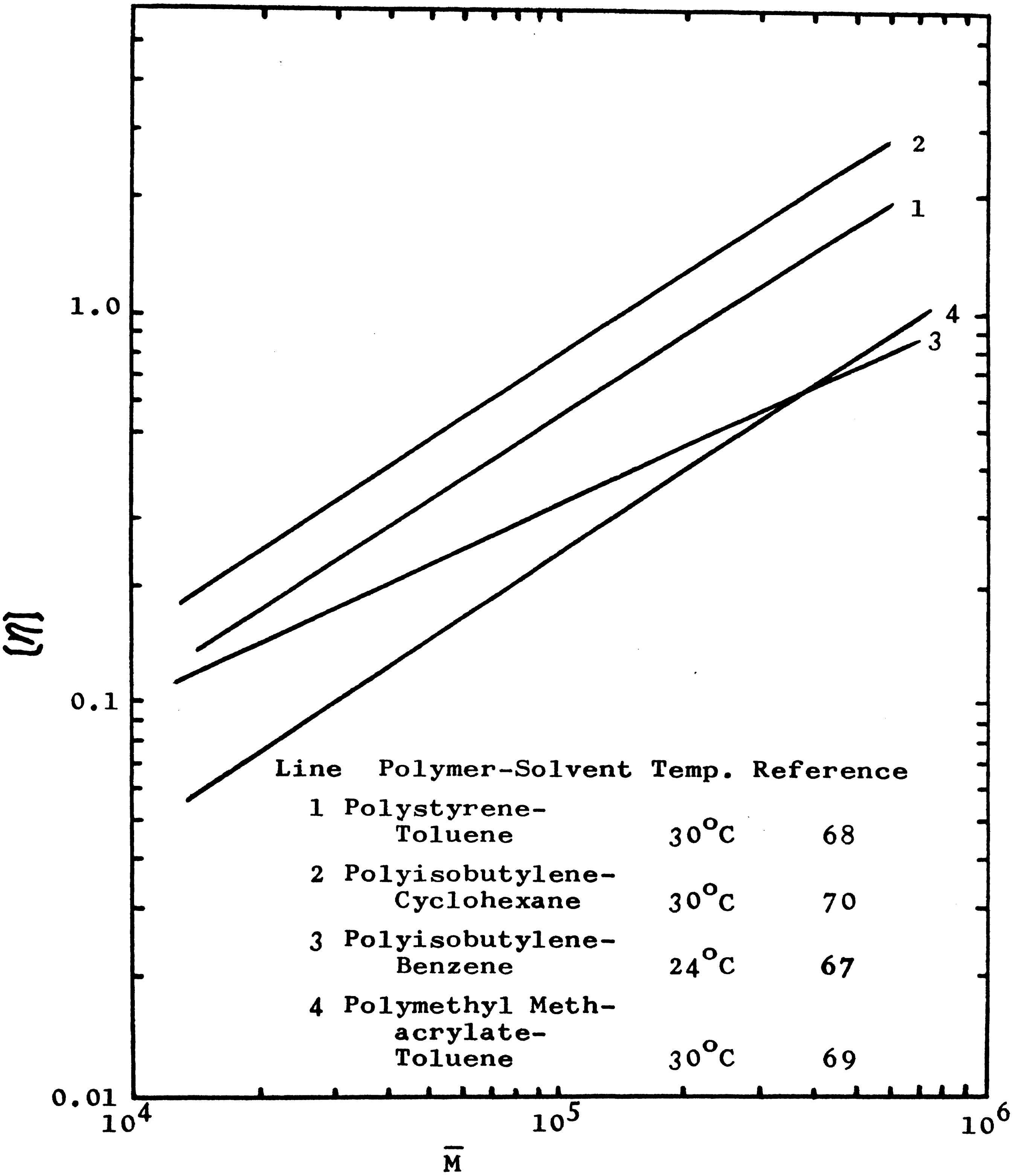
TABLE VI

Constants for Equation (9)

Polymer	Solvent	Temp. °C	$K \times 10^4$	a	Reference
Polystyrene	Toluene	30	1.40	0.72	68
Polyisobutylene	Cyclohexane	30	2.77	0.70	70
Polyisobutylene	Benzene	24	1.07	0.50	67
Polymethyl Methacrylate	Toluene	30	0.70	0.71	69

Plots of these equations are shown in Figure 11, page 55.

The molecular weights of all polymer samples used in this work were estimated from equation (9) or Figure 11 and are listed in Table V, page 53. The intrinsic viscosity measurements of the polyisobutylene-cyclohexane system were made at 25°C, the temperature of the pumping experiments. Unfortunately, published results were available at 30°C only. However, for this good solvent, the difference in the intrinsic viscosities at 25°C and 30°C



Line	Polymer-Solvent	Temp.	Reference
1	Polystyrene-Toluene	30°C	68
2	Polyisobutylene-Cyclohexane	30°C	70
3	Polyisobutylene-Benzene	24°C	67
4	Polymethyl Methacrylate-Toluene	30°C	69

Figure 11. Intrinsic Viscosity vs. Molecular Weight of Polymer-Solvent Systems Studied.

is small. Therefore, the molecular weights of polyisobutylene in cyclohexane at 25°C were estimated from the 30°C data in the literature (see Table VI, page 54).

Table V, page 53, also lists experimentally obtained values of k', the Huggins constant. For polystyrene in toluene at high molecular weights k' is equal to about 0.32, which is close to many values previously reported. However, the low molecular weight polystyrene sample ($\overline{M}_v$ = 19,000) gave k' = 0.44. A similar increase in k' for polystyrene at molecular weights below 50,000 has been reported by Simha and Zakin (71) and by McCormick (72). Values of k' for polyisobutylene in benzene, a poor solvent (theta) are expectedly higher than cyclohexane, a good solvent.

Values of molecular weight for the three polyisobutylene samples were estimated from intrinsic viscosity measurements in both cyclohexane (25°C) and benzene (24°C) solutions. For the low molecular weight samples the agreement is good (less than 10 per cent deviation), but there is considerable difference in the two estimates for the high molecular weight sample (PIB L-80).

Both estimates are subject to some error. The intrinsic viscosity in cyclohexane is large enough so that there is a possibility of the viscosity measurements being shear dependent. This seems unlikely in view of the Newtonian character of initial pumping solutions up to concentrations of 0.3 per cent (55). Also, as noted above, the molecular weight was estimated from a published relationship for 30°C although measurements were made at 25°C.

The benzene measurements were compared with a theta solvent equation. However, the benzene used in this experiment was commercial grade and no effort was made to purify it.

In view of these considerations, an average of the two estimated molecular weights, 726,000, was taken as the molecular weight of PIB L-80.

Intrinsic viscosities estimated from one-point methods are shown for the four polymer-solvent systems in Table VII, page 58. The results for polystyrene in toluene, polyisobutylene in cyclohexane, polymethyl methacrylate in toluene and two samples of polyisobutylene in benzene show fairly good agreement with extrapolated values based on the dilution method. Equation (5) could only be used for polystyrene in toluene where the value of γ was well-known. Except for polyisobutylene L-80 in benzene, the one-point method using equation (6) generally gives results within 6 per cent of the extrapolated value. For this high molecular weight sample in its theta solvent, the agreement is poor. This poor agreement is probably related to the very high Huggins values shown by this sample. Thus, the

TABLE VII

Intrinsic Viscosities Calculated from One-Point Method

Polymer	Conc.	η_{sp}	Intrinsic Viscosity	$[\eta]$, dl/gm	
	gm/dl		Eq. 5	Eq. 6	graph
a. Polystyrene-E in Toluene at 30°C					
A	1.037	0.186	0.168*	0.169	0.166
B	1.000	0.608	0.510*	0.516	0.523
C	1.505	1.580	0.742*	0.747	0.773
D	1.519	1.779	0.807*	0.810	0.832
E	1.979	3.437	1.017*	0.997	1.026
b. Polyisobutylene in Cyclohexane at 25°C					
LMMH	1.542	0.870	-	0.453	0.467
LMMS	1.236	0.695	-	0.468	0.489
L-80	0.302	0.132	-	3.240	3.440
c. Polyisobutylene in Benzene at 24°C					
LMMH	1.500	0.414	-	0.245	0.228
LMMS	1.497	0.420	-	0.249	0.232
L-80	0.612	0.857	-	1.128	0.819
d. Polymethyl Methacrylate in Toluene at 30°C					
G	0.552	1.167	-	1.608	1.703

* $\gamma = 2.73$ (Ref. 14, 15)

one-point method appears to be useful for samples whose k' values are no larger than about 0.6. This conclusion is in general agreement with Pechoc (17), who showed data indicating the method was valid only for k' values greater than 0.3 and less than 0.45.

B. Degradation by Pumping

For the investigation of degradation by pumping of dilute solutions of polyisobutylene L-80 in cyclohexane and in benzene and polymethyl methacrylate-G in toluene, samples were taken directly from the pumping system. Initial samples were taken after the solution had been pumped sufficiently to ensure a uniform concentration of the polymer. Final samples were taken after the pumping experiment was completed. Intermediate samples were also taken for some of the polymer solutions. All experimental results of intrinsic viscosity measurements on these samples are contained in Appendix C. The plots η_{sp}/C vs. C are shown in Figures 12 to 14, pages 60 to 62, respectively. Table VIII, page 63, summarizes the results.

Results of concentration measurements using the gravimetric method described earlier of the three polymer-solvent systems used in studying degradation are listed in Table IX, page 64. Two or three concentration levels were studied for each system. Nominal concentrations, based on the weight of

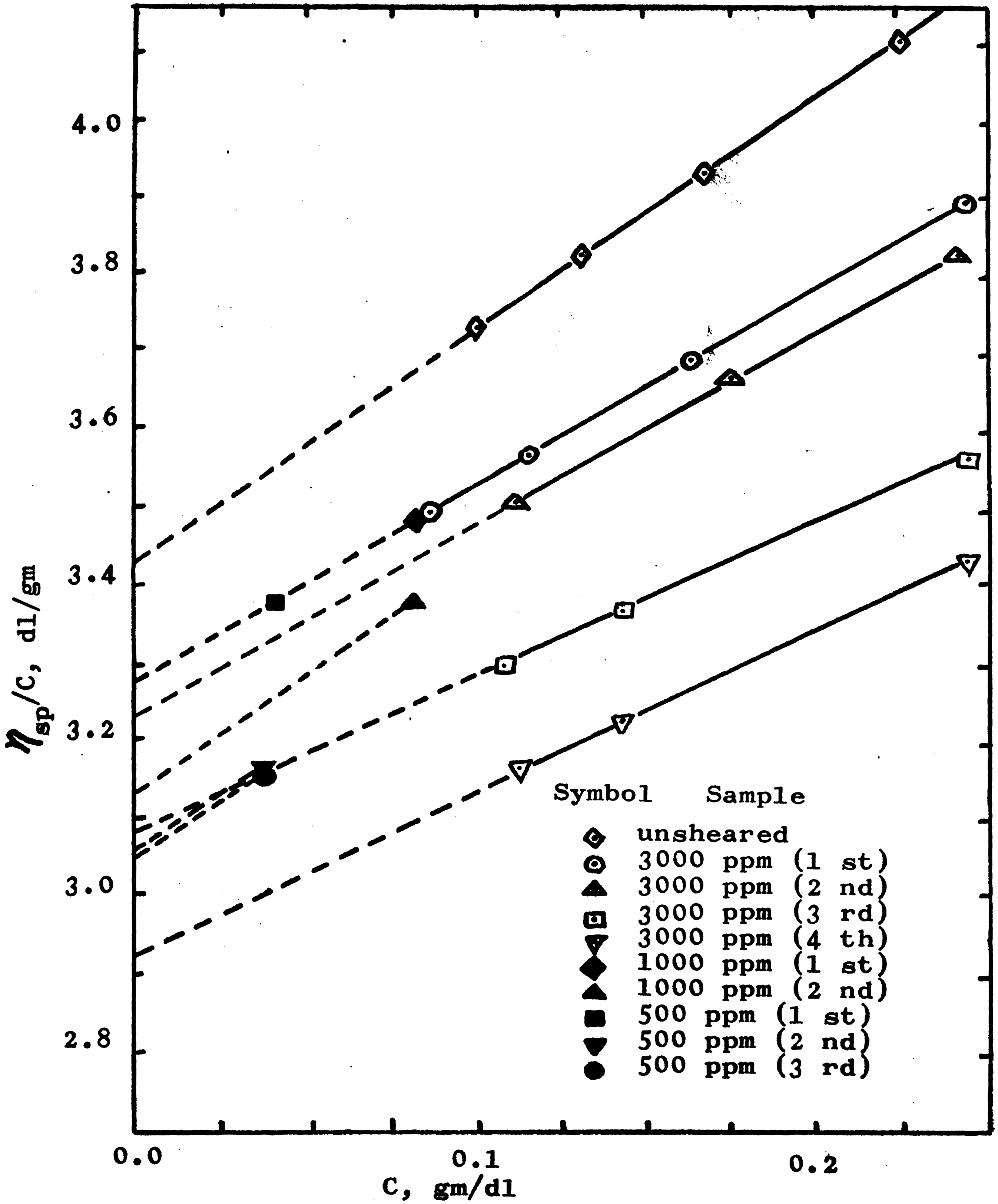


Figure 12. Degradation of Polyisobutylene L-80 in Cyclohexane at 25°C.

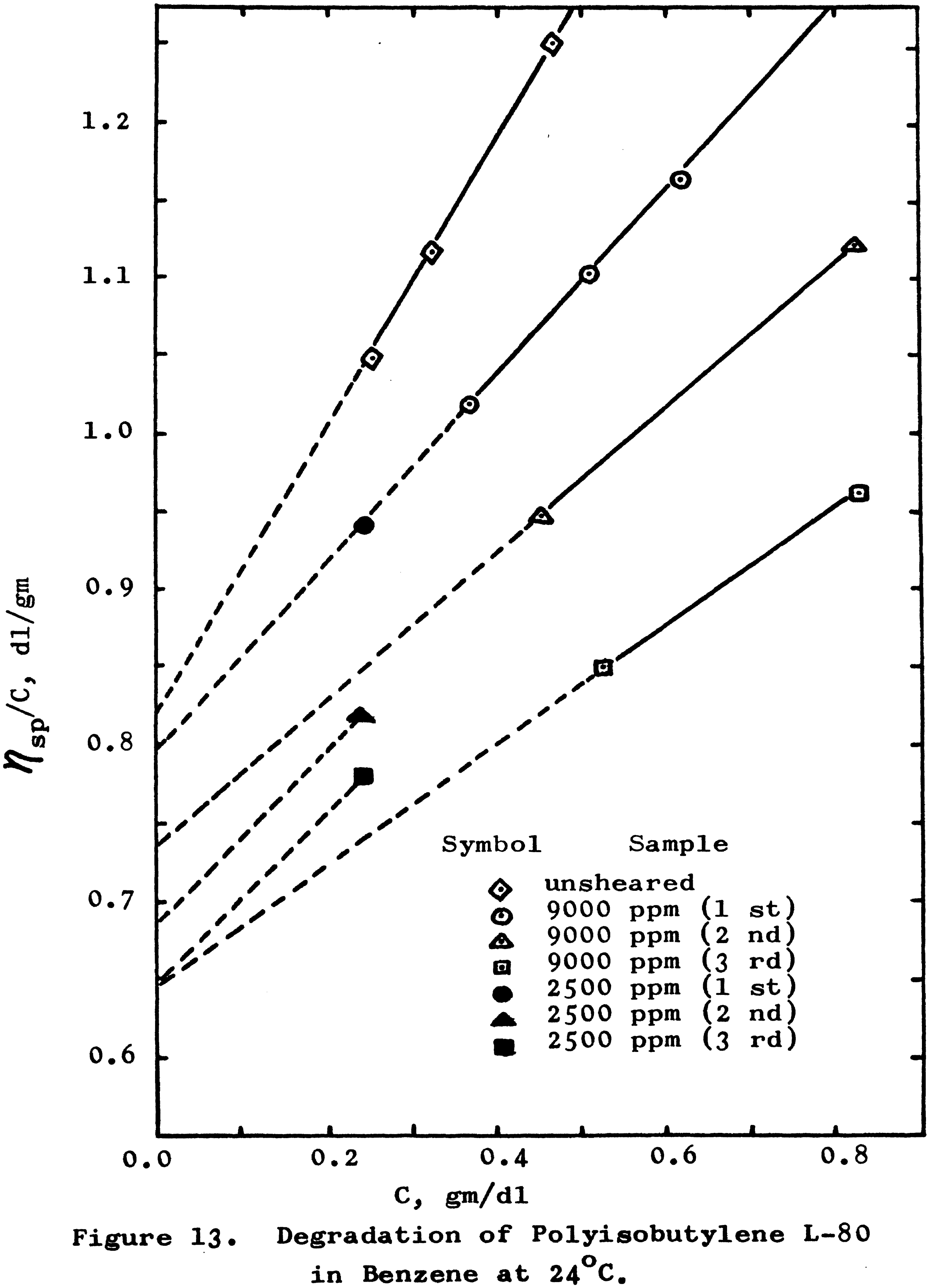


Figure 13. Degradation of Polyisobutylene L-80 in Benzene at 24°C.

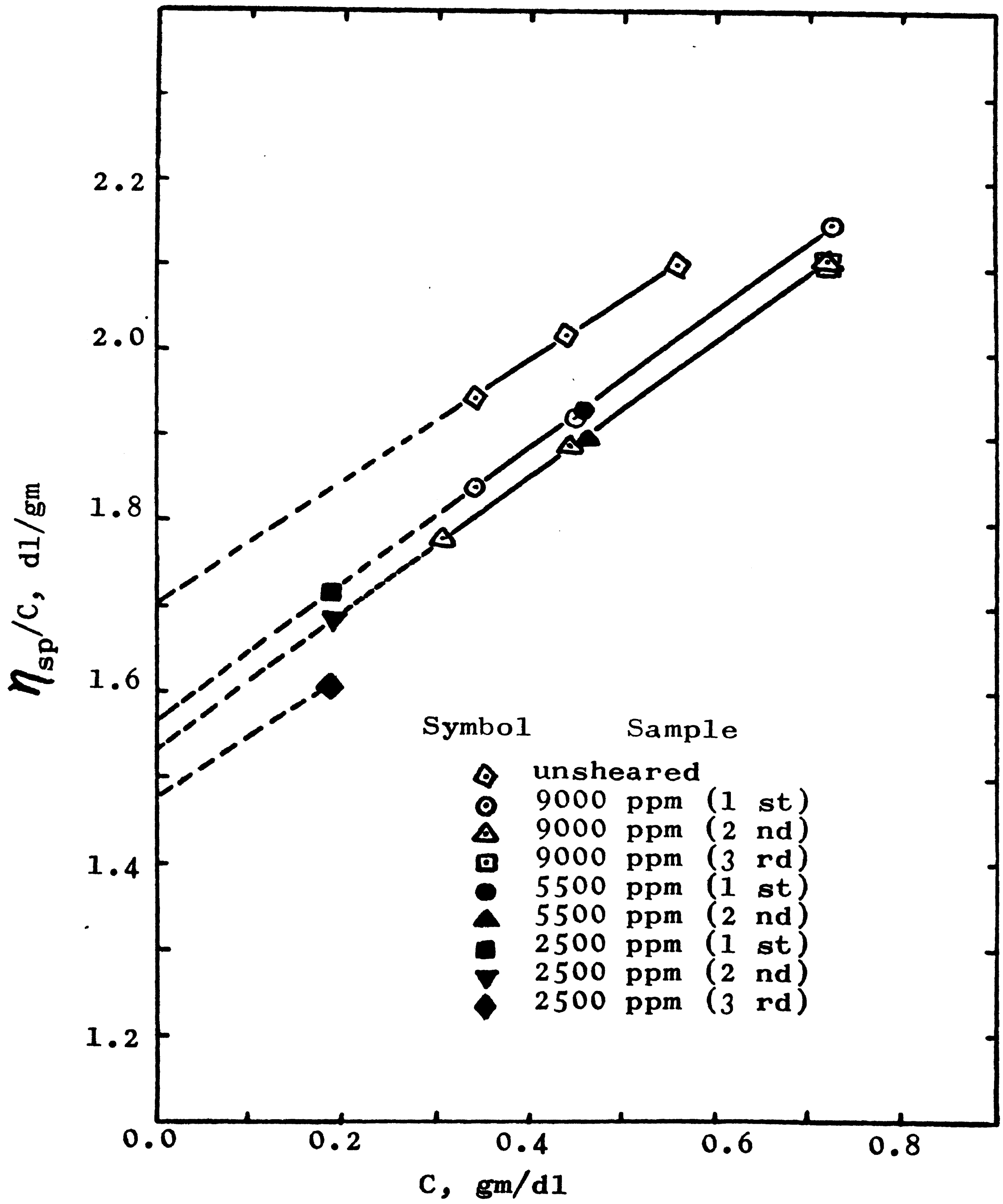


Figure 14. Degradation of Polymethyl Methacrylate-G in Toluene at 30°C.

TABLE VIII

Effect of Degradation Time on Polymer Intrinsic Viscosity

Test	Sample	Degradation Time min	$[\eta]$ dl/gm	$[\eta]_s/[\eta]_o$	M_s/M_o #
a.	PIB L-80 in Cyclohexane at 25°C				
1.	unsheared	-	3.436	-	-
2.	3000 ppm (1 st)	0	3.279	1.000	1.000
3.	3000 ppm (2 nd)	440	3.246	0.990	0.986
4.	3000 ppm (3 rd)	1000	3.086	0.941	0.911
5.	3000 ppm (4 th)	1440	2.930	0.894	0.852
6.	1000 ppm (1 st)	0	3.278	1.000	1.000
7.	1000 ppm (2 nd)	555	3.134*	0.956	0.938
8.	500 ppm (1 st)	0	3.279	1.000	1.000
9.	500 ppm (2 nd)	525	3.053*	0.931	0.902
10.	500 ppm (3 rd)	1380	3.048*	0.930	0.902
b.	PIB L-80 in Benzene at 24°C				
1.	unsheared	-	0.819	-	-
2.	9000 ppm (1 st)	0	0.791	1.000	1.000
3.	9000 ppm (2 nd)	385	0.735	0.929	0.862
4.	9000 ppm (3 rd)	875	0.647	0.817	0.667
5.	2500 ppm (1 st)	0	0.791	1.000	1.000
6.	2500 ppm (2 nd)	215	0.677**	0.856	0.731
7.	2500 ppm (3 rd)	540	0.641**	0.811	0.657
c.	PMMA-G in Toluene at 30°C				
1.	unsheared	-	1.703	-	-
2.	9000 ppm (1 st)	0	1.547	1.000	1.000
3.	9000 ppm (2 nd)	287	1.528	0.988	0.983
4.	9000 ppm (3 rd)	799	1.528	0.988	0.983
5.	5500 ppm (1 st)	0	1.547	1.000	1.000
6.	5500 ppm (2 nd)	325	1.532*	0.991	0.987
7.	2500 ppm (1 st)	0	1.547	1.000	1.000
8.	2500 ppm (2 nd)	577	1.511*	0.975	0.965
9.	2500 ppm (3 rd)	1072	1.463*	0.946	0.925

* One-point method (equation 6)

** k' in equation (3) taken as 0.80

\# $M_s/M_o = ([\eta]_s/[\eta]_o)^{1/a}$

TABLE IX

Concentrations of Polymer Solutions Used in Degradation Studies

Sample	Concentration, gm/dl		
	Nominal	Measured	Estimated (from viscosity measurement)
a. PIB L-80 in Cyclohexane at 25°C			
3000 ppm	0.232	0.238	-
1000 ppm	0.077	0.083	0.076
500 ppm	0.0387	0.045	0.037
b. PIB L-80 in Benzene at 24°C			
9000 ppm	0.778	0.821	-
2500 ppm	0.219	0.222	0.240
c. PMMA-G in Toluene at 30°C			
9000 ppm	0.774	0.717	-
5500 ppm	0.472	0.454	0.442
2500 ppm	0.215	0.208	0.194

polymer and volume of solvent added to the pumping system are also tabulated. In all but one case, the differences are less than 10 per cent. However, in view of the poor checks obtained for polyisobutylene L-80 in benzene (see Table III, page 45), it was felt that these concentration values were not reliable enough to obtain consistent intrinsic viscosity results. Since only relative values, or changes of intrinsic viscosity were needed for the degradation study, the following procedure was adopted.

Gravimetrically determined concentrations of the most concentrated initial pumping solution for each system were used in calculating the intrinsic viscosities. In each case the intrinsic viscosity was lower than for the unpumped polymer solution (see Table VIII, page 63). The values of k' in the Huggins equation (equation (3)) were found. Assuming that all lower concentrations of initial pumping solutions for a given polymer-solvent system had the same intrinsic viscosity, their concentrations were estimated using the measured values of η_{sp} and the Huggins equation. These concentrations are tabulated in Table IX, page 64, and were taken to be the same for all degraded samples in that run.

Successive concentrations used in the pumping experiments with polyisobutylene L-80 were increased by factors of at least two (Table VIII, page 63). Thus, the effect of previous pumping degradation on the molecular weight (and intrinsic viscosity) of the initial pumping solution of the next (higher) concentration was minimized. Hence the assumption that all of the initial pumping solutions had the same intrinsic viscosity, that is, same polymer molecular weight, as that of the most concentrated of the same polymer-solvent system is a reasonable approximation. Further, since only relative values of intrinsic viscosity are being considered, little error is introduced even if the estimated actual concentrations and/or intrinsic viscosities are somewhat in error.

For polymethyl methacrylate-G in toluene, the concentration increments were smaller. However, the amounts of degradation, as measured by intrinsic viscosity, were also generally small.

For polyisobutylene L-80 in cyclohexane at 25°C, intrinsic viscosities of four 3,000 ppm, two 1,000 ppm, and three 500 ppm samples were measured. Unfortunately, anomalous results were obtained on diluting the 1,000 ppm and the 500 ppm solutions. Thus, a one-point method using equation (6), which was found to be satisfactory for this system (Table VII, page 58), was used to evaluate the intrinsic viscosities at these low concentrations (see Table VIII, page 63, and Figure 12, page 60).

Similarly, the intrinsic viscosities of two 9,000 ppm, and three 2,500 ppm samples of polyisobutylene L-80 in benzene at 24^{o}C, and three 9,000 ppm, two 5,500 ppm, and three 2,500 ppm samples of polymethyl methacrylate-G in toluene at 30^{o}C were obtained (see Table VIII, page 63, and Figures 13 and 14, pages 61 and 62, respectively). Except for the 9,000 ppm samples in both of these systems and 2,500 ppm polyisobutylene L-80 in benzene, intrinsic viscosities of the degraded solutions were evaluated by the same one-point method. For the two degraded 2,500 ppm samples of polyisobutylene L-80 in benzene, intrinsic viscosities were evaluated by the Huggins equation. The Huggins constant was taken as the average of two values obtained from degraded 9,000 ppm samples.

Degradation times and the intrinsic viscosity ratio, which is the ratio of the intrinsic viscosity at finite time to the intrinsic viscosity at zero time (initial pumping solutions), are both listed in Table V, page 53, along with an estimate of the ratio of the residual to the initial molecular weight. The plots of $[\eta]_s/[\eta]_o$ vs. time are shown in Figures 15 to 17, pages 68 to 70, respectively.

Examination of Figures 15 to 17 shows that except for one point, values of $[\eta]_s/[\eta]_o$ are lower, the lower the concentration, for equal pumping times. This does not necessarily mean that more polymer bonds were broken in low

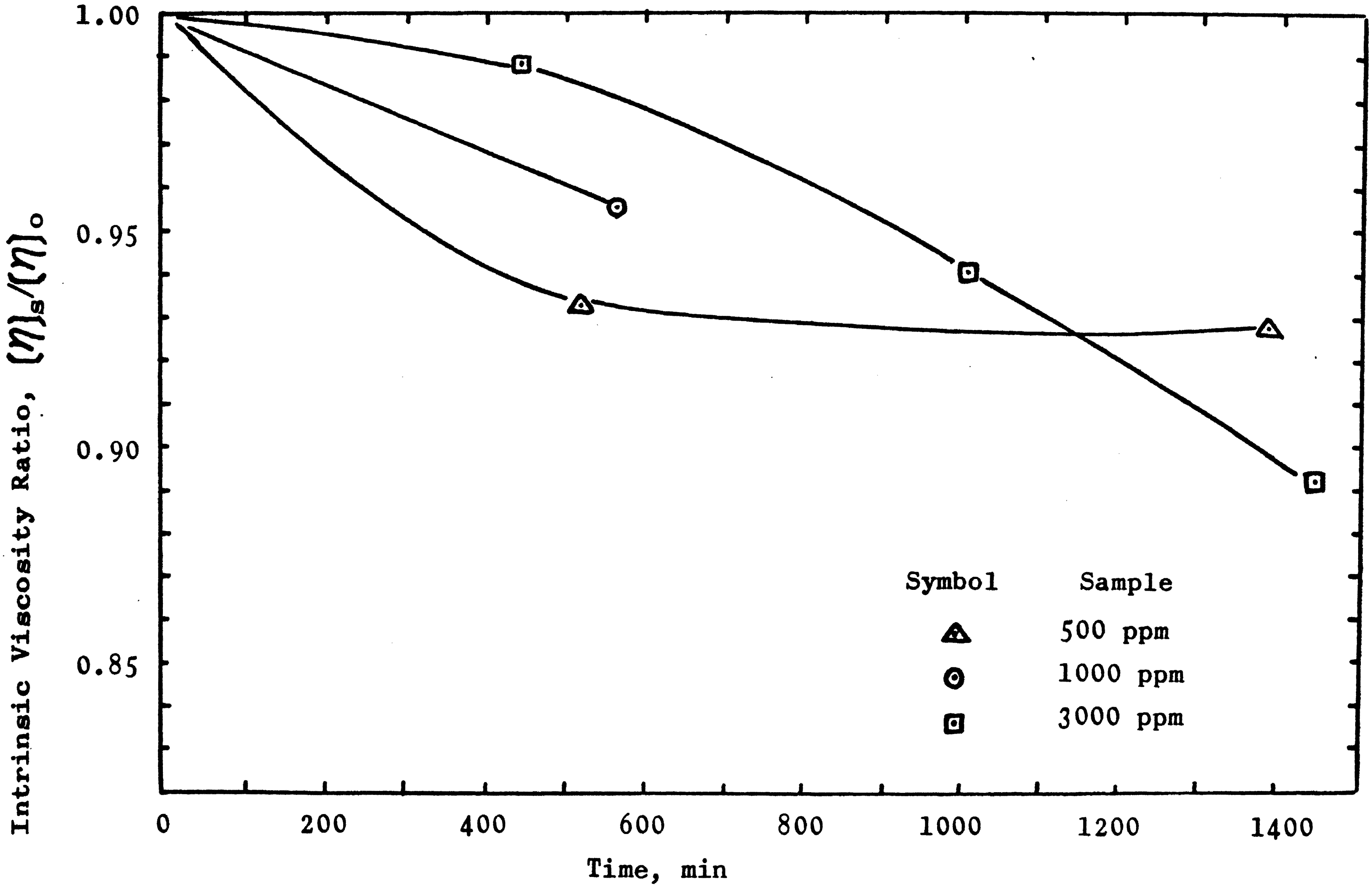


Figure 15. Effect of Pumping Time on Intrinsic Viscosity Ratio for Polyisobutylene L-80 in Cyclohezane.

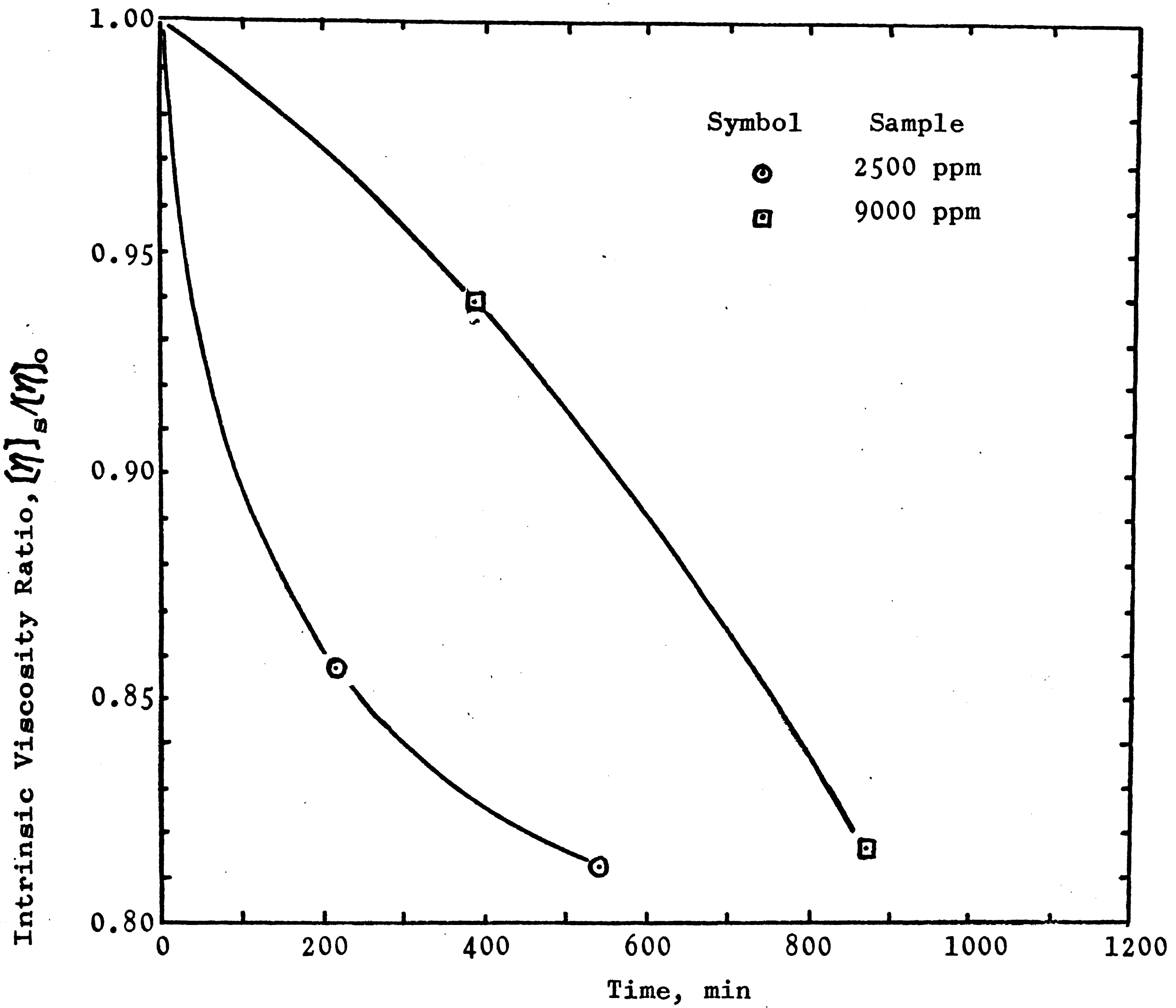


Figure 16. Effect of Pumping Time on Intrinsic Viscosity Ratio for Polyisobutylene L-80 in Benzene.

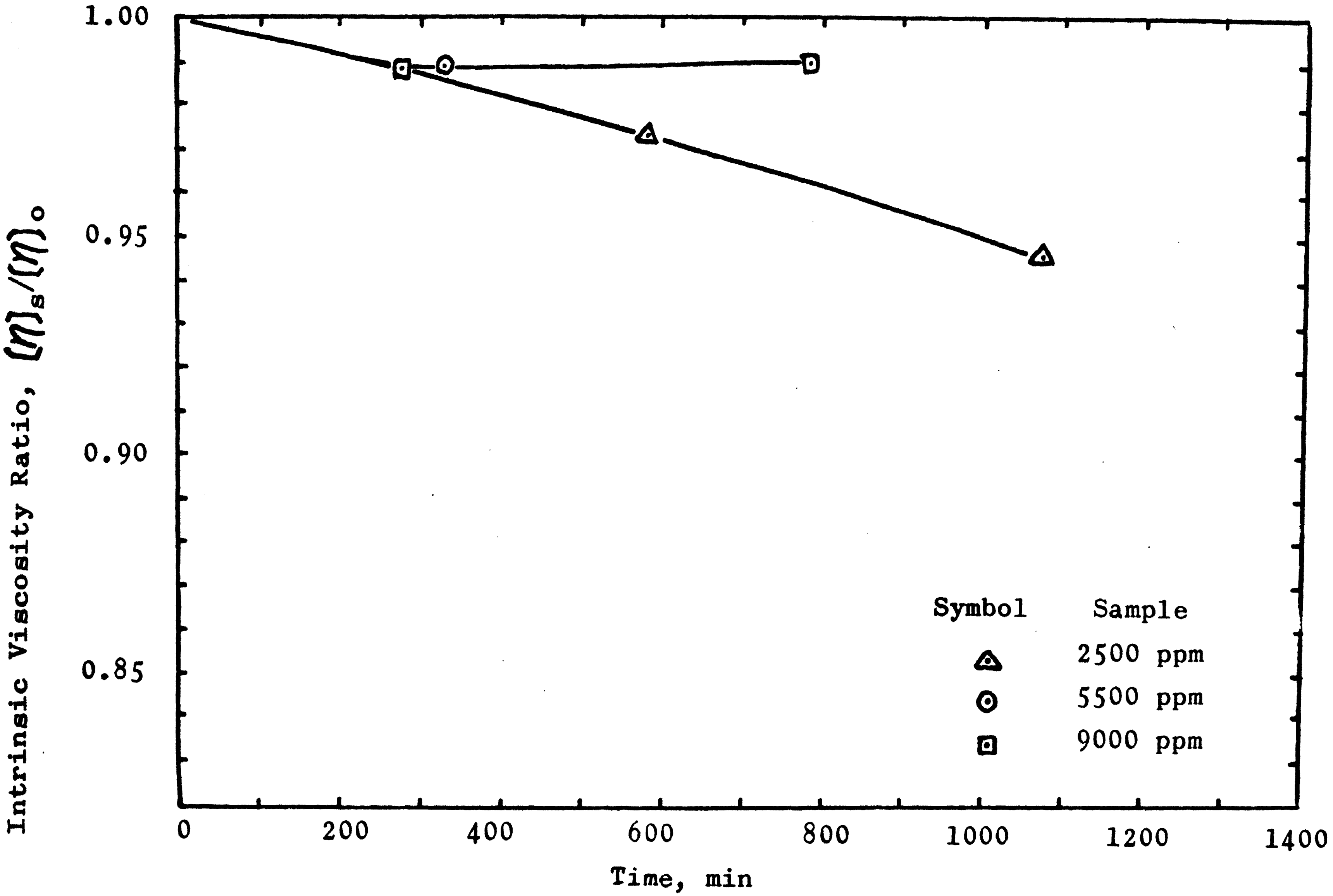


Figure 17. Effect of Pumping Time on Intrinsic Viscosity Ratio for Polymethyl Methacrylate-G in Toluene.

concentration solutions. However, since a smaller number of molecules were present in these solutions, the effect of each broken bond on the average molecular weight, and hence on the intrinsic viscosity, was larger. Number average molecular weights would be needed to determine whether more bonds were broken per unit pumping time in the more concentrated or in the less concentrated solutions.

It is clear that degradation occurred in all solutions and that no critical value of $(\overline{M}_v V)$ exists for PIB L-80 in cyclohexane in the range of concentrations studied (0.05 per cent to 0.3 per cent by weight) nor in benzene (0.25 per cent and 0.9 per cent by weight). Values of $(\overline{M}_v V)$ studied ranged from about 3×10^2 to 6×10^3. Hence, the critical value of $(\overline{M}_v V)$ of 16,000 suggested by Porter and Johnson (34), based on results for more concentrated solutions, does not apply to these dilute solutions. Furthermore, the degradation was found to occur in polymer solutions which were Newtonian from a shear rate of 3×10^2 to 1×10^5 $\sec^{-1}$ (55). Also, contrary to the results of Merrill, Mickley, and Ram (40), degradation occurred in PIB L-80 in cyclohexane, a polymer solvent combination in which they found no degradation in their splashing experimentals with dilute solutions. Thus, the combination of pumping and turbulent flow in pilot scale equipment gives more degradation than the results of these previous investigations might have predicted.

Comparison of the results for PIB L-80 in benzene and in cyclohexane at approximately equal concentrations (2,500 ppm and 3,000 ppm, respectively) shows that degradation is much more rapid in the benzene solution. The reason for this surprising result is not known. It may be related to the lower viscosity (0.76 centipoise) of the benzene solution compared with the cyclohexane solution (1.72 centipoise). Merrill, Mickley, and Ram (40) found a similar viscosity effect in their splashing experiments.

Comparison of Figures 15 and 17, pages 68 and 70, respectively, shows that for approximately equal concentrations of PMMA-G ($\overline{M}_v = 1.5 \times 10^6$)in toluene (2,500 ppm) and PIB L-80 ($\overline{M}_v = 7.26 \times 10^5$) in cyclohexane (3,000 ppm), the rates of degradation are about equal.

The effects of degradation on friction factors* in drag-reduction fluids** caused by pumping are shown in Figures 18 and 19, pages 73 and 74, respectively. At the highest

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* Fanning friction factor, $f = \frac{D \, \Delta P}{4 \, L} \Big/ \frac{\rho \, V^2}{2 \, g_c}$ (14)

** Drag-reduction refers to the phenomenon in which lower friction factors occur at the same flow rate in turbulent flow region with the addition of small amounts of polymer additives to the solvent.

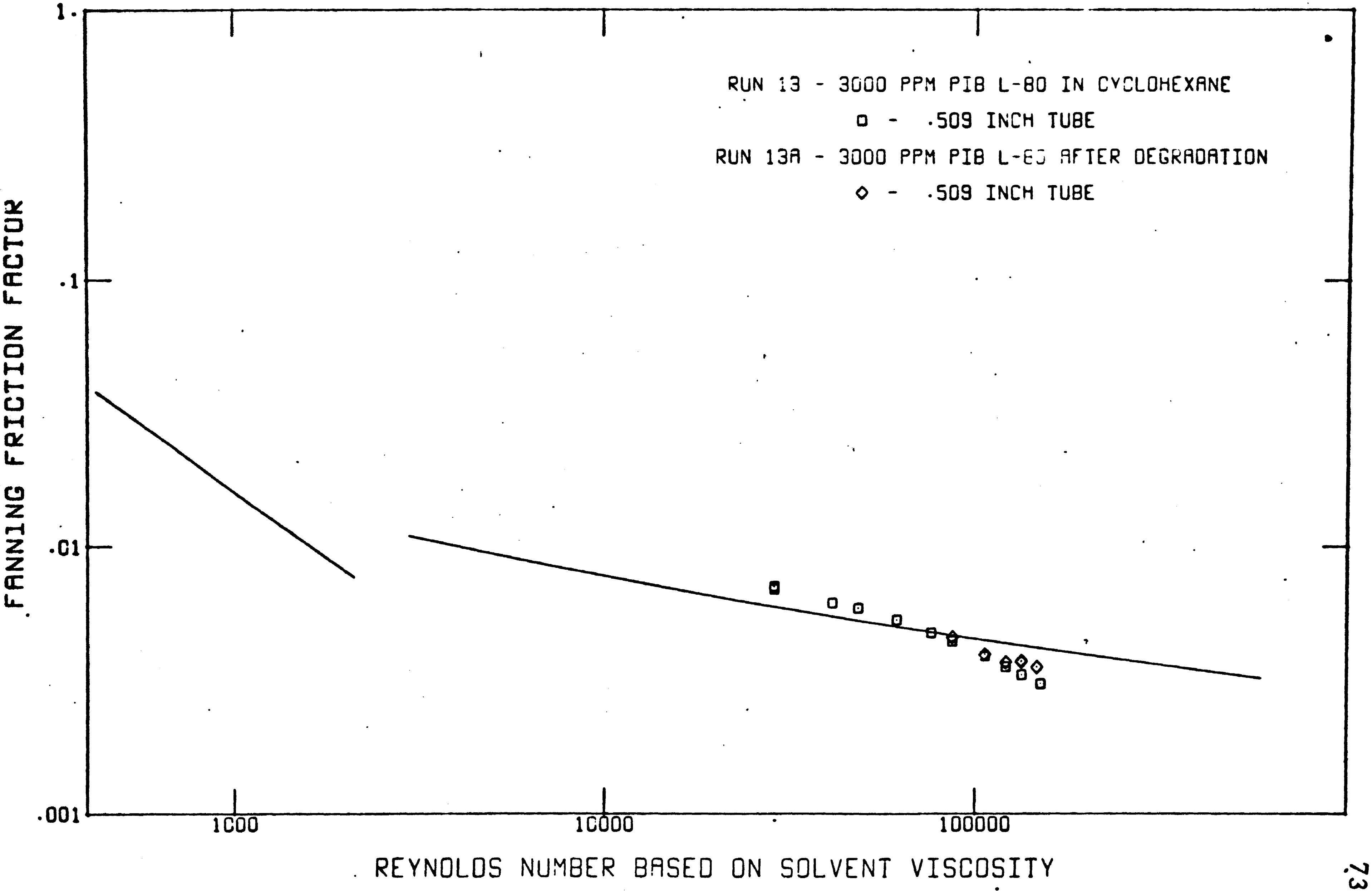

Figure 18. PLOT OF SOLVENT REYNOLDS NUMBER VERSUS FANNING FRICTION FACTOR (55)

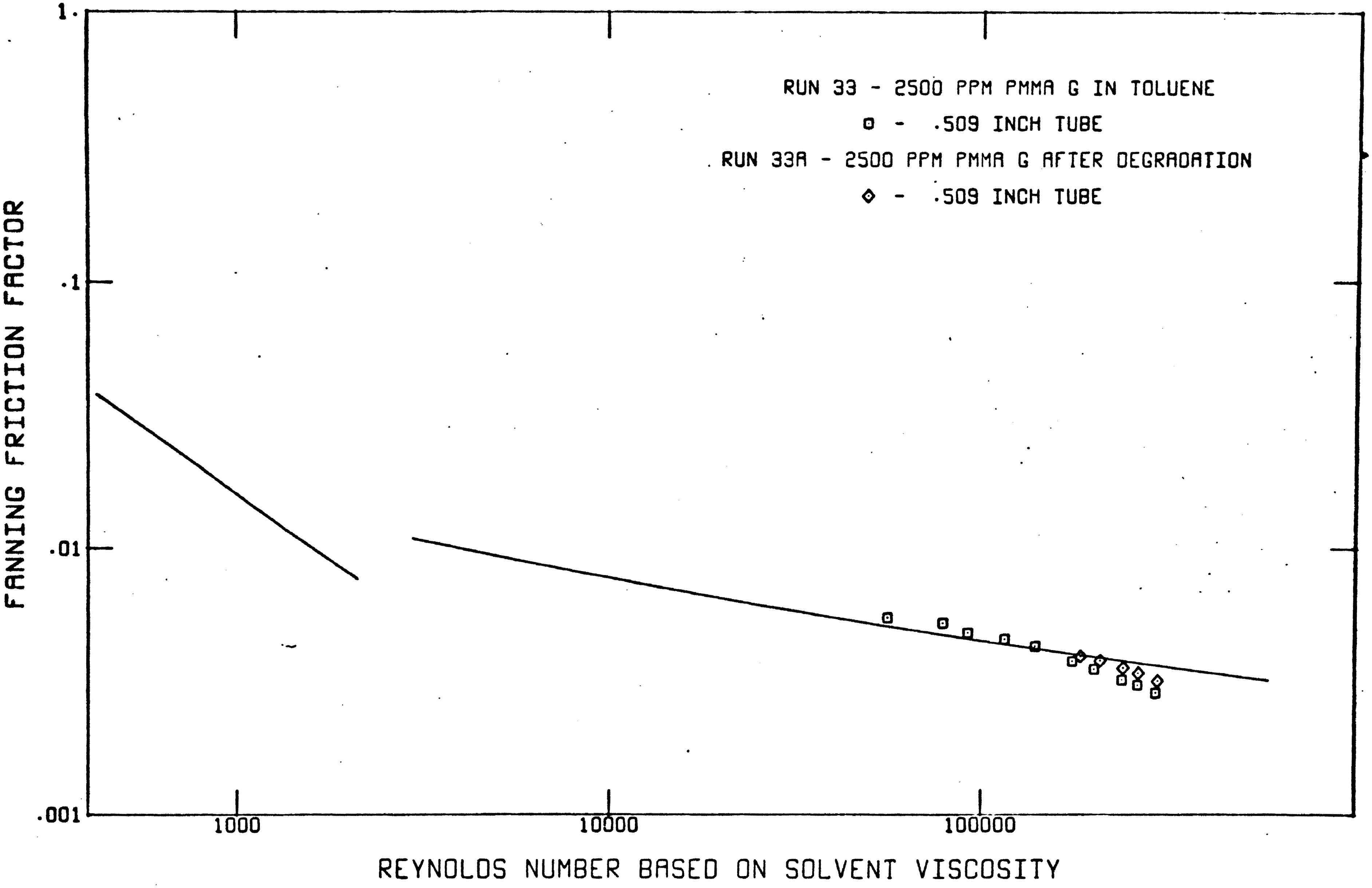

Figure 19. PLOT OF SOLVENT REYNOLDS NUMBER VERSUS FANNING FRICTION FACTOR (55).

Reynolds number (based on solvent viscosity), the 3,000 ppm PIB L-80 in cyclohexane solution showed a reduction in friction factor of 27 per cent at 570 minutes after pumping began compared with that calculated for the pure solvent. At the end of 1,385 minutes of pumping, the reduction in friction factor was only 16 per cent. Similar results were obtained for 2,500 ppm PMMA-G in toluene.

These results and the estimated ratios of degraded molecular weights to initial pumping solution molecular weights are shown in Table X, page 76.

It is of interest to note that the loss in drag reduction is about 40 per cent for both solutions, while their ratios of molecular weight at the time of the final measurements to that at the time of the initial measurements are both about 0.89.

Thus, a relatively large decrease in drag reduction is accompanied by a relatively small change in average molecular weight. This suggests that drag reduction may be dependent on the presence of a minor amount of very high molecular weight material which is very susceptible to rapid mechanical degradation, but which has a relatively small effect on the average molecular weight.

TABLE X

The Effect of Pumping Time on Degradation

Elapsed Pumping Time min	Max. % Drag Reduction (0.509" tube)*	% Mol. Wt. Reduction (based on initial pumping solution)
a. 3000 ppm PIB L-80 in Cyclohexane		
70	27	0.97
1385	16	0.86
b. 2500 ppm PMMA-G in Toluene		
0	21	1.00
1072	12	0.89

* Ref. (55)

C. Turbine Meter Calibration Study

The flow meter calibration data with various dilute polymer solutions are in Appendix E. Flow rate vs. meter reading in cycles per second (cps) for the 1 1/2-inch turbine flow meter is shown in Figure 20, page 78. A similar plot is shown in Figure 21, page 79, for the 3/4-inch turbine flow meter. Because of the large number of points obtained at many of the meter readings, vertical bars are used to show the range of the flow data.

A first degree least-squares line was drawn on each plot. For the 1 1/2-inch meter the standard deviation was 0.674 and the average per cent error was 1.77. For the 3/4-inch meter the standard deviation was 0.145 and the average per cent error was 1.95. Thus, it can be seen that over a wide range of flow rates, for fluids ranging in viscosity from 0.607 to 6.676 centistokes, a straight line fits the calibration data quite satisfactorily.

Figures 22 and 23, pages 80 and 81, respectively, show plots of the calibration factor, f/Q vs. $\log (f/\nu)$ for both meters. With the expanded vertical scale used, the data show considerable scatter but no trend of calibration factor values with variations in f/ν over ranges of about 40 : 1 for the 1 1/2-inch meter and about 12 : 1 for the 3/4-inch meter. Thus, the meter calibrations are linear in the ranges of f/ν studied. The average values of the

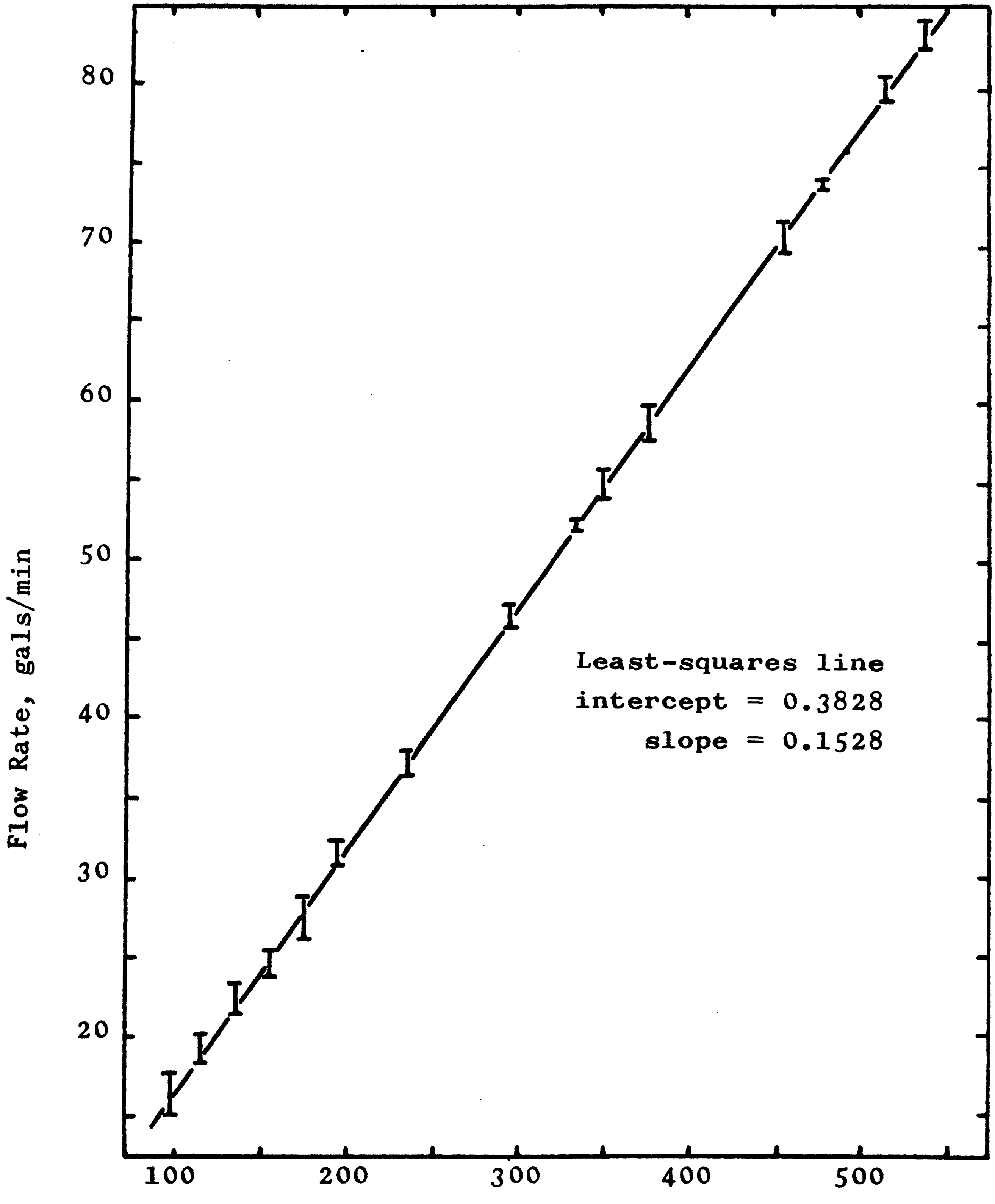

Figure 20. Flow Rate vs. Meter Reading for 1 1/2" Turbine Flow Meter.

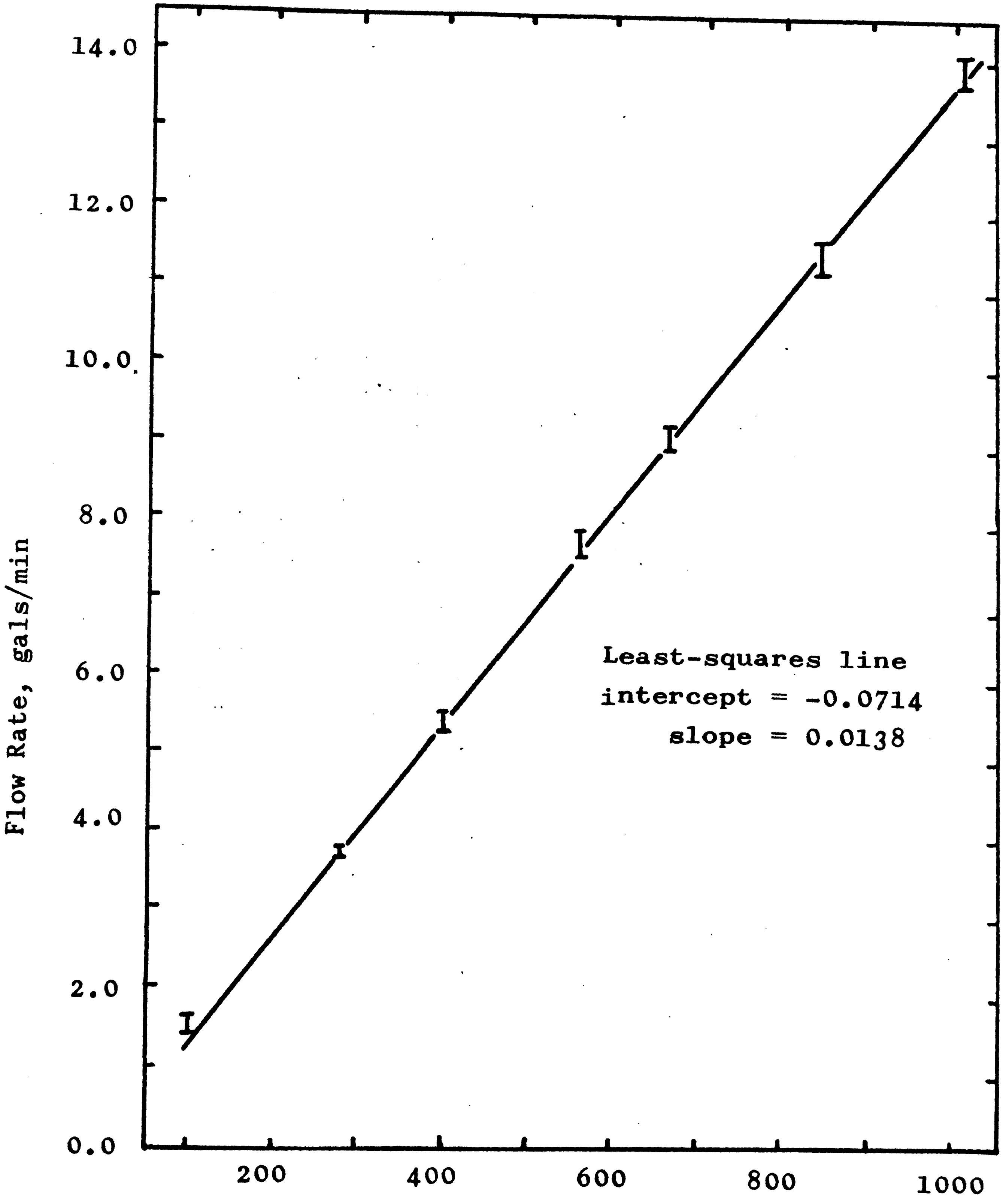

Figure 21. Flow Rate vs. Meter Reading for 3/4" Turbine Flow Meter.

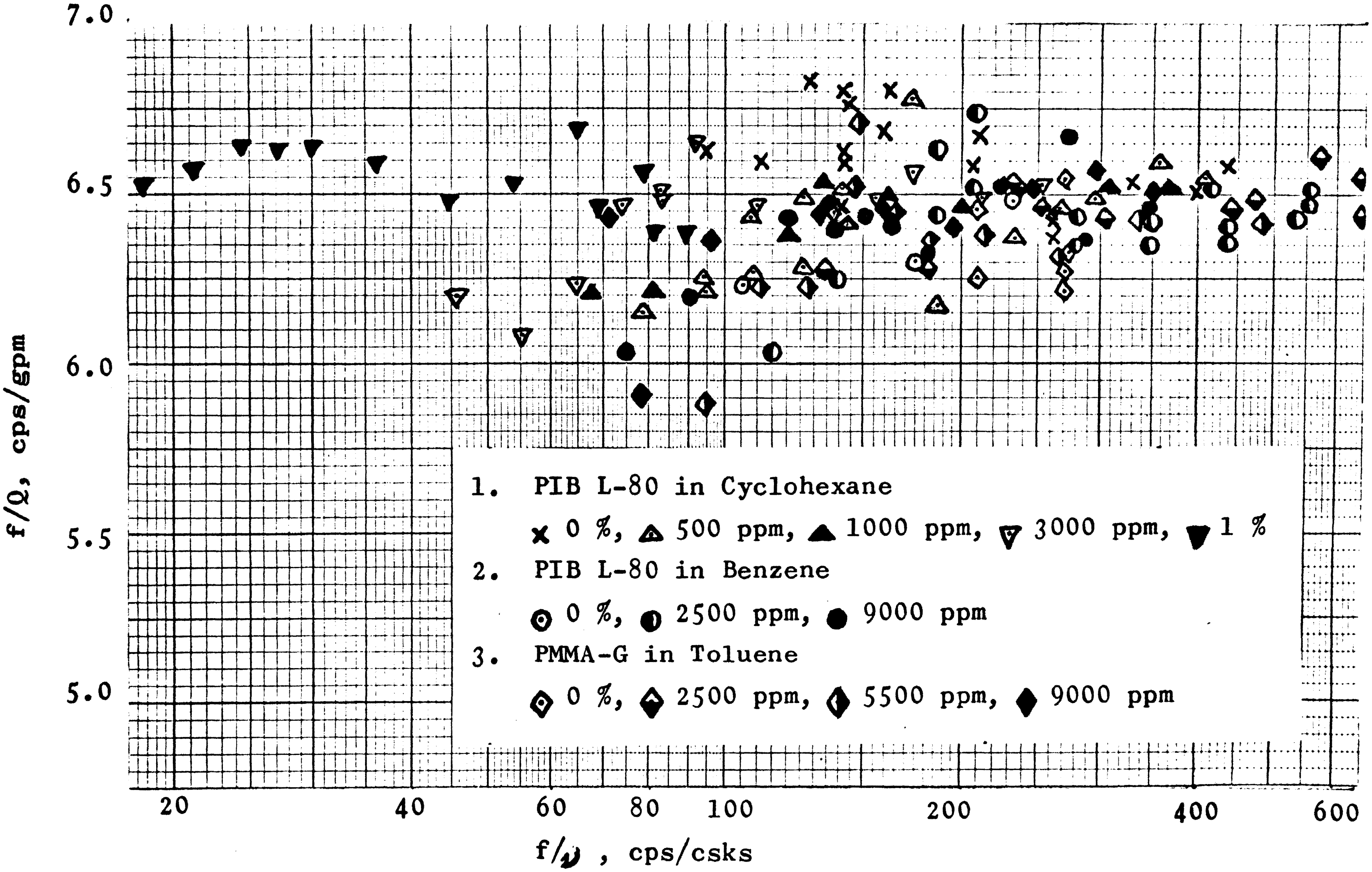

Figure 22. Effect of Flow Rate and Viscosity on the Calibration Factor 1 1/2" Turbine Flow Meter.

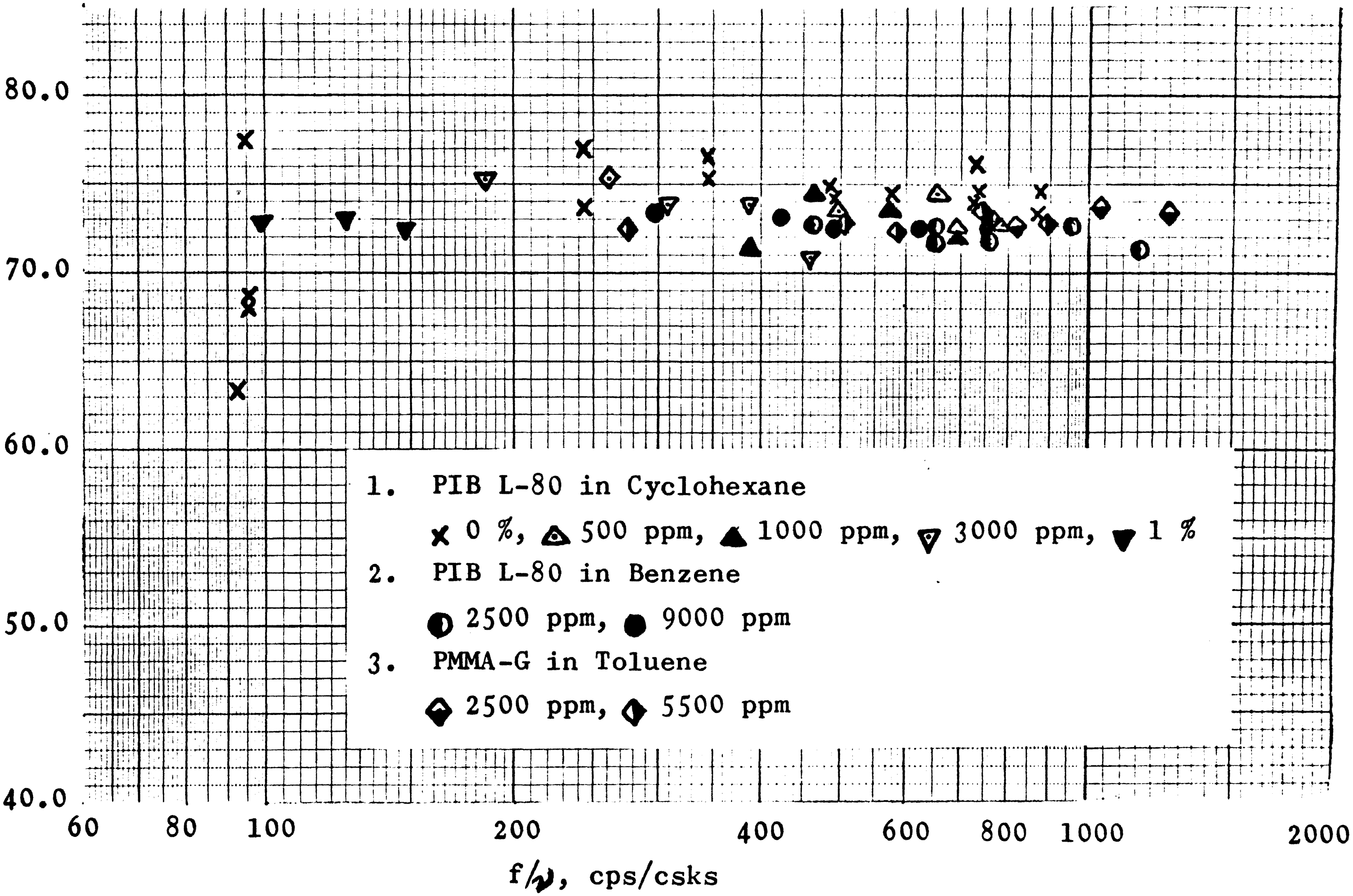

Figure 23. Effect of Flow Rate and Viscosity on the Calibration Factor 3/4" Turbine Flow Meter.

calibration factors obtained in this installation with organic solvents and solutions compared with the manufacturer's calibration with water are shown in Table XI.

TABLE XI

Calibration Factors for Turbine Meters

Meter Size inches	$(f/Q)_{mean}$ cycles/gallon	Manufacturer's (42) Calibration Factor cycles/gallon
3/4	4390.2	4362.0
1-1/2	394.8	397.0

The differences between the calibrations are less than 0.7 per cent.

One solution studied, 1.0 per cent PIB L-80 in cyclohexane, was non-Newtonian. Its rheological characteristics in capillary flow at high shear rate can be expressed by the equation: (73)

$$(-\Delta P\ D/4\ L) = 0.124\ (8\ V/D)^{0.88} \qquad (15)$$

where $\Delta P/L$ = pressure gradient, dynes/centimeter^3

V = average flow velocity, centimeters/second

D = tube diameter, centimeters.

In plotting f/ν for this solution, its low shear rate (Newtonian) viscosity was used. The data points for this non-Newtonian solution are indistinguishable from the rest of the data.

V. SUMMARY AND CONCLUSIONS

Intrinsic viscosities of five samples of polystyrene in toluene, three samples of polyisobutylene in cyclohexane and benzene and one sample of polymethyl methacrylate in toluene were determined by linear extrapolation of viscosity-concentration data using the Huggins equation. Molecular weights estimated from these results were used for selecting samples for turbulent pumping experiments.

Intrinsic viscosities calculated by one-point methods were within 6 per cent of the extrapolated values for all samples where the Huggins constant, k', was less than 0.6. For polyisobutylene of $\bar{M}_v \approx 726{,}000$ in benzene where k' = 1.2, the one-point method was unsatisfactory.

Huggins constants of about 0.32 were found for four polystyrene samples of molecular weights between 97,000 and 242,000 in toluene. A higher value of k' = 0.44 was obtained for a 19,000 molecular weight sample, confirming previous reports that the k' value rises at molecular weights below 50,000.

A gravimetric method for determining the concentration of a polymer solution was found to be satisfactory for polystyrene ($\bar{M}_v \approx 242{,}000$) up to 0.86 gm/dl. However, erratic results were obtained with a low molecular weight ($\bar{M}_v \approx 50{,}000$) polyisobutylene in cyclohexane. Apparent thermal degradation led to consistently low concentration values for high molecular weight polyisobutylene ($\overline{M}_v \approx$ 726,000) in benzene.

The effect of pumping and turbulent flow on the degradation of a polymer in dilute solution was studied. The solutions studied were polyisobutylene ($\overline{M}_v \approx$ 726,000) in cyclohexane (0.05 to 0.3 per cent), polyisobutylene in benzene (0.25 to 0.9 per cent) and polymethyl methacrylate ($\overline{M}_v \approx 1.5 \times 10^6$) in toluene (0.25 to 0.9 per cent).

Samples were taken at the start of pumping, and after pumping was completed, as well as at some intermediate times. All pumped samples showed degradation.

For equal pumping times, low concentration polymer solutions degraded to lower molecular weights than higher concentration solutions. This may reflect the same rate of bond breaking in both solutions, but with a higher proportion of molecules present in the less concentrated solution being affected.

No critical value of molecular weight times volume fraction ($\overline{M}_v$ V) was found for polyisobutylene solutions in benzene or cyclohexane. Degradation occurred in a 726,000 molecular weight sample at concentrations ranging from 0.05 to 0.9 per cent. This is contrary to previous published reports which state that no degradation was observed below

$\overline{M}_v$ = 2,200,000 or $(\overline{M}_v V)_c \approx$ 16,000. However, the latter value was based on experiments in more concentrated solutions.

For equal pumping times and nearly equal concentrations, a polyisobutylene sample showed much more degradation in benzene solution than in cyclohexane. This may be due to the lower viscosity of the benzene solution.

For approximately equal concentrations of the 1.5×10^6 molecular weight sample of polymethyl methacrylate and the 7.26×10^5 molecular weight sample of polyisobutylene in cyclohexane, the rates of degradation were about the same, about 7 per cent of molecular weight in 1,000 minutes of pumping.

Friction factor measurements in flow of the solutions through a 0.509-inch tube showed that there is a decrease in the maximum amount of drag reduction attainable, with 3,000 ppm PIB L-80 in cyclohexane and 2,500 ppm PMMA-G in toluene, as pumping proceeds. This coincides with mechanical degradation of the polymer molecules. For both solutions, the loss in per cent drag reduction caused by degradation is considerably greater than the per cent loss in molecular weight. This suggests that drag reduction may be dependent on the presence of a minor amount of very high molecular weight material which is very susceptible to degradation, but which has a relatively small effect on the average molecular weight.

A 3/4-inch and a 1 1/2-inch turbine flow meter were calibrated with organic solutions which ranged from 0.6 to 6.7 centistokes in kinematic viscosity. Plots of frequency vs. flow rate were linear for both meters. The calibration factors, f/Q, were constant over the range of f/ν values studied (40 : 1 for the 1 1/2-inch meter and 12 : 1 for the 3/4-inch meter). The average of the calibration factors for organic solutions differed from the manufacturer's calibrations with water by less than 0.7 per cent. Data for a non-Newtonian fluid gave the same calibration factor as for Newtonian fluids.

VI. APPENDICES

A list of materials used in the investigation is given in Appendix A. Appendix B contains the calibration data for the pycnometer. All experimental data for the intrinsic viscosity measurements collected during the investigation are listed in Appendix C. The concentration analysis data are given in Appendix D. The flow meter calibration data are listed in Appendix E. All sample calculations are listed in Appendix F.

APPENDIX A

List of Materials and Their Specifications

A. Polymers

Three kind of linear high polymers were used in this investigation: polystyrene, polyisobutylene, and polymethyl methacrylate.

Polystyrene. Five polystyrene samples were donated by the Dow Chemical Co., Midland, Michigan. They were:

Designation	Grade	Lot Number
A	Dow Resin PS 2	71237-62-000
B	Styron 678	83131-67-000
C	Styron 666	82888-67-000
D	Styron 683	83170-67-000
E	Styron 690	83365-67-000

They were all thermally polymerized with a molecular weight distribution having an $\bar{M}_w/\bar{M}_n$ ratio of 2.2 to 2.7. Polymers B and C had, respectively, 4 per cent and 1 per cent mineral oil additives. The only other impurities present in all these samples would be small amounts of volatiles present due to incomplete devolatilization during production.

Polyisobutylene. Three polyisobutylene samples were donated by the Humble Oil and Refining Co., Baton Rouge, Louisiana. They were:

Type	Grade	Lot Number
LM Vistanex	MH	-
LM Vistanex	MS	-
MM Vistanex	L-80	B40828 230

They were produced at very low temperatures (~ -140°F) using Friedel-Craft-type catalyst and alkyl halide solvents for the catalyst and feed. They were catalyst-free with trace amounts of antioxidant (butylated hydroxytoluene) and sodium stearate; molecular weight distribution unknown.

Polymethyl Methacrylate. Polymethyl Methacrylate-G, produced in the form of 1/4-inch plexiglass sheet, was donated by the Rohm and Haas Co., Philadelphia, Pa.

B. Solvents

Three organic solvents were used in this investigation: toluene, cyclohexane, and benzene.

Toluene (A). Mallinckrodt Purified (Toluol); sp. gr. 0.861; 35 lb st. dr.

Toluene (B). Purity (weight per cent toluene) 99.5 per cent minimum; impurities - heptane isomers 0.5 per cent maximum boiling range 1.0°C, including 110.6°C; sp. gr. between 0.869 and 0.873 at 15.5°C; nitration grade; purchased from G. S. Robins Co., St. Louis, Mo.

Cyclohexane. Purity (weight per cent cyclohexane) 99.9 per cent minimum; impurities non volatiles, water, benzene 0.1 per cent maximum; sp. gr. range 0.780 to 0.784 at 15.5°C; purchased from G. S. Robins Co., St. Louis, Mo.

<u>Benzene</u>. Sp. gr. range 0.882 to 0.886; maximum boiling range 1°C, including 80.1°C; color (Saybolt) 30; acid wash color - 0 to 1; acidity-negative; corrosion-16 maximum; sulfur as H_2S/SO_2 negative; thiophene free; purchased from Independent Petrochemical Corp., St. Louis, Mo.

APPENDIX B

Calibration Data for the Pycnometer

At 30^{o}C Density of Water = 0.99567 gm/ml (64)

Pycnometer Reading	Weight of Water in Air gm	Weight of Water in Vacuo gm	Calculated Volume ml
10.46	5.0964	5.0987	5.1209
6.32	5.0481	5.0473	5.0693
12.28	5.1165	5.1219	5.1441
11.61	5.1080	5.1141	5.1363
10.38	5.0947	5.1000	5.1222
7.08	5.0569	5.0561	5.0781
5.81	5.0412	5.0465	5.0684
4.62	5.0275	5.0612	5.0832
3.60	5.0139	5.0192	5.0410
.60	4.9804	4.9797	5.0013
.22	4.9766	4.9759	4.9975
9.75	5.0885	5.0877	5.1099
3.44	5.0126	5.0118	5.0336
14.63	5.1438	5.1430	5.1654
13.53	5.1312	5.1304	5.1527
12.38	5.1172	5.1164	5.1387
11.60	5.1072	5.1064	5.1286
10.58	5.0973	5.0965	5.1187
9.32	5.0825	5.0817	5.1038
8.97	5.0784	5.0776	5.0997
8.15	5.0685	5.0677	5.0898
7.33	5.0587	5.0579	5.0799
6.68	5.0513	5.0505	5.0725
5.75	5.0396	5.0388	5.0608
5.12	5.0322	5.0314	5.0533
4.45	5.0240	5.0232	5.0451
4.12	5.0195	5.0187	5.0406
2.33	4.9980	4.9972	5.0190
1.47	4.9898	4.9891	5.0107
.28	4.9754	4.9747	4.9963
10.25	5.0990	5.0982	5.1204
9.52	5.0849	5.0841	5.1062
8.91	5.0781	5.0773	5.0994
14.37	5.1414	5.1406	5.1630
8.57	5.0738	5.0730	5.0951
2.80	5.0052	5.0044	5.0262

Calibration Data for the Pycnometer

At 20^{o}C Density of Water = 0.99823 gm/ml (64)

Pycnometer Reading	Weight of Water in Air gm	Weight of Water in Vacuo gm	Calculated Volume ml
13.20	5.1407	5.1399	5.1490
12.00	5.1259	5.1251	5.1342
11.18	5.1154	5.1146	5.1237
10.08	5.1018	5.1010	5.1101
9.05	5.0931	5.0923	5.1014
8.11	5.0815	5.0807	5.0897
3.75	5.0301	5.0293	5.0383
1.15	4.9994	4.9986	5.0075
14.00	5.1515	5.1507	5.1599
3.22	5.0231	5.0223	5.0313
.60	4.9943	4.9935	5.0024
13.80	5.1487	5.1479	5.1571
10.05	5.1036	5.1028	5.1119
9.21	5.0964	5.0956	5.1047
7.60	5.0765	5.0757	5.0847
4.95	5.0447	5.0439	5.0529
12.55	5.1337	5.1329	5.1420
10.02	5.1018	5.1010	5.1101
6.65	5.0641	5.0633	5.0723
.16	4.9881	4.9874	4.9962
2.34	5.0128	5.0120	5.0209

APPENDIX C

Intrinsic Viscosity Measurement Data

No.	Solvent Wt. added gm	Conc. gm/dl	Density gm/ml	Efflux Time sec	ν csks	η_{sp}	η_{sp}/C dl/gm
Polystyrene-A in Toluene (B) at 30°C							
1**	14.1819	1.0000	.8591	547.82	.7180	.1858	.1858
2	5.2688	.7287	.8586	524.26	.6869	.1338	.1836
3	4.1272	.6010	.8584	512.83	.6718	.1086	.1807
4	4.7036	.5009	.8582	504.27	.6605	.0897	.1791
5	14.0331	.3347	.8579	490.13	.6418	.0586	.1750
6	8.7270	.2774	.8578	485.30	.6354	.0479	.1727
7	9.8800	.2324	.8577	481.52	.6305	.0396	.1703
8	7.8552	.2059	.8577	479.39	.6276	.0349	.1695
9	9.5359	.1808	.8576	477.29	.6249	.0303	.1674
10	12.6997	.1556	.8576	475.48	.6225	.0263	.1689
Polystyrene-B in Toluene (A) at 30°C							
1**	13.1647	1.0000	.8587	738.40	.9692	.6076	.6076
2	4.8425	.7304	.8579	658.24	.8636	.4310	.5901
3	6.0042	.5474	.8573	604.53	.7928	.3128	.5715
4	3.9288	.4703	.8571	582.95	.7643	.2653	.5642
5	37.9901	.1991	.8563	511.43	.6699	.1080	.5426
* 6	23.3724	.1470	.8561	498.25	.6525	.0790	.5378
Polystyrene-C in Toluene (B) at 30°C							
1**	16.5078	1.5048	.8602	1190.13	1.5640	1.5798	1.0498
2	10.3290	.9245	.8592	865.50	1.1366	.8727	.9439
3	15.0471	.5920	.8586	704.04	.9240	.5213	.8805
4	20.7031	.3960	.8583	618.55	.8113	.3352	.8464

** solution

* nonlinear point

Intrinsic Viscosity Measurement Data

No.	Solvent Wt. added gm	Conc. gm/dl	Density gm/ml	Efflux Time sec	ν csks	η_{sp}	η_{sp}/C dl/gm
Polystyrene-D in Toluene (B) at 30°C							
1**	14.8046	1.5186	.8605	1270.81	1.6702	1.7630	1.1609
2	8.1445	.9784	.8594	929.80	1.2213	1.0178	1.0403
3	4.8634	.8069	.8590	833.98	1.0951	.8086	1.0020
4	5.4960	.6736	.8587	763.67	1.0025	.6551	.9725
5	7.1924	.5538	.8585	703.29	.9230	.5233	.9449
* 6	10.4231	.4403	.8583	652.74	.8563	.4129	.9378
* 7	9.9255	.3684	.8581	621.13	.8147	.3439	.9335
* 8	16.4315	.2900	.8579	587.44	.7702	.2704	.9323
* 9	13.9314	.2457	.8578	572.01	.7499	.2367	.9633
Polystyrene-E in Toluene (B) at 30°C							
1**	14.9653	1.9792	.8616	2036.13	2.6770	3.4340	1.7351
2	5.9175	1.4164	.8604	1453.64	1.9107	2.1604	1.5253
3	6.5619	1.0768	.8596	1159.22	1.5233	1.5174	1.4092
4	6.4496	.8715	.8592	997.34	1.3102	1.1642	1.3359
5	8.0880	.7033	.8588	874.53	1.1485	.8963	1.2745
6	9.5313	.5730	.8586	786.56	1.0327	.7045	1.2295
7	9.4855	.4838	.8584	729.38	.9574	.5798	1.1985
8	8.5826	.4240	.8582	692.35	.9086	.4990	1.1769
9	15.6064	.3463	.8581	646.02	.8475	.3980	1.1494
10	7.2758	.3190	.8580	630.73	.8273	.3647	1.1432
PIB-LMMH in Cyclohexane at 25°C							
1**	13.0846	1.7031	.7781	1729.88	2.2741	.9899	.5813
2	1.3560	1.5423	.7777	1626.50	2.1381	.8699	.5640
3	1.9845	1.3551	.7772	1524.50	2.0039	.7514	.5545
4	2.2761	1.1895	.7767	1436.83	1.8886	.6497	.5462
5	3.7689	.9893	.7762	1329.96	1.7480	.5258	.5315
6	9.8059	.6880	.7754	1179.54	1.5500	.3516	.5111
7	20.3650	.4215	.7747	1056.20	1.3877	.2090	.4958
8	23.2754	.2921	.7744	999.62	1.3132	.1436	.4915

Intrinsic Viscosity Measurement Data

No.	Solvent Wt. added gm	Conc. gm/dl	Density gm/ml	Efflux Time sec	ν csks	η_{sp}	η_{sp}/C dl/gm
PIB-LMMS in Cyclohexane at $25^{o}C$							
1**	13.7535	1.2357	.7724	1478.34	1.9432	.6879	.5567
2	3.8520	.9657	.7727	1331.68	1.7502	.5208	.5393
3	4.8332	.7579	.7729	1226.04	1.6112	.4004	.5283
4	5.1726	.6160	.7730	1155.65	1.5186	.3201	.5197
5	3.1687	.5526	.7731	1125.57	1.4790	.2858	.5172
6	1.5628	.5259	.7731	1113.85	1.4636	.2724	.5180
*7	2.5961	.4869	.7731	1096.96	1.4414	.2532	.5200
8	2.6179	.4530	.7732	1079.92	1.4189	.2337	.5160
9	6.2218	.3886	.7732	1049.21	1.3785	.1987	.5112
*10	10.9768	.3107	.7733	1015.78	1.3345	.1605	.5165
PIB L-80 in Cyclohexane at $25^{o}C$							
1**	19.6618	.3015	.7868	1992.39	2.6195	1.3179	4.3710
2	6.8769	.2224	.7834	1655.98	2.1769	.9178	4.1269
3	8.8645	.1662	.7809	1434.42	1.8854	.6557	3.9460
4	9.8100	.1299	.7793	1300.50	1.7092	.4979	3.8344
5	14.8256	.0976	.7779	1187.78	1.5609	.3654	3.7437
* 6	15.0848	.0779	.7770	1121.34	1.4734	.2875	3.6896
* 7	7.7831	.0706	.7767	1097.85	1.4425	.2600	3.6833
PIB-LMMH in Benzene at $24^{o}C$							
1**	15.7154	1.4995	.8742	745.61	.9787	.4174	.2784
2	1.3870	1.3775	.8739	725.65	.9524	.3789	.2751
3	3.3921	1.1489	.8735	688.47	.9034	.3073	.2675
4	5.1312	.9184	.8730	653.05	.8568	.2391	.2604
5	10.5021	.6510	.8725	613.85	.8051	.1637	.2514
* 6	22.9645	.3978	.8720	580.20	.7607	.0989	.2486
* 7	21.8109	.2905	.8718	569.97	.7472	.0792	.2725

Intrinsic Viscosity Measurement Data

No.	Solvent Wt. added gm	Conc. gm/dl	Density gm/ml	Efflux Time sec	ν csks	η_{sp}	η_{sp}/C dl/gm
PIB-LMMS in Benzene at 24°C							
1**	20.0929	1.4972	.8750	748.24	.9822	.4238	.2831
2	2.0422	1.3585	.8747	725.56	.9523	.3799	.2797
3	2.0578	1.2426	.8744	706.90	.9277	.3438	.2767
4	4.5392	1.0457	.8739	675.28	.8861	.2828	.2704
5	9.6544	.7821	.8732	634.53	.8323	.2041	.2609
6	12.9118	.5849	.8727	605.67	.7943	.1484	.2537
7	16.5440	.4421	.8724	585.84	.7681	.1101	.2490
* 8	21.1378	.3370	.8721	573.60	.7520	.0864	.2565
PIB L-80 in Benzene at 24°C							
1**	14.8495	1.4024	.8773	2497.08	3.2833	3.7590	2.6804
2	3.9457	1.1070	.8766	1742.85	2.2912	2.3180	2.0940
3	4.1722	.9054	.8760	1374.50	1.8066	1.6146	1.7834
4	11.0472	.6108	.8752	979.19	1.2863	.8600	1.4081
5	10.7837	.4635	.8749	835.16	1.0967	.5851	1.2622
6	19.0136	.3253	.8745	724.00	.9503	.3729	1.1463
7	18.7077	.2515	.8743	667.98	.8764	.2659	1.0575
PMMA-G in Toluene (B) at 30°C							
1 **	10.0478	1.1084	.8613	–	–	–	–
2	1.6747	.9494	.8607	1573.28	2.0681	2.4220	2.5510
3	3.8281	.7150	.8599	1205.60	1.5843	1.6190	2.2642
4	4.5794	.5520	.8593	998.45	1.3117	1.1668	2.1139
5	5.5689	.4322	.8589	864.65	1.1355	.8749	2.0244
6	7.0088	.3394	.8585	767.85	1.0080	.6637	1.9555

Intrinsic Viscosity Measurement Data

No.	Solvent Wt. added	Conc.	Density	Efflux Time	ν	η_{sp}	η_{sp}/C
	gm	gm/dl	gm/ml	sec	csks		dl/gm
500 ppm (1 st) PIB L-80 in Cyclohexane at 25°C							
1	**14.6232	.0372	.7738	985.75	1.2950	.1268	3.4090
* 2	6.4989	.0258	.7737	952.90	1.2517	.0891	3.4602
* 3	5.9282	.0201	.7737	936.98	1.2308	.0708	3.5228
500 ppm (2 nd) PIB L-80 in Cyclohexane at 25°C							
1	**17.1646	.0372	.7738	977.76	1.2845	.1177	3.1630
*2	6.5204	.0270	.7737	951.07	1.2493	.0870	3.2281
*3	7.6463	.0204	.7737	935.01	1.2282	.0686	3.3656
*4	5.8859	.0172	.7737	926.62	1.2171	.0590	3.4365
500 ppm (3 rd) PIB L-80 in Cyclohexane at 25°C							
1	**15.9034	.0372	.7738	977.63	1.2843	.1175	3.1590
* 2	5.0474	.0282	.7737	954.56	1.2539	.0910	3.2238
* 3	9.2532	.0196	.7737	931.81	1.2240	.0649	3.3144
1000 ppm (1 st) PIB L-80 in Cyclohexane at 25°C							
1	**16.1442	.0756	.7739	1105.45	1.4525	.2642	3.4942
* 2	11.6292	.0439	.7738	1009.21	1.3259	.1537	3.4984
* 3	9.7942	.0325	.7737	974.24	1.2798	.1136	3.4970
* 4	10.9769	.0251	.7737	953.88	1.2530	.0902	3.5893
1000 ppm (2 nd) PIB L-80 in Cyclohexane at 25°C							
1	**14.5045	.0756	.7739	1098.33	1.4432	.2560	3.3863
2	6.8700	.0513	.7738	1020.18	1.3403	.1663	3.2425
* 3	7.9275	.0374	.7737	985.41	1.2945	.1264	3.3786
3000 ppm (1 st) PIB L-80 in Cyclohexane at 25°C							
1	**18.0301	.2378	.7745	1684.97	2.2151	.9293	3.9076
2	8.6680	.1605	.7742	1391.70	1.8292	.5926	3.6913
3	10.8408	.1142	.7740	1230.66	1.6173	.4078	3.5723
4	13.7169	.0836	.7739	1130.75	1.4858	.2931	3.5068
* 5	12.0781	.0676	.7738	1081.82	1.4214	.2370	3.5035

Intrinsic Viscosity Measurement Data

No.	Solvent Wt. added gm	Conc. gm/dl	Density gm/ml	Efflux Time sec	ν csks	η_{sp}	η_{sp}/C dl/gm
3000 ppm (2 nd) PIB L-80 in Cyclohexane at 25°C							
1	**13.4420	.2378	.7745	1669.17	2.1943	.9112	3.8314
2	5.1580	.1718	.7742	1426.20	1.8746	.6322	3.6798
3	11.0942	.1076	.7740	1204.21	1.5825	.3775	3.5084
*4	10.0281	.0804	.7739	1118.27	1.4694	.2788	3.4674
*5	6.0380	.0698	.7739	1065.20	1.3996	.2180	3.1228
*6	14.0572	.0534	.7738	1023.90	1.3452	.1706	3.1946
3000 ppm (3 rd) PIB L-80 in Cyclohexane at 25°C							
1	**11.5070	.2378	.7745	1616.49	2.1250	.8508	3.5776
2	7.8601	.1412	.7741	1290.91	1.6966	.4770	3.3775
3	6.6789	.1050	.7740	1177.51	1.5474	.3469	3.3034
3000 ppm (4 th) PIB L-80 in Cyclohexane at 25°C							
1	**14.2655	.2378	.7745	1588.70	2.0884	.8190	3.4437
2	5.7976	.1690	.7742	1358.70	1.7858	.5549	3.2825
3	4.0917	.1404	.7741	1270.39	1.6696	.4535	3.2304
4	6.3472	.1112	.7740	1182.44	1.5539	.3525	3.1716
* 5	16.0186	.0729	.7739	1082.19	1.4219	.2375	3.2587
* 6	9.3942	.0606	.7738	1039.53	1.3658	.1885	3.1097
2500 ppm (1 st) PIB L-80 in Benzene at 24°C							
1	**12.9083	.2400	.8740	646.88	.8486	.2254	.9390
2	3.1983	.1923	.8739	620.35	.8136	.1748	.9086
* 3	5.4948	.1434	.8739	596.87	.7827	.1299	.9063
4	7.4550	.1066	.8738	577.56	.7572	.0931	.8735
* 5	6.6874	.0866	.8738	568.28	.7450	.0754	.8701
2500 ppm (2 nd) PIB L-80 in Benzene at 24°C							
1	**13.3797	.2400	.8740	631.67	.8286	.1964	.8184
* 2	4.9274	.1754	.8739	603.24	.7911	.1421	.8105
* 3	4.2172	.1425	.8739	588.92	.7722	.1148	.8055
* 4	8.8737	.1022	.8738	572.42	.7504	.0833	.8148
* 5	6.1427	.0855	.8738	565.48	.7413	.0701	.8193

Intrinsic Viscosity Measurement Data

No.	Solvent Wt. added gm	Conc. gm/dl	Density gm/ml	Efflux Time sec	ν csks	η_{sp}	η_{sp}/C dl/gm
2500 ppm (3 rd) PIB L-80 in Benzene at 24°C							
1 **	12.8711	.2400	.8740	626.20	.8214	.1860	.7750
* 2	3.9662	.1834	.8739	597.76	.7839	.1317	.7181
* 3	3.8631	.1492	.8739	585.69	.7679	.1087	.7284
* 4	5.8016	.1165	.8738	573.37	.7517	.0851	.7307
* 5	9.6123	.0855	.8738	560.78	.7351	.0611	.7147
* 6	5.5260	.0742	.8737	550.92	.7221	.0423	.5705
9000 ppm (1 st) PIB L-80 in Benzene at 24°C							
1 **	12.7625	.8214	.8750	1097.40	1.4419	1.0845	1.3204
2	4.3627	.6119	.8747	902.84	1.1858	.7136	1.1662
3	3.5100	.5077	.8745	823.25	1.0810	.5618	1.1066
4	7.7658	.3688	.8743	725.31	.9520	.3750	1.0169
* 5	10.0238	.2725	.8741	676.44	.8876	.2818	1.0339
9000 ppm (2 nd) PIB L-80 in Benzene at 24°C							
1 **	13.9019	.8214	.8750	1012.02	1.3296	.9221	1.1226
2	5.2601	.5956	.8747	843.54	1.1077	.6007	1.0085
3	6.1772	.4503	.8744	752.40	.9877	.4268	.9478
* 4	7.7404	.3449	.8742	692.04	.9081	.3116	.9036
* 5	3.6833	.3103	.8742	671.95	.8817	.2733	.8808
* 6	9.1436	.2485	.8741	640.60	.8403	.2135	.8592
9000 ppm (3 rd) PIB L-80 in Benzene at 24°C							
1 **	15.4688	.8214	.8750	943.76	1.2397	.7922	.9644
2	8.6520	.5264	.8745	763.27	1.0020	.4477	.8504
* 3	9.2256	.3807	.8743	707.57	.9286	.3413	.8965
* 4	2.4986	.3541	.8742	692.08	.9082	.3117	.8803
* 5	8.1837	.2883	.8741	656.68	.8615	.2442	.8470
* 6	13.4721	.2207	.8740	624.60	.8192	.1829	.8289
2500 ppm (1 st) PMMA-G in Toluene at 30°C							
1 **	15.5257	.1941	.8581	616.55	.8086	.3339	1.7199
2	6.7809	.1351	.8579	567.21	.7436	.2262	1.6746
* 3	5.8644	.1069	.8578	543.85	.7127	.1752	1.6384
4	9.3949	.0802	.8577	522.79	.6849	.1293	1.6118

Intrinsic Viscosity Measurement Data

No.	Solvent Wt. added gm	Conc. gm/dl	Density gm/ml	Efflux Time sec	ν csks	η_{sp}	η_{sp}/C dl/gm
2500 ppm (2 nd) PMMA-G in Toluene at $30^{\circ}C$							
1 **	12.8385	.1940	.8581	606.59	.7955	.3122	1.6094
2	5.4578	.1361	.8579	561.54	.7361	.2139	1.5715
3	9.0296	.0911	.8577	526.86	.6903	.1382	1.5166
* 4	8.5404	.0694	.8576	510.92	.6693	.1034	1.4893
2500 ppm (3 rd) PMMA-G in Toluene at $30^{\circ}C$							
1 **	12.8245	.1940	.8581	613.14	.8041	.3265	1.6828
2	7.1338	.1246	.8578	556.74	.7297	.2034	1.6319
* 3	6.8194	.0929	.8577	532.09	.6972	.1496	1.6104
* 4	6.4877	.0747	.8576	519.06	.6800	.1211	1.6202
5500 ppm (1 st) PMMA-G in Toluene at $30^{\circ}C$							
1 **	11.0051	.4420	.8584	854.50	1.1222	.8516	1.9267
2	8.4002	.2505	.8579	667.83	.8762	.4451	1.7765
* 3	4.8635	.2003	.8578	625.72	.8207	.3533	1.7640
* 4	6.7800	.1565	.8577	582.66	.7639	.2596	1.6580
5500 ppm (2 nd) PMMA-G in Toluene at $30^{\circ}C$							
1 **	12.4346	.4420	.8584	849.55	1.1156	.8408	1.9024
* 2	8.3164	.2647	.8580	677.49	.8890	.4661	1.7608
* 3	6.6895	.2002	.8578	621.38	.8150	.3439	1.7181
* 4	10.6972	.1440	.8577	579.64	.7600	.2529	1.7566
9000 ppm (1 st) PMMA-G in Toluene at $30^{\circ}C$							
1 **	11.2130	.7166	.8596	1175.65	1.5449	1.5527	2.1668
2	7.0249	.4401	.8587	851.47	1.1182	.8457	1.9216
3	5.4552	.3387	.8584	749.89	.9844	.6243	1.8434
* 4	6.9482	.2618	.8582	672.98	.8830	.4567	1.7443
9000 ppm (2 nd) PMMA-G in Toluene at $30^{\circ}C$							
1 **	14.8241	.7166	.8596	1160.56	1.5251	1.5199	2.1210
2	9.4696	.4368	.8587	842.65	1.1066	.8265	1.8922
3	10.9392	.3010	.8583	708.75	.9302	.5346	1.7759
* 4	8.6175	.2418	.8581	656.64	.8615	.4210	1.7410
9000 ppm (3 rd) PMMA-G in Toluene at $30^{\circ}C$							
1 **	15.4598	.7166	.8596	1161.57	1.5264	1.5221	2.1241

APPENDIX D

Concentration Analysis Data

Test No.	Density gm/ml	Wt. of Solution gm	Wt. of Polymer gm	Calculated Concentration gm/dl
a. 500 ppm (1 st) PIB L-80 in Cyclohexane				
1	.77375	16.7399	.0098	.0453
2	.77375	17.0681	.0101	.0458
b. 500 ppm (2 nd) PIB L-80 in Cyclohexane				
1	.77375	16.4317	.0094	.0443
2	.77375	18.2936	.0026	.0110 *
c. 500 ppm (3 rd) PIB L-80 in Cyclohexane				
1	.77375	19.5178	.0063	.0250 *
2	.77375	17.0419	.0049	.0222 *
d. 1000 ppm (1 st) PIB L-80 in Cyclohexane				
1	.77390	20.6050	.0135	.0507 *
2	.77390	17.7679	.0195	.0849
e. 1000 ppm (2 nd) PIB L-80 in Cyclohexane				
1	.77390	15.0937	.0163	.0836
2	.77390	18.0819	.0193	.0826
f. 3000 ppm (1 st) PIB L-80 in Cyclohexane				
1	.77412	20.6441	.0620	.2325
2	.77412	22.4717	.0682	.2349
g. 3000 ppm (2 nd) PIB L-80 in Cyclohexane				
1	.77412	22.7458	.0429	.1460 *
2	.77412	18.2499	.0565	.2397
h. 3000 ppm (3 rd) PIB L-80 in Cyclohexane				
1	.77412	17.4667	.0539	.2389
2	.77412	16.9838	.0537	.2448
i. 3000 ppm (4 th) PIB L-80 in Cyclohexane				
1	.77412	19.2839	.0586	.2352
2	.77412	17.9614	.0554	.2388

* **Anomalous data not included in average**

Concentration Analysis Data

Test No.	Density gm/ml	Wt. of Solution gm	Wt. of Polymer gm	Calculated Concentration gm/dl
j.	2500 ppm (1 st) PIB L-80 in Benzene			
1	.87365	14.8544	.0377	.2217
2	.87365	14.3769	.0369	.2242
k.	2500 ppm (2 nd) PIB L-80 in Benzene			
1	.87365	12.3638	.0316	.2233
2	.87365	18.3126	.0469	.2237
l.	2500 ppm (3 rd) PIB L-80 in Benzene			
1	.87365	11.6078	.0297	.2235
2	.87365	11.5810	.0289	.2180
m.	9000 ppm (1 st) PIB L-80 in Benzene			
1	.87401	13.4567	.1270	.8249
2	.87401	14.9646	.1391	.8124
n.	9000 ppm (2 nd) PIB L-80 in Benzene			
1	.87401	12.1095	.1137	.8206
2	.87401	13.5506	.1262	.8140
o.	9000 ppm (3 rd) PIB L-80 in Benzene			
1	.87401	13.5884	.1289	.8291
2	.87401	13.4614	.1274	.8272
p.	2500 ppm (1 st - 3 rd) PMMA-G in Toluene			
1	.85812	9.7410	.0254	.2238
2	.85812	13.1929	.0318	.2068
3	.85812	10.5393	.0238	.1938
q.	5500 ppm (1 st - 2 nd) PMMA-G in Toluene			
1	.85837	16.4110	.0858	.4488
2	.85837	10.8245	.0577	.4576
r.	9000 ppm (1 st - 3 rd) PMMA-G in Toluene			
1	.85956	9.6738	.0788	.7002
2	.85956	10.7982	.0904	.7196
3	.85956	8.8905	.0755	.7300

APPENDIX E

Flow Meter Calibration Data

1 1/2-inch Turbine Flow Meter:

Meter Reading		Flow Rate		f/Q	f/ν
Read	Corrected				
	cps	lbs/min	gals/min	cps/gpm	cps/csks
a. Cyclohexane at 25°C					
100	109.52	106.50	16.49	6.63	95.23
120	128.50	125.50	19.44	6.60	111.73
140	147.50	139.00	21.53	6.84	128.26
160	163.20	155.25	24.05	6.78	141.91
160	163.20	154.75	23.97	6.80	141.91
160	162.00	157.96	24.47	6.62	140.86
160	165.80	158.00	24.47	6.77	144.17
160	162.50	162.00	25.09	6.47	141.30
160	162.50	158.75	24.59	6.60	141.30
160	162.40	162.25	25.13	6.46	141.21
160	162.40	154.25	23.89	6.79	141.21
180	185.80	176.25	27.30	6.80	161.56
180	181.80	175.50	27.18	6.68	158.08
200	204.75	194.25	30.09	6.80	178.04
240	240.00	234.99	36.40	6.59	208.69
240	242.60	234.61	36.34	6.67	210.95
300	300.00	300.00	46.47	6.45	260.86
300	300.00	301.00	46.62	6.43	260.86
300	300.00	303.50	47.01	6.38	260.86
380	380.00	375.00	58.09	6.54	330.43
380	381.60	376.00	58.24	6.55	331.82
b. 500 ppm PIB L-80 in Cyclohexane at 25°C					
100	101.00	106.00	16.41	6.15	78.78
120	121.00	124.80	19.32	6.25	94.38
140	141.00	145.20	22.48	6.26	109.98
160	161.00	165.00	25.55	6.29	125.58
160	161.00	160.00	24.78	6.49	125.58
180	181.00	182.00	28.18	6.42	141.18
180	181.00	179.25	27.76	6.51	141.18
220	222.70	211.80	32.80	6.78	173.71
240	240.58	241.94	37.47	6.42	187.65

Flow Meter Calibration Data

Meter Reading		Flow Rate		f/Q	f/ν
Read	Corrected				
	cps	lbs/min	gals/min	cps/gpm	cps/csks
300	300.00	304.00	47.08	6.37	234.00
340	340.00	339.50	52.58	6.46	265.21
380	380.00	378.00	58.54	6.49	296.41
460	460.70	450.75	69.81	6.59	359.36
520	521.80	514.50	79.68	6.54	407.02
c. 1000 ppm PIB L-80 in Cyclohexane at 25°C					
100	101.00	105.00	16.25	6.21	67.42
120	121.00	125.60	19.44	6.22	80.77
140	141.00	146.25	22.64	6.22	94.12
160	161.00	161.50	25.00	6.43	107.47
180	181.00	183.12	28.35	6.38	120.82
200	200.98	198.44	30.72	6.54	134.16
240	240.58	238.94	37.00	6.50	160.60
300	300.00	299.00	46.30	6.47	200.26
380	380.81	375.75	58.18	6.54	254.21
460	463.80	459.00	71.07	6.52	309.61
540	547.40	543.00	84.08	6.51	365.42
d. 3000 ppm PIB L-80 in Cyclohexane at 25°C					
100	100.00	104.16	16.12	6.20	45.91
120	120.20	127.50	19.73	6.08	55.18
140	140.50	145.25	22.48	6.24	64.50
160	160.60	160.31	24.81	6.47	73.73
180	180.80	179.96	27.85	6.48	83.01
180	180.80	179.33	27.76	6.51	83.01
180	180.80	176.33	27.29	6.62	83.01
200	200.98	194.95	30.17	6.65	92.27
240	240.58	240.00	37.15	6.47	110.45
300	300.00	300.00	46.44	6.45	137.74
340	340.75	339.00	52.47	6.49	156.45
380	380.81	374.25	57.93	6.57	174.84
460	463.90	461.25	71.40	6.49	212.99
540	547.40	541.00	83.75	6.53	251.33

Flow Meter Calibration Data

Meter Reading Read	Corrected	Flow Rate		f/Q	f/ν
	cps	lbs/min	gals/min	cps/gpm	cps/csks
e. 1 % PIB L-80 in Cyclohexane at 25°C					
100	100.51	101.50	15.68	6.40	15.05
120	121.80	120.40	18.60	6.54	18.24
140	141.60	139.00	21.48	6.59	21.21
160	162.40	158.00	24.41	6.65	24.32
180	181.00	176.25	27.24	6.64	27.11
200	201.01	195.31	30.18	6.65	30.10
240	240.40	236.00	36.47	6.59	36.00
300	300.00	299.00	46.21	6.49	44.93
360	360.00	355.80	54.99	6.54	53.92
380	380.00	378.75	58.53	6.49	56.92
460	462.00	462.00	71.40	6.47	69.20
520	522.70	515.00	79.59	6.56	78.29
540	540.80	548.00	84.69	6.38	81.00
f. Benzene at 24°C					
120	120.20	139.00	19.06	6.30	173.19
160	160.61	180.50	24.75	6.48	231.42
g. 2500 ppm PIB L-80 in Benzene at 24°C					
100	100.00	120.60	16.53	6.04	115.44
100	100.00	120.83	16.56	6.03	115.44
120	120.20	140.20	19.22	6.25	138.76
120	120.20	136.90	18.77	6.40	138.76
140	140.40	159.80	21.91	6.40	162.08
140	140.40	159.25	21.83	6.42	162.08
160	160.61	181.75	24.92	6.44	185.41
160	160.61	176.56	24.20	6.63	185.41
180	180.80	195.75	26.84	6.73	208.72
180	180.80	202.50	27.76	6.51	208.72
200	201.01	227.50	31.19	6.44	232.05
200	201.01	225.67	30.94	6.49	232.05
240	241.41	276.99	37.97	6.35	278.70
240	241.41	273.00	37.43	6.44	278.70

Flow Meter Calibration Data

Meter Reading		Flow Rate		f/Q	f/ν
Read	Corrected				
	cps	lbs/min	gals/min	cps/gpm	cps/csks
300	300.00	344.50	47.23	6.35	346.34
300	300.00	340.50	46.68	6.42	346.34
360	360.30	402.50	55.18	6.52	415.95
380	380.81	433.50	59.43	6.40	439.63
380	380.81	436.50	59.85	6.36	439.63
460	461.70	523.50	71.77	6.43	533.01
480	481.82	540.00	74.04	6.50	556.24
480	481.82	543.00	74.45	6.47	556.24
h. 9000 ppm PIB L-80 in Benzene at 24°C					
100	100.00	121.00	16.57	6.03	74.96
120	120.20	141.40	19.36	6.20	90.10
140	140.40	164.50	22.52	6.23	105.24
160	160.61	182.00	24.92	6.44	120.39
180	180.80	203.75	27.90	6.47	135.53
200	201.01	228.12	31.24	6.43	150.68
240	241.41	278.33	38.11	6.33	180.96
300	300.00	335.00	45.88	6.53	224.88
360	360.30	394.50	54.02	6.66	270.08
380	380.81	436.00	59.71	6.37	285.46
460	461.70	522.00	71.49	6.45	346.10
* 480	481.90	525.75	72.00	6.69	361.24
i..Toluene at 30°C					
120	125.00	138.00	19.28	6.48	205.93
120	125.00	143.00	19.98	6.25	205.93
120	125.00	144.40	20.18	6.19	205.93
160	165.00	186.00	25.99	6.34	271.82
160	165.00	187.50	26.20	6.29	271.82
160	165.00	180.50	25.23	6.53	271.82
160	165.00	180.00	25.16	6.55	271.82
160	165.00	189.50	26.48	6.22	271.82

Flow Meter Calibration Data

Meter Reading		Flow Rate		f/Q	f/ν
Read	Corrected				
	cps	lbs/min	gals/min	cps/gpm	cps/csks
j. 2500 ppm PMMA-G in Toluene at 30°C					
100	107.76	122.83	17.15	6.28	134.19
120	127.40	140.40	19.60	6.49	158.65
140	146.60	166.80	23.29	6.29	182.56
160	166.00	183.25	25.59	6.48	206.72
180	185.50	205.00	28.62	6.47	231.00
180	185.50	202.81	28.32	6.54	231.00
200	204.70	226.25	31.59	6.47	254.91
240	242.80	270.33	37.75	6.43	302.36
360	360.00	399.00	55.72	6.46	448.31
380	380.00	419.50	58.58	6.48	473.22
460	460.00	498.75	69.65	6.60	572.85
520	520.00	568.00	79.32	6.55	647.57
520	520.00	578.00	80.71	6.44	647.57
* 560	560.00	578.00	80.71	6.93	697.38
k. 5500 ppm PMMA-G in Toluene at 30°C					
100	105.94	129.00	18.01	5.88	94.58
120	125.80	144.60	20.18	6.23	112.32
140	145.50	166.75	23.28	6.24	129.91
160	165.40	176.25	24.60	6.72	147.67
160	165.40	181.25	25.30	6.53	147.67
180	185.20	205.41	28.67	6.45	165.35
200	205.30	230.94	32.24	6.36	183.30
240	242.90	272.67	38.06	6.38	216.87
300	300.00	339.50	47.39	6.32	267.85
380	380.00	423.00	59.05	6.43	339.28
460	460.00	503.25	70.26	6.54	410.71
540	540.20	603.00	84.18	6.41	482.32

* anomalous result in high flow rate region not included in data analysis

Flow Meter Calibration Data

Meter Reading		Flow Rate		f/Q	f/ν
Read	Corrected				
	cps	lbs/min	gals/min	cps/gpm	cps/csks
1. 9000 ppm PMMA-G in Toluene at 30°C					
100	109.50	122.00	17.00	6.43	71.33
120	120.00	145.60	20.29	5.91	78.17
140	147.70	166.25	23.17	6.37	96.22
160	166.70	184.75	25.75	6.47	108.59
200	205.30	228.13	31.80	6.45	133.74
240	242.90	268.67	37.45	6.48	158.24
300	300.00	335.00	46.70	6.42	195.43
360	360.00	396.00	55.21	6.52	234.52
380	380.00	416.25	58.03	6.54	247.55
460	460.00	501.75	69.95	6.57	299.67
* 520	520.10	559.50	78.00	6.66	338.82
540	540.40	595.00	82.95	6.51	352.05

Flow Meter Calibration Data

3/4-inch Turbine Flow Meter:

Meter Reading Read	Corrected	Flow Rate		f/Q	f/ν
	cps	lbs/min	gals/min	cps/gpm	cps/csks
a. Cyclohexane at $25^{\circ}C$					
100	104.85	10.70	1.65	63.25	91.17
100	109.25	9.08	1.40	77.63	95.00
100	110.00	10.43	1.61	68.03	95.65
100	110.00	10.35	1.60	68.60	95.65
280	280.40	23.50	3.64	77.02	243.82
280	280.40	24.50	3.79	73.87	243.82
400	400.00	33.66	5.21	76.69	347.82
400	402.00	34.43	5.33	75.35	349.56
560	558.50	48.16	7.46	74.84	485.65
560	563.90	48.66	7.53	74.79	490.34
560	563.90	48.91	7.57	74.41	490.34
660	656.00	56.75	8.79	74.61	570.43
660	662.00	57.62	8.92	74.15	575.65
840	837.00	71.00	10.99	76.09	727.82
840	837.00	72.37	11.21	74.65	727.82
840	843.00	73.00	11.30	74.54	733.04
840	837.00	73.37	11.36	73.63	727.82
840	837.00	73.62	11.40	73.38	727.82
840	837.00	73.12	11.32	73.88	727.82
1000	1002.02	86.66	13.42	74.63	871.32
1000	1000.00	87.83	13.60	73.49	869.56
1000	1005.07	88.66	13.73	73.17	873.97
b. 500 ppm PIB L-80 in Cyclohexane at $25^{\circ}C$					
840	842.00	72.87	11.28	74.59	656.78
1000	1005.08	89.16	13.81	72.77	783.99
c. 1000 ppm PIB L-80 in Cyclohexane at $25^{\circ}C$					
560	562.50	50.91	7.88	71.34	388.46
660	668.80	58.12	9.00	74.31	461.87
840	838.00	73.37	11.36	73.75	578.72
1000	1000.90	89.66	13.88	72.08	691.23

Flow Meter Calibration Data

Meter Reading Read	Corrected cps	Flow Rate lbs/min	gals/min	f/Q cps/gpm	f/ν cps/csks
d. 3000 ppm PIB L-80 in Cyclohexane at 25°C					
400	401.04	34.43	5.33	75.22	184.13
560	568.40	49.50	7.66	74.17	260.97
660	664.30	58.00	8.97	73.98	305.00
840	843.00	73.75	11.41	73.83	387.05
1000	1002.51	91.33	14.13	70.90	460.28
e. 1 % PIB L-80 in Cyclohexane at 25°C					
660	656.80	58.37	9.02	72.79	98.38
840	836.00	74.00	11.43	73.09	125.22
1000	1000.00	89.14	13.77	72.58	149.79
f. 2500 ppm PIB L-80 in Benzene at 24°C					
400	400.00	39.12	5.46	73.20	497.51
560	560.00	55.16	7.70	72.68	696.51
660	654.60	64.33	8.98	72.86	814.17
g. 9000 ppm PIB L-80 in Benzene at 24°C					
400	401.02	40.00	5.47	73.20	299.26
560	566.80	56.33	7.71	73.46	422.98
660	663.10	66.62	9.12	72.67	494.85
840	834.00	83.87	11.48	72.60	622.38
1000	1005.10	101.83	13.94	72.07	750.07
h. 2500 ppm PMMA-G in Toluene at 30°C					
400	401.02	40.17	5.50	72.79	462.96
560	564.50	57.25	7.84	71.91	651.69
560	566.80	57.08	7.82	72.41	654.35
660	661.40	67.16	9.20	71.81	763.56
660	663.10	66.32	9.09	72.91	765.52

Flow Meter Calibration Data

Meter Reading		Flow Rate		f/Q	f/ν
Read	Corrected				
	cps	lbs/min	gals/min	cps/gpm	cps/csks
840	837.90	84.62	11.60	72.21	967.32
840	834.00	83.75	11.48	72.62	962.82
1000	1005.00	102.37	14.03	71.59	1160.24
1000	1005.10	102.33	14.03	71.63	1160.35
i. 5500 ppm PMMA-G in Toluene at 30°C					
400	400.00	39.50	5.51	72.53	357.14
560	560.00	55.00	7.67	72.92	500.00
660	657.60	65.00	9.07	72.46	587.14
840	837.30	81.75	11.41	73.36	747.58
1000	1000.00	98.25	13.71	72.90	892.85

APPENDIX F

Sample Calculations

A numerical example of each calculation used in this investigation is presented:

1. Calculation of Density and Concentration During Dilution for Intrinsic Viscosity Measurements.

Example: 1.0 gm/dl Polystyrene-A in Toluene at 30°C.

Density of Solvent = 0.8556 gm/ml (toluene at 30°C)

Point	Sample	Weight gm	Density gm/ml	Concentration gm/dl
1.	Solution	14.3469	0.8595	1.0000
2.	Solvent added	2.0720	0.8590	0.8733
3.	Solvent added	7.5310	0.8579	0.5980
4.	Solvent added	7.7271	0.8574	0.4518

$$\rho_1 = 0.8595 \text{ gm/ml}$$

$$\rho_2 = (2.072 + 14.3469)/[(2.072/0.8556) + (14.3469/0.8595)]$$

$$= 0.8590 \text{ gm/ml}$$

$$C_1 = 1.0000 \text{ gm/dl}$$

$$C_2 = [(1.0 \times 14.3469)/0.8595]/[(2.072/0.8556) + (14.3469/0.8595)]$$

$$= 0.8733 \text{ gm/dl}$$

A Fortran program was written and IBM 1620 computer was used for these calculations.

2. Calculation of Specific Viscosity.

Example: 1.7031 gm/dl Polyisobutylene LMMH in Cyclohexane at 25^{o}C.

Density of Solvent = 0.7736 gm/ml.

Density of Solution = 0.7781 gm/ml.

Efflux Time of Solvent = 875.25 sec.

Efflux Time of Solution = 1,729.88 sec.

According to equation (12):

Absolute Viscosity of Solvent = η_o

$= 0.7736 \left[(A \times 875.25) - (B / 875.25)\right] = 0.8892$ centipoise.

Absolute Viscosity of Solution = η

$= 0.7781 \left[(A \times 1729.88) - (B / 1729.88)\right] = 1.7897$ centipoise.

where $A = 0.001315$ and $B = 1.34$.

Therefore, Specific Viscosity $= \eta_{sp} = (\eta - \eta_o)/\eta_o$

$= (1.7897 - 0.8892)/0.8892 = 0.9913$.

3. Calculation of Density.

Example: 0.3015 gm/dl Polyisobutylene L-80 in Cyclohexane at 25^{o}C.

Test No.	Pycnometer Reading	Volume* ml	Weight of Solution gm	Density gm/ml
1.	9.18	5.1080	4.0189	0.7868
2.	5.97	5.0700	3.9897	0.7869
3.	1.12	5.0127	3.9441	0.7868
			Average=	0.7868

* Volume = 4.9995 + {0.01182 x Pycnometer Reading}.

4. <u>Determination of the Concentration of Polymer in Solution</u>.

Example: 0.9784 gm/dl Polystyrene-E in Toluene at 30°C.

Density of Solution = 0.85938 gm/ml

Test No.	Weight of Solution gm	Weight of Dried Sample gm	Concentration Actual gm/dl	Concentration Measured gm/dl	% Error
1.	19.4416	0.2193	0.9784	0.9693	-0.92
2.	9.2556	0.1043	0.9784	0.9684	-1.02

Measured Concentration = {0.2193 x 0.85938 x 100}/19.4416

= 0.9693 gm/dl.

5. Calculation of Shear Rates in Viscometer (63).

Average Shear Rate $= \overline{G} = 8\ V'/3\pi\ r^3\ t$ (16)

For Viscometer A-1:

$V' = 5.0$ ml $r = 0.02$ cm $t_{min} = 460$ sec.

Therefore,

$$\overline{G}_{max} = (8 \times 5)/[3 \times 3.1416 \times (0.02)^3 \times 460] = 1120\ \text{sec}^{-1}.$$

6. Least-Squares Program (74).

The best-fitting straight line through the data is the line which makes the sum of the squares of the deviation of measured y (dependent variable) values from predicted Y values a minimum.

$$Y = a + b\,(x - \overline{x})$$

When the differentiations are carried out and the resulting expressions solved for a and b, there results:

$$a = \frac{\sum^{n_i} y_i}{n_i} = \overline{y}$$

and,

$$b = \frac{\sum^{n_i} y_i\ (x_i - \overline{x})}{\sum^{n_i} (x_i - \overline{x})^2}\ .$$

A least-squares curve-fitting routine for the IBM 1620 was written for this purpose by Hershey (75), and was used frequently in this investigation for calculating intrinsic viscosities, for fitting the calibration data for the pycnometer and the flow meters, etc.

7. Turbine Flow Meter Calibration.

Example: For 1 1/2-inch Turbine Flow Meter:

Density of Test Fluid = 0.77358 gm/ml
(cyclohexane at 25°C).

Frequency Meter Reading = 160.0 cps.

Flow Rate = 155.25 lbs/min.

Sine Wave Generator Reading	100	200	300	400	500	.....
Frequency Meter Reading	95	198	300	400	500	.....

Therefore,

Corrected Frequency Meter Reading

$$= 200 - \left[(198 - 160)/(198 - 95)\right] (200 - 100) = 163.2 \text{ cps.}$$

$$^{*}\text{Flow Rate} = 155.25 \left[(453.5924)/(0.77358 \times 3785)\right] = 24.05 \text{ gpm.}$$

* where one gallon equals 3785 ml.

VII. NOMENCLATURE

Arabic Symbols:

a = exponent (in equations (8) and (9))

a = weight of a unit volume of air (in equation (13)), grams/milliliter

A = viscometer calibration constant

B = viscometer kinetic energy correction constant

C = concentration, grams/deciliter

d = density of the substance, grams/milliliter

d' = density of the brass weights, grams/milliliter

D = meter bore diameter (in equation (10)), centimeter or inch

D = tube diameter (in equations (14) and (15)), centimeter

f = Fanning friction factor (in equation (14))

f = frequency (in equation (10) and (11)), cycles/second

g_c = force-mass conversion factor

$\overline{G}$ = average shear rate, second^{-1}

k' = Huggins constant

k'' = $1/2 - k'$

k_A = Arrhenius constant (in equation (1))

K = constant in Flory viscosity equation

K_F = constant in Flory viscosity equation

K_m = constant in equation (8)

K_s = constant in equation (7)

L = tube length (in equations (14) and (15)), centimeter

M = molecular weight, gram/gram mole

M_o = molecular weight of initial sample, gram/gram mole

M_s = molecular weight of sheared sample, gram/gram mole

$\bar{M}_v$ = viscosity average molecular weight, gram/gram mole

$\bar{M}_w$ = weight average molecular weight, gram/gram mole

n = rotor angular velocity, second^{-1}

ΔP = pressure drop, $\text{dynes/centimeter}^2$

Q = volumetric flow rate, pounds/minute or gallons/minute

r = radius of capillary, centimeters

t = efflux time, seconds

V = polymer volume fraction

V = average flow velocity (in equations (14) and (15)), centimeters/second

V' = bulb volume (in equation (16)), milliliters

W = weight of substance in air, grams

W^o = weight of substance in vacuo, grams

Subscripts:

c = critical value

o = initial sample

s = sheared sample

Greek Symbols:

γ = k'/k" (in equation (5))

η = absolute viscosity, centipoise

η_o = absolute viscosity of solvent, centipoise

η_{rel} = relative viscosity

η_{sp} = specific viscosity

$[\eta]$ = intrinsic viscosity, deciliters/gram

$[\eta]_o$ = intrinsic viscosity of initial sample, deciliters/gram

$[\eta]_s$ = intrinsic viscosity of sheared sample, deciliters/gram

ν = kinematic viscosity, centistokes

π = geometric constant (=3.1416)

ρ = density, grams/milliliter.

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