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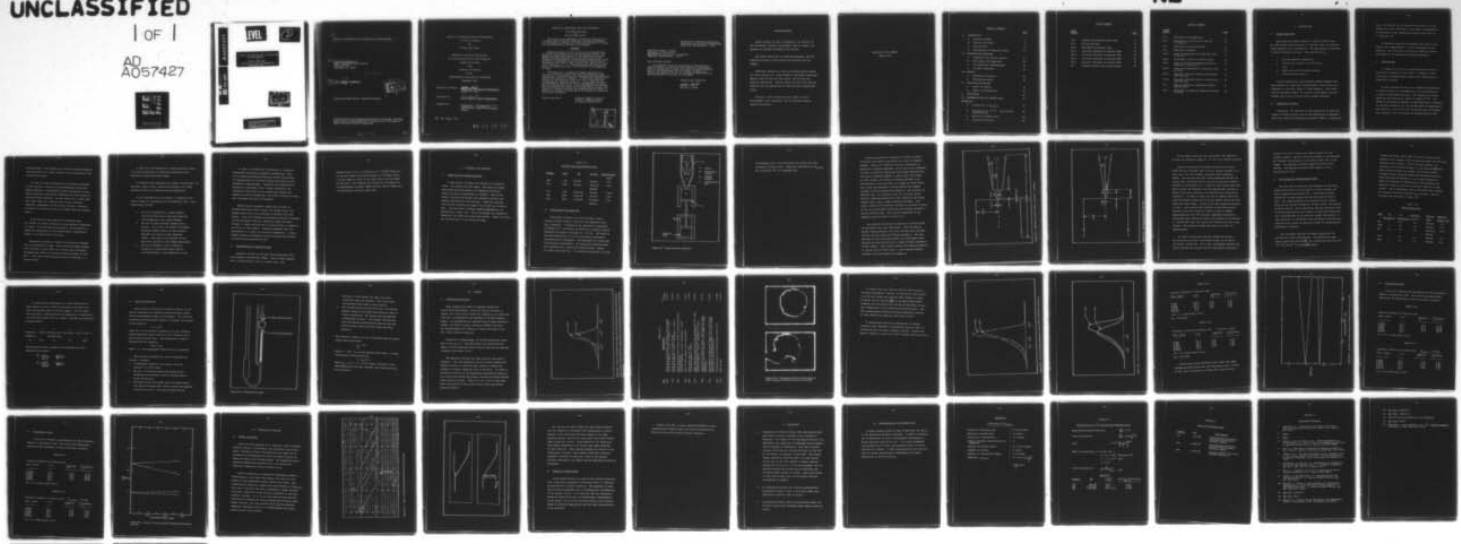

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Effects of Extensional Flow on Polystyrene in Dilute Solutions

by
William Alan Sweet
Department of Chemical Engineering
September 1978

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Effects of Extensional Flow on Polystyrene in Dilute Solutions

by

William Alan Sweet

Submitted in Partial Fulfillment
of the Requirements for the Degrees of
Master of Science
and
Bachelor of Science
at the
Massachusetts Institute of Technology
September 1978

Signature of Author: William Sweet
Department of Chemical Engineering
August 11, 1978

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E. W. Merrill, Thesis Supervisor

Accepted by: _____
James Wei, Chairperson
Departmental Committee on Graduate Theses

EFFECTS OF EXTENSIONAL FLOW ON POLYSTYRENE

IN DILUTE SOLUTIONS

by
William Alan Sweet

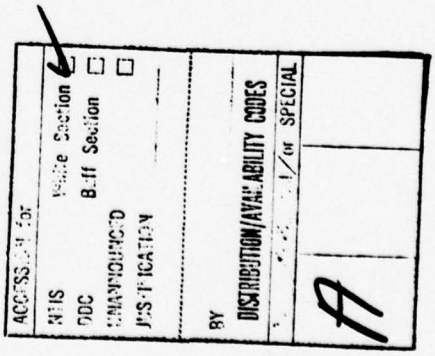
Submitted to the Department of Chemical Engineering on 11 August 1978 in partial fulfillment of the requirements for the degrees of Master of Science and Bachelor of Science at the Massachusetts Institute of Techology.

ABSTRACT

Dilute solutions (0.025 to 0.05 wt.%) of polystyrene in toluene were placed in an extensional flow field. The molecular weight distribution of the polymer was studied before and after being placed in the flow field by gel permeation chromatography. Monodispersed polystyrene showed no change in molecular weight distribution after passing through the flow field. These results are contrary to those of P. Leopairat (1). It is suggested that the degradation Leopairat observed was due to an artifact in the apparatus he used.

Polystyrene in a solution of higher concentration (0.2 wt.%) did show significant shift in molecular weight distribution as measured by gel permeation chromatography and verified by intrinsic viscosity. A relatively concentrated solution of polyethylene oxide (0.05 wt.%) also degraded as measured by intrinsic viscosity. It is suggested that the degradation observed is due to intermolecular entanglements of the polymer chains. Where degradation was observed, the concentration was above the critical concentration; the critical concentration being the concentration at which the domain of a polymer molecule begins to overlap the domain of its nearest neighbors.

Thesis Supervisor: Professor Edward W. Merrill
Carbon P. Dubbs Professor
of Chemical Engineering



Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Professor George C. Newton
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dear Professor Newton:

In accordance with the regulations of the Faculty, I herewith submit a thesis entitled "Effects of Extensional Flow on Polystyrene in Dilute Solutions" in partial fulfillment of the requirements for the degrees of Master of Science and Bachelor of Science in Chemical Engineering at the Massachusetts Institute of Technology.

Respectively Submitted,

William A. Sweet

ACKNOWLEDGEMENTS

Special thanks are due to Professor E. W. Merrill for his enthusiasm, constant encouragement and, of course, the guidance he provided throughout this project.

The author would like to thank Dan Dershowitz for his guidance and help in this project and Jim Moore for his company.

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Finally, I wish to thank my wife, Cindi, for her encouragement and, especially, for her patience with me during this project.

DEDICATED TO MY PARENTS

AND MY WIFE

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I. INTRODUCTION

A. Problem Statement

High molecular weight polymers in dilute solutions can be used as drag reducing agents in turbulent flow, as viscosity index improvers or as flocculants. The applications of polymers in dilute solutions are many. They can be used to:

1. Increase pipeline capacities;
2. Increase the viscosity of lubrication oils;
3. Reduce drag on ocean-going vessels;
4. Flocculate waste water.

During repeated use, high molecular weight polymers have been observed to loose their effectiveness. This is due to a reduction in the chain length of these polymers. This reduction of molecular weight, as a result of main chain scission, reduces the utility of these dilute polymer solutions.

B. Objective of Theses

Originally, the objective of this thesis was to study the effect of varying strain rates on the degradation of polyethylene oxide (PEO) and polydimethyl siloxane (PDMS) in extensional

flow. The effects of the characteristic ratio C of the polymer was to be correlated to the extent of degradation in extensional flow, comparing my results with those of P. Leopairat (2).

In following Leopairat's procedure, his results were found to be irreproducible, in that no degradation was observed. The flow field was varied in order to uncover the source of the degradation Leopairat observed.

C. Previous Work

P. Leopairat (3) gives a detailed account of most of the recent literature in this field. A summary of this literature is presented here, along with a description of Leopairat's findings.

In 1961, Johnson and Price (4) studied the degradation of dilute solutions of polyisobutylene and polystyrene as a result of high speed stirring. The scission of covalent bonds was monitored by the uptake of iodine (I^{131}). The number of main chain scissions, as calculated from a decrease in intrinsic viscosity, was of the same order of magnitude as free radicals. This led to the conclusion that the degradation process is due to scission of covalent bonds in the

chain backbone. The authors also noted that maximum degradation took place in a "poor" solvent, at low temperatures and at high shear rates.

In 1961, A. Ram (5) observed an irreversible descrease in the intrinsic viscosity of polyisobutylene during high shear viscometry. Ram observed greater degradation in more dilute solutions, noting that turbulence was also greater in the more dilute solutions. He also noted, for a given shear rate, that there is a limiting value of the intrinsic viscosity, independent of the initial intrinsic viscosity, as long as the initial viscosity is higher than the limiting value.

In his work on drag reduction in turbulent flow, A.G. Fabula (6) noted a decrease in drag reduction downstream in a pipe. He attributed the decrease in drag reduction to mechanical degradation of the macromolecules (polyethylene oxide) in the first half of the pipe.

Harrington and Zimm (7) studied the mechanical degradation of polystyrene and DNA. They found the polymer degradation to follow a first order law, and the rate of breakage of polystyrene chains to be nearly constant between 15^{o} and 45^{o} C. They also found the polymer easier to degrade in a "poor" solvent.

H. Shin (8) found molecules of higher molecular weight to be more susceptible to mechanical degradation than molecules of lower molecular weight.

In turbulent and capillary flow, Fisher and Rodriguez (9) and then, later, Cutler, Zaskin and Patterson (10) found entrance effects to be dominant during degradation.

In the introduction to his thesis, P. Leopairat (11) lists a number of shortcomings of this previous work. These shortcomings include:

1. The use of turbulence, a highly complex flow field from which a physical mechanism for degradation is not easily deduced.
2. The use of broad molecular weight distributions. As H. Shin (12) showed, the higher molecular weight polyers are more readily degraded than those of lower molecular weight. Data such as the location of the main chain scission is not readily obtainable.
3. The use of averages, such as intrinsic viscosity, or qualitative data, such as the effectiveness in the reduction of drag.

In order to overcome the limitations, P. Leopairat worked with anionically polymerized polystyrene, which has a nearly monodispersed molecular weight distribution. He characterized the molecular weight distribution by gel permeation chromatography. Leopairat also subjected the polymers to extensional flow. Unlike turbulence, the extensional flow field can be analytically solved and, subject to certain assumptions, the strain to which the polymer is exposed can also be calculated.

Models used by Leopairat showed that in order to develop sufficient force to break the polymer chain, the polymer would have to be stretched to 99.39% of its full length. Since the randomly coiled polymer molecule is exposed to the extensional flow for a period of about 100 microseconds, it seems unlikely that it would be able to extend to 99.39% of its full length. Leopairat suggested that the degradation is a result of internal entanglements. A small segment between entanglements may be stretched sufficiently and break during extensional flow.

D. Shortcomings of Leopairat's Work

Leopairat did most of his work with polystyrene (PSt) and polymethyl methacrylate (PMMA). Both of these polymers have a characteristic ratio C of about nine. The

characteristic ratio C is defined as $C = \bar{r}_o^2/n\ell^2$, where $\bar{r}_o^2$ is the mean square end-to-end distance of a polymer chain, n is the number of units in the chain and ℓ is the length of each unit. The original plan called for this thesis to use polydimethyl siloxane (PDMS) and PEO, both of which have a characteristic ratio of about four.

II. APPARATUS AND PROCEDURE

A Preparation of Polymer Solution

A known weight of polymer was placed in a volumetric flask. The solvent was then added. The flask was capped and stored until the polymer was completely dissolved (about one day for polystyrene in toluene). During this period, stirring and shaking were avoided to prevent any unwanted degradation of the polymer. Light was excluded from the PEO solutions by wrapping the flasks with aluminum foil. This was done to prevent unwanted degradation, as observed by J. Moore (13). After the polymer was completely dissolved, the flask was filled with solvent. Table II-1 gives the concentrations of the solutions used.

Table II-1

Polymers and Concentrations Used

Polymer	Code	MW	Solvent	Concentration (wt%)
PSt	800	390,000	Toluene	0.05
PSt	1600	390,000	Dichloro-Methane	0.05
PSt	1700	2,000,000	Toluene	0.025
PSt	1800	2,000,000	Toluene	0.19
PEO	2000	1,200,000	Dichloro-Methane	0.05

B. Extensional Flow Apparatus

The polymer solution was forced through a narrow orifice at high velocity, using the flow apparatus built by P. Leopairat. A diagram of the apparatus is presented in Figure II-1. The piston is driven by a hydraulic system described by Leopairat on pages 34 - 40 (14). The speed of the retracting piston P2 in the low pressure cylinder R was measured by a kymograph. The kymograph was a pump with a multi-speed transmission. Its horizontal rotating screw was converted into a vertically rotating shaft, using a 1:1 right angle gear box. A cylindrical drum with a 25 inch

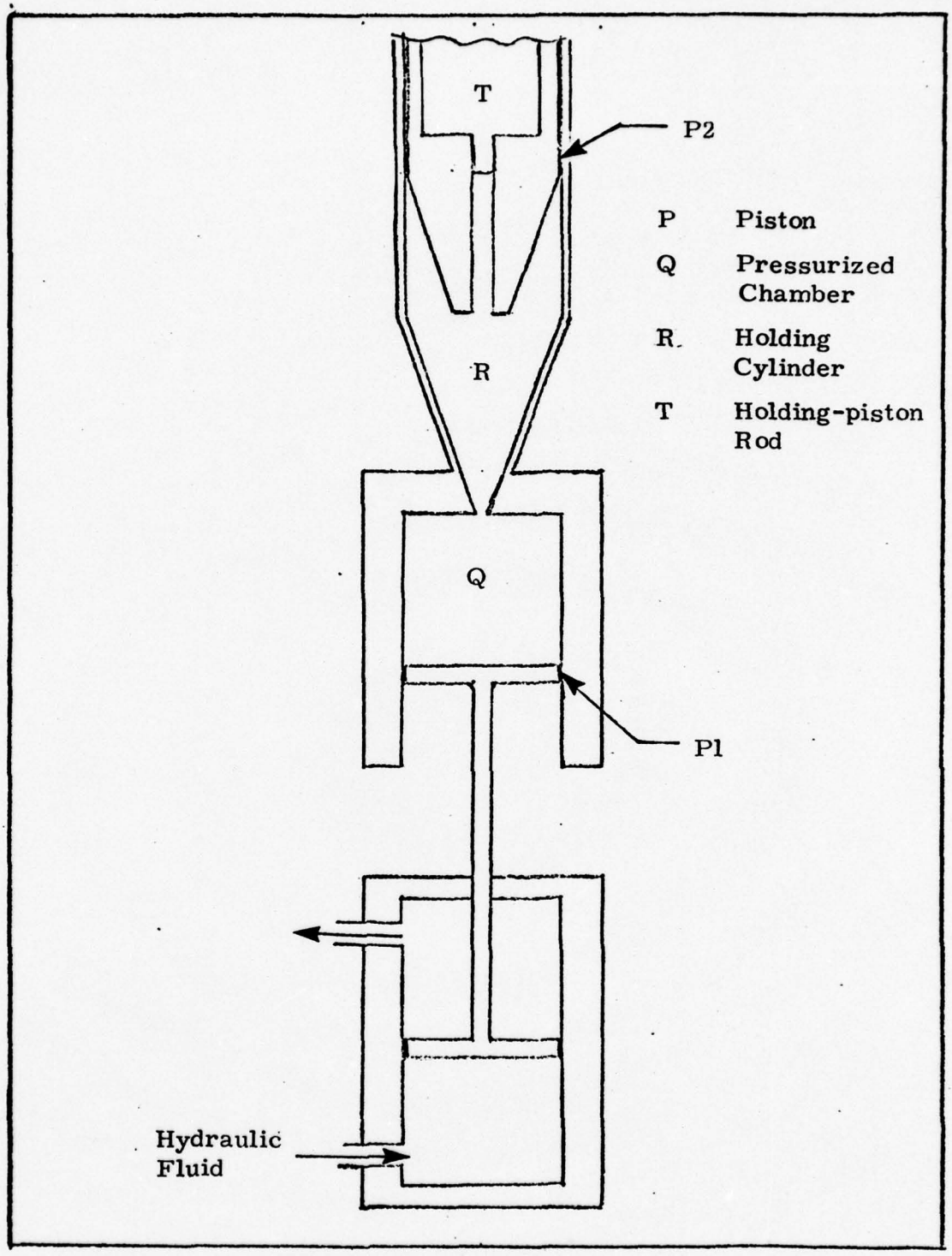

Figure II-1. Extensional Flow Apparatus

circumference and a six inch height was fitted onto this vertically rotating shaft. Appendix A describes how $\bar{V}_{orifice}$ was calculated from the kymograph data.

Careful examination of Leopairat's holding cylinder R revealed the interior dimensions not to be as Leopairat thought. Figure II-2 shows the interior dimensions of Leopairat's original apparatus, to the best of our knowledge. In order to avoid any turbulence which might develop where the orifice suddenly expands in radius from 0.023 inches to 0.063 inches, the orifice of holding cylinder R was drilled with a 3/16 inch drill to a depth of 0.258 inches, and a piece was machined to insert between the holding cylinder R and the pressurized chamber Q. The orifice was machined into .303 stainless steel by a process called Electric Discharge Machining by Jake Avakian of the Draper Machine Shop, using a Copper-Tungsten electrode. This insert, along with the holding cylinder R, was held in place by the six screws which originally held holding cylinder R and the orifice plate. The interior dimensions of the apparatus used are shown in Figure II-3.

The interior dimensions of Leopairat's original holding cylinder R were also duplicated. This was done by having a plug machined to fit into the hole which had been drilled into the bottom of holding cylinder R. The plug was made of 3/16 inch brass stock, cut 0.258 inches long. The plug was then drilled with a number 56 drill (diameter = 0.0465 inches). After being inserted into holding cylinder R, various orifice plates were inserted between holding cylinder R and the pressurized chamber Q.

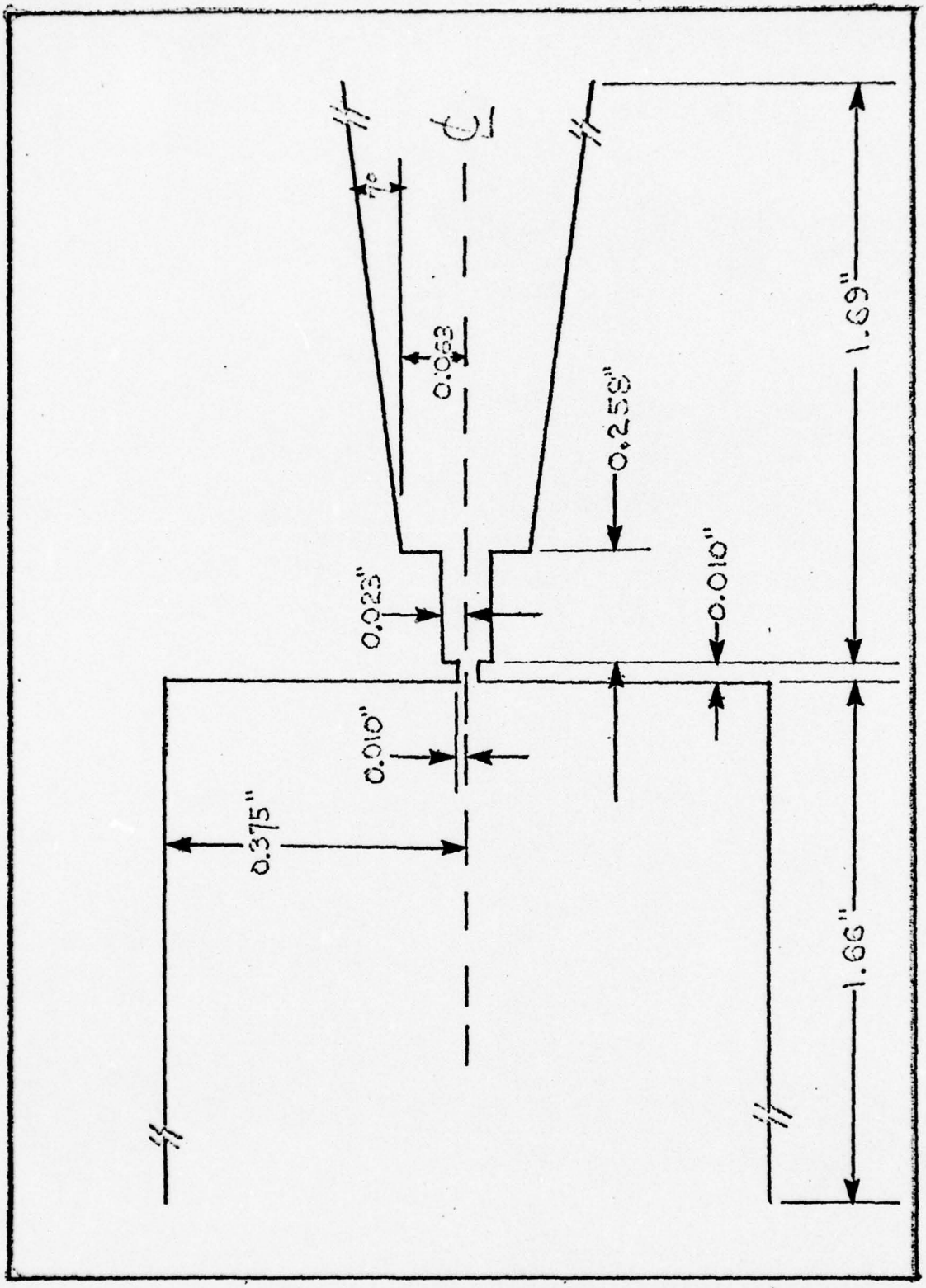

Figure II-2. Dimensions of Flow Field as used by P. Leopairat

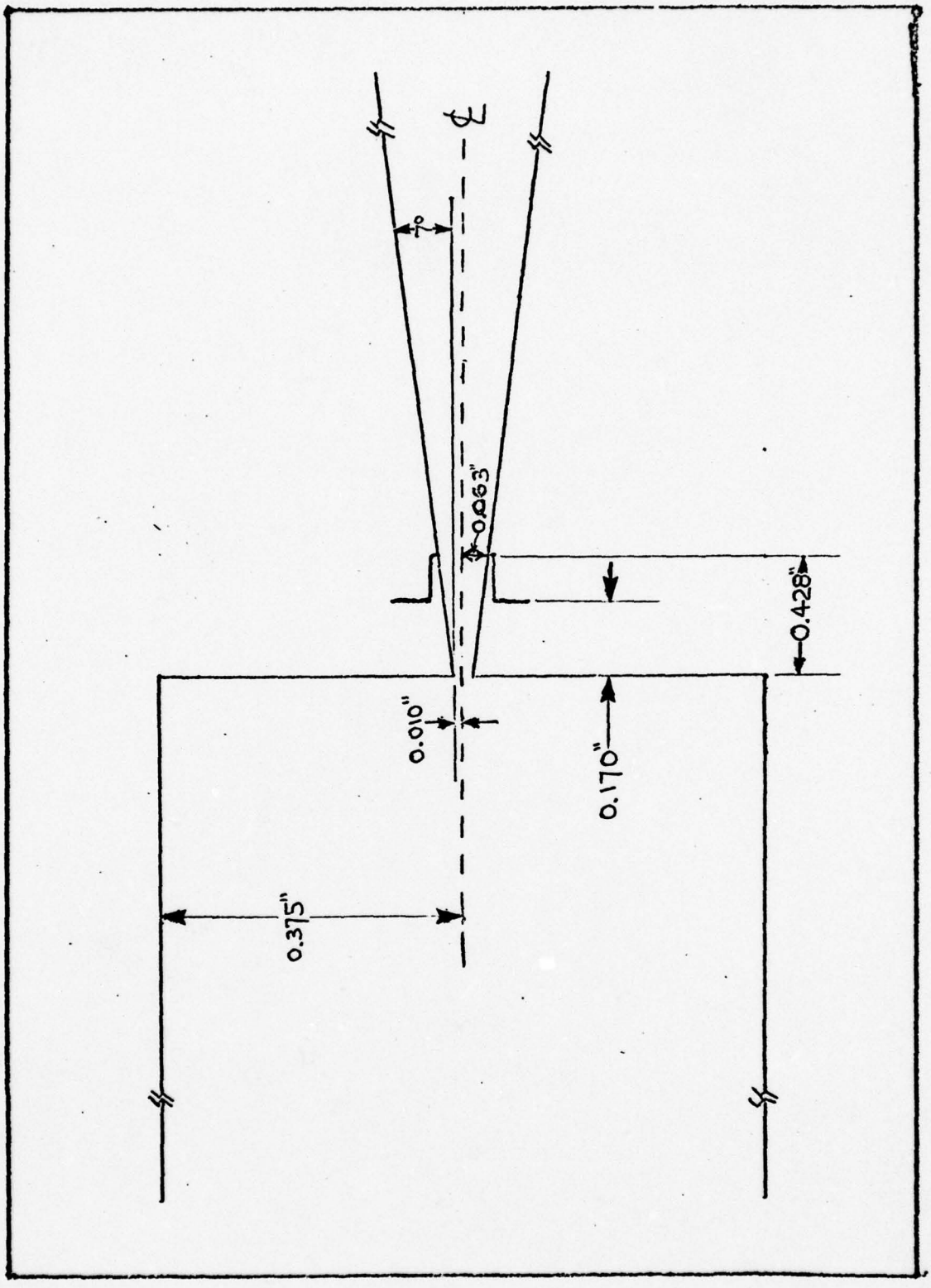

Figure II-3. Dimensions of Flow Field Used

The procedure used with the extensional flow apparatus as given by Leopairat, pages 67 - 69 (15), was closely followed.

Fourteen milliliters of polymer solution were slowly drawn from its container into a 20 mls. syringe through a 6.5 inch long, 1/16 inch diameter stainless steel hypodermic needle. The solution was then slowly discharged through the central hole of piston head P2 into the low-pressure holding cylinder R (see Figure II-1). Piston P1 was slowly drawn downward, sucking the solution into the high-pressure cylinder Q. piston P1 was then lowered to the bottom of the low-pressure cylinder R. In order to drive out any air bubbles which may have been caught, piston P1 was thrust slowly forward and then drawn back three times. Piston P2 was then sealed by screwing in rod T. The solution then remained in the high-pressure cylinder Q for five minutes in order to come to thermal equilibrium with the 25^{o}C constant temperature bath which circulated water around the outside of cylinder Q and cylinder R. During this time, the syringe was rinsed twice with clean solvent. The hydraulic system was then set to give the desired speed.

In order to force the solution through the orifice, the switch for piston P1 was turned on and, at the end of its stroke, turned off. As P1 rose, the polymer solution was forced through the orifice into the low-pressure cylinder R.

Piston P2 and rod T rose as the liquid entered the low-pressure chamber, and this rise was recorded on the kymograph. The solution was unloaded in the reverse order that it was loaded. The apparatus was then washed twice with clean solvent. The degraded solutions were stored in 20 cc scintillation vials.

C. Gel Permeation Chromatography (GPC)

GPC was used to quantitatively determine the molecular weight distribution of the polymer in solution before and after undergoing extensional flow. The solution passes through GPC columns packed with gel particles of varying size. The larger molecules are excluded from the smaller pores and are flushed through the columns first; the smaller molecules follow. The UV absorbance and the refractive index of the solution exiting the columns is continually monitored and a chromatograph of the molecular weight distribution is thus obtained. A calibration curve was made by plotting peak retention time versus log molecular weight for monodispersed polystyrene standards.

The instrument used was the Waters Associates (16) ALC GPC 244 liquid chromatograph. The packing gels were Waters Associates Styragel®. The columns used were the 10^3, 10^4, 10^5 and 10^6 Å Styragel® columns.

A Waters Associates Model 6000 A solvent delivery system pumped solvent through a Waters Associates Model U6K Universal Injector to the columns. Prior to being injected, all solutions were filtered through a 0.5 μm Millipore® filter. After passing through the columns, the solution passed through a Waters Associates Model 440 Absorbance Detector, which monitored UV absorbance, and a Waters Associates Model 401 Differential Refractometer, which measured the refractive index of the exiting solution relative to pure solvent. The UV absorbance and RI difference were recorded on a Houston Instrument Omni-Scribe$_{TM}$ recorder. The GPC settings used are shown in Table II-2.

Table II-2

GPC Settings Used

Code	UV Attenuation	RI Attenuation	Flow Rate (ml/min.)	Solvent Used	Injection Volume (ml)
800	--	2X	1.8	Toluene	0.5
1600	--	2X	1.8	Toluene	0.5
900	0.2	2X	1.8	Dichloro-Methane	0.35
1700	--	1X	1.8	Toluene	0.5
1800	--	1X	1.8	Toluene	0.5

To analyze the chromatograph, a linear baseline was drawn under the curve, using the baseline from before and after the polymer came out of the columns. Once the baseline was drawn, the peak height was measured as a function of the retention volume every 0.2 inches. The data was tabulated as shown below.

1	2	3	4	5
Retention Volume or	Height	MW from calibration curve	Col 2/Col 3	Col 2 x Col 3
V_r	N_iM_i	M_i	N_i	$N_iM_i^2$

The molecular weight averages were calculated from the equations given below.

$$\bar{M}_n = \frac{\sum M_i N_i}{\sum N_i} = \frac{\sum \text{Col 2}}{\sum \text{Col 4}}$$

$$\bar{M}_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i} = \frac{\sum \text{Col 5}}{\sum \text{Col 2}}$$

D. Intrinsic Viscosity

The intrinsic viscosity of a polymer solution can be used to determine the viscosity average molecular weight and the hydrodynamic volume of the polymer. The intrinsic viscosity and the molecular weight of a polymer are related by the equation:

$$(n) = K M^{a}$$

where (n) is the intrinsic viscosity, M is the viscosity average molecular weight and K and a are constants for a given polymer-solvent pair. The hydrodynamic volume is obtained from the equation:

$$(n)M = V \phi$$

where V is the hydrodynamic volume and ϕ is a constant.

The following procedure was used in measuring the intrinsic viscosity.

1. An Ubbelohde viscometer (see Figure II-4) was secured in a 25.0°C bath.
2. Ten mls. of filtered solvent was placed in the viscometer and allowed to come to thermal equilibrium (10 minutes).
3. The liquid level was brought above the upper graduation mark by sealing tube 2 with a finger and applying a suction to tube 3. The time required for the

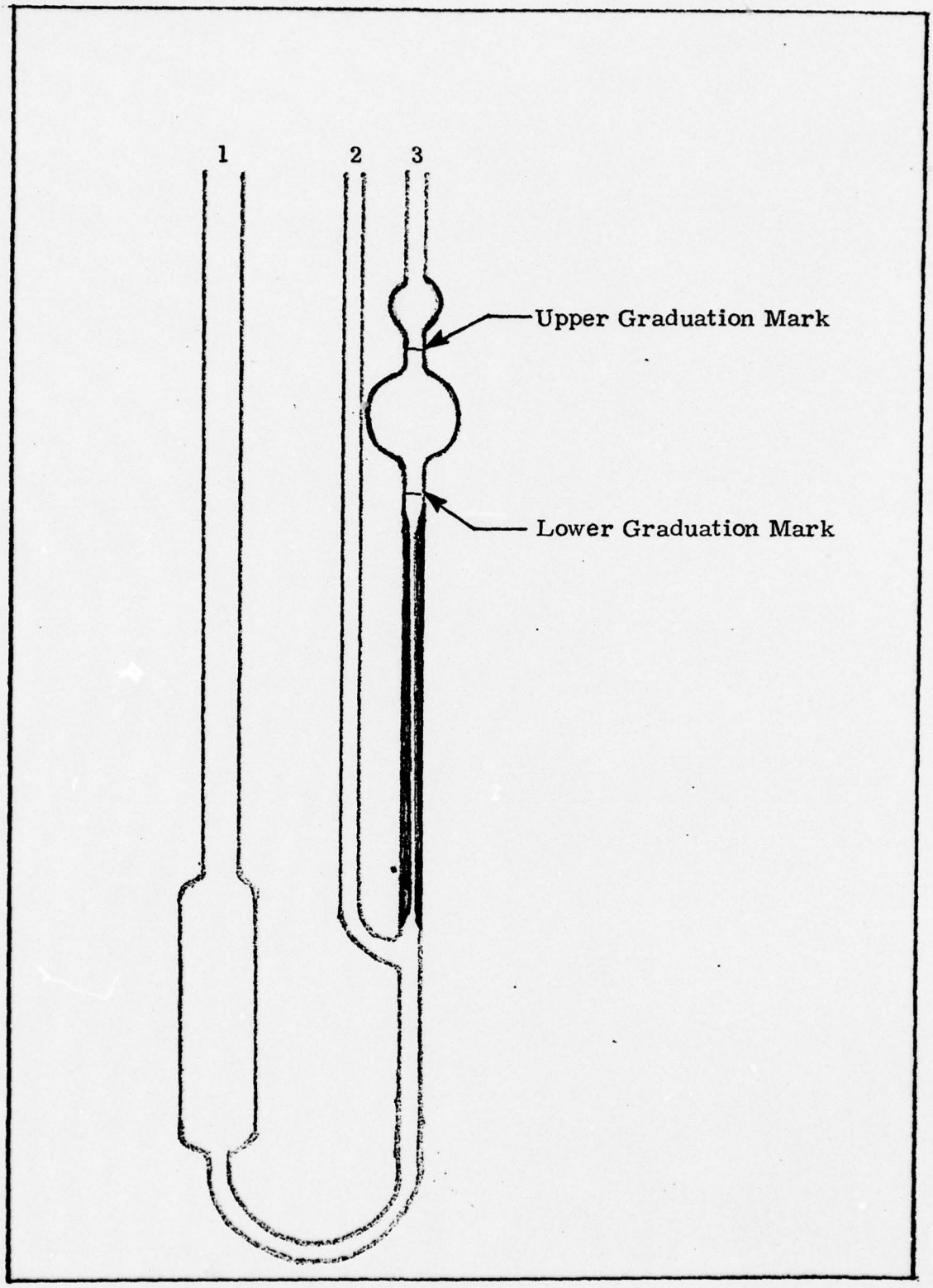

Figure II-4. Ubbelohde Viscometer

meniscus to fall between the upper and lower graduation marks was measured. The efflux time was measured three times by this process.

4. The viscometer was drained and 10 mls. of filtered polymer solution were added and allowed to come to thermal equilbrium. The efflux time was measured as described in step 3. The polymer solution was then successively diluted three times by five mls. and the efflux times of each of these solutions measured.

The intrinsic viscosity (n) was calculated from the experimental data by plotting:

$$\frac{n_r}{C} \text{ vs } C$$

where $n = t/t_o$ (t_o is the solvent efflux time, C is the concentration) and by plotting:

$$\ln \; n_{sp} \text{ vs } C$$

where $n_{sp} = n_r - 1$. (n) is the common intercept at zero concentration for the best straight lines through the two sets of points.

III. RESULTS

A. Polystyrene Solutions

Many attempts were made to reproduce Leopairat's results with polystyrene. Using the orifice as shown in Figure II-3, with orifice velocities ranging up to 11,000 cm/s (run 801), no degradation was observed on the GPC chromatographs. No degradation was observed using a higher molecular weight (run 1702) or using a different solvent (run 901). All chromatographs were identical, within the error of the GPC, unlike those of Leopairat.

Leopairat's chromatographs all showed significant breakdown of the polymer. The peak height was lowered and the amount of lower molecular weight species observed was markedly increased (see Figure III-1).

The apparatus used was the same one built and used by Leopairat. The only difference was the orifice leading into holding cylinder R, which had been altered to reduce any tendency to produce turbulent flow in this area. In order to discover the source of the degradation observed by Leopairat, the orifice was varied and polymer solution was forced through these various orifices. Table III-1 is a list of runs made and a description of the orifice used in each run and the orifice velocity.

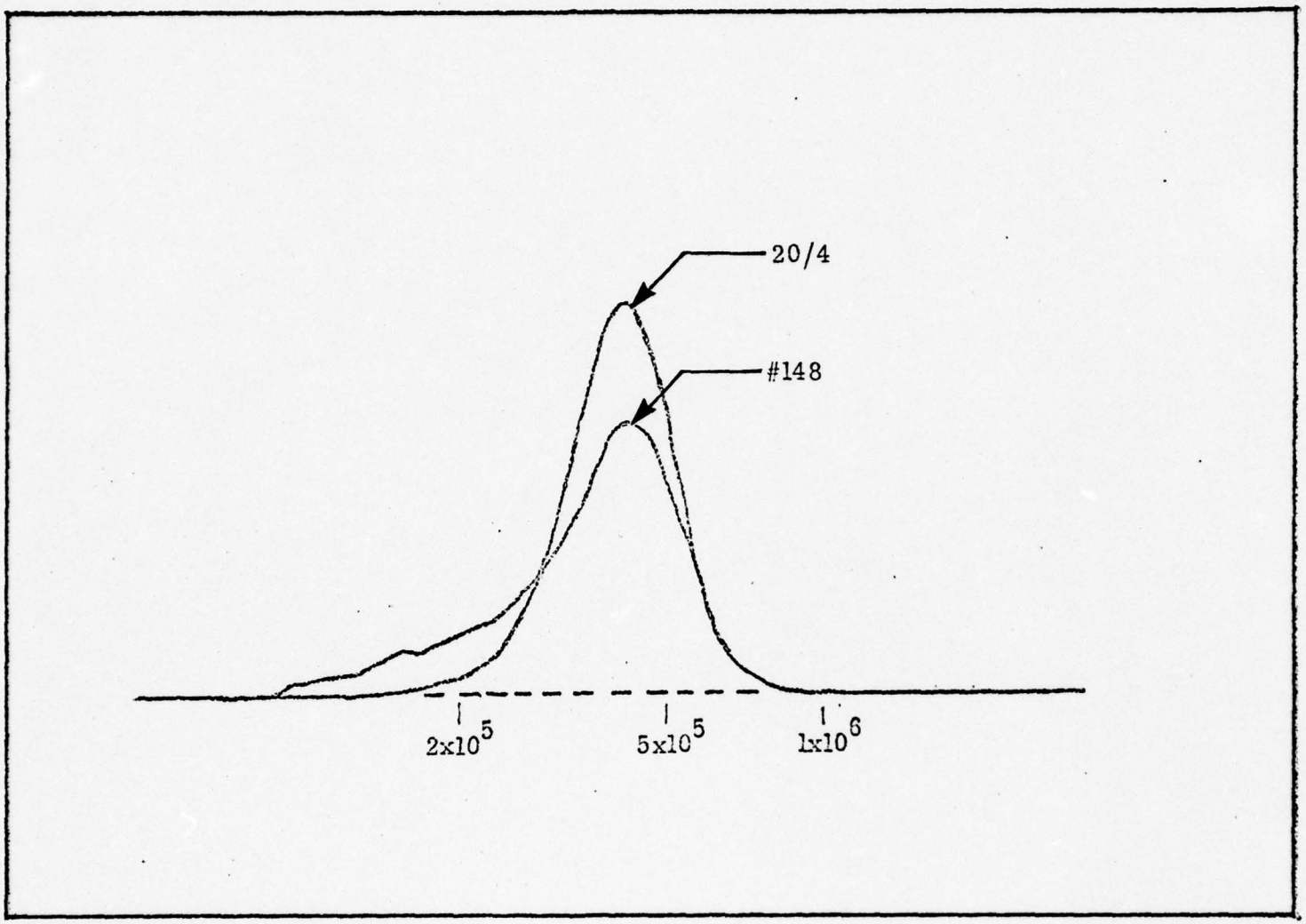

Figure III-1. Trace of Leopairat's run #148 over that of PS 20/4 showing marked decrease in the number of high molecular weight species and corresponding increase in low molecular weight species.

TABLE III-1

RUN	DESCRIPTION	$\overline{V}_{orifice}$
1601	Using plug and original Leopairate orifice plate (orifice diameter = 0.020", thickness = 0.010")	12,600
1603	Using plug and thick orifice plate (orifice diameter = 0.018", thickness = 0.094")	13,200
1604	Using plug and brass orifice plate drilled with burrs, burrs placed up (orifice diameter = 0.020", thickness = 0.010")	11,600
1605	Same as 1604, except burrs placed down	11,200
1606	Using plug, but no plate (orifice diameter = 0.046")	4,090
1607	Using plug and brass plate with obstructions and sharp edges in/around orifice (see Figure III-2) (oridice diameter = 0.020", thickness = 0.010")	16,900
1608	Using orifice described above, digs and burrs were created on top side of plus in an attempt to create turbulence	16,100
1612	Using smooth orifice (see Figure II-3), only 10 ml were used in an attempt to create jet flow through orifice which struck piston P2	12,300
1613	Using plug with no orifice plate, only 10 ml	5,360
1703	Same as 1601	15,700

Figure III-2. Photographs of hole in orifice plates as used by Leopairat (above) and as used in run 1608.

In order to be sure that the GPC was able to detect molecular degradation, 100 mls. of solution 16 were placed in a 250 mls. beaker and sonified three minutes at about 60 Watts, using a Sonifier(R) cell disruptor Model W185D. Aluminum foil was placed over the top of the beaker to prevent evaporation of the solvent during sonification. The GPC chromatograph indicated molecular degradation similar to that observed by Leopairat (see Figure III-3).

A concentrated solution of polystyrene in toluene (solution 1800) degraded in extensional flow (run 1801) as revealed by both intrinsic viscocity and GPC. Results are shown in Tables II-2 and III-3 and in Figures III-4 and III-5.

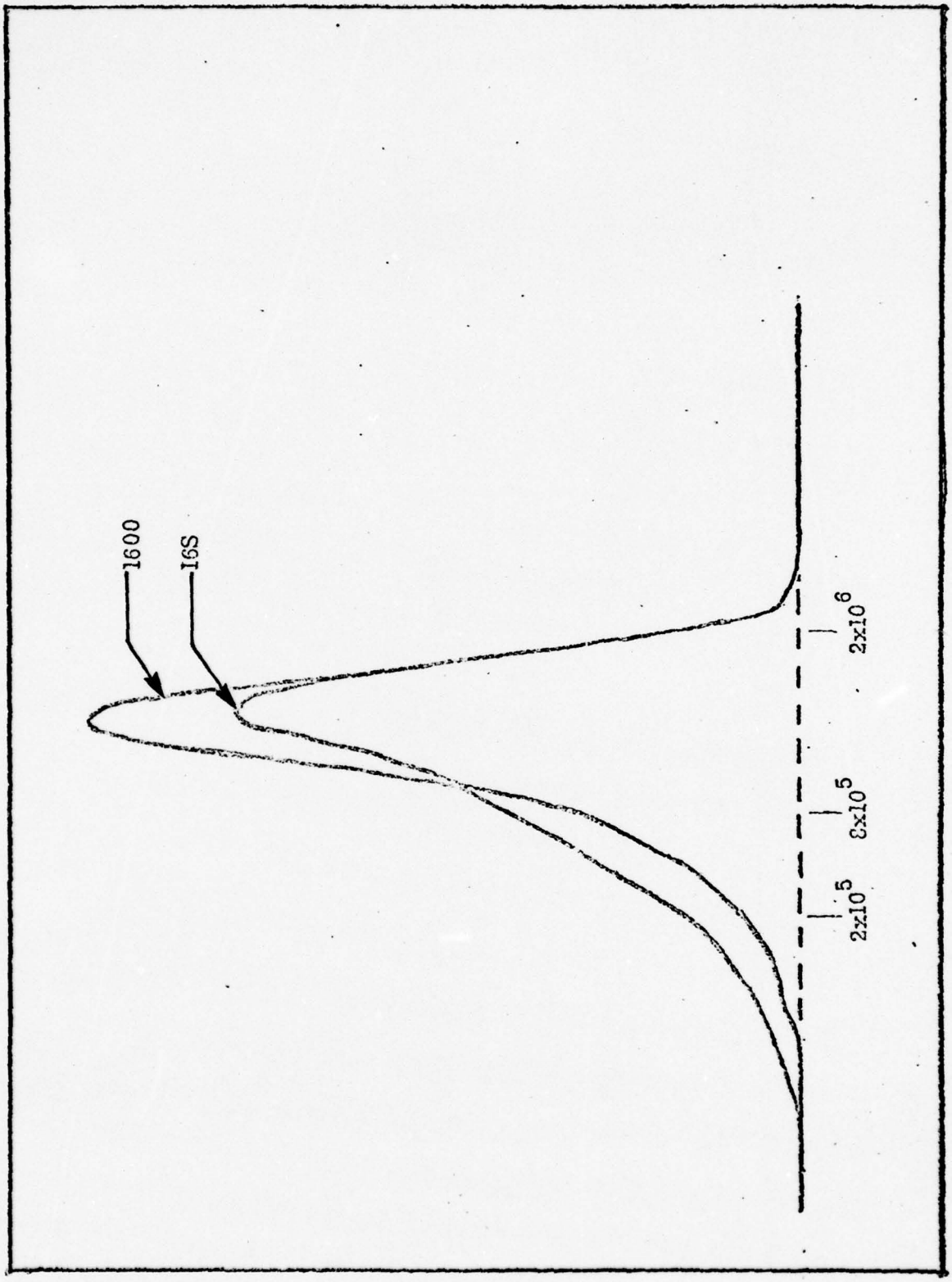

Figure III-3. Trace of sonified polystyrene solution (16S) compared to solution 16.

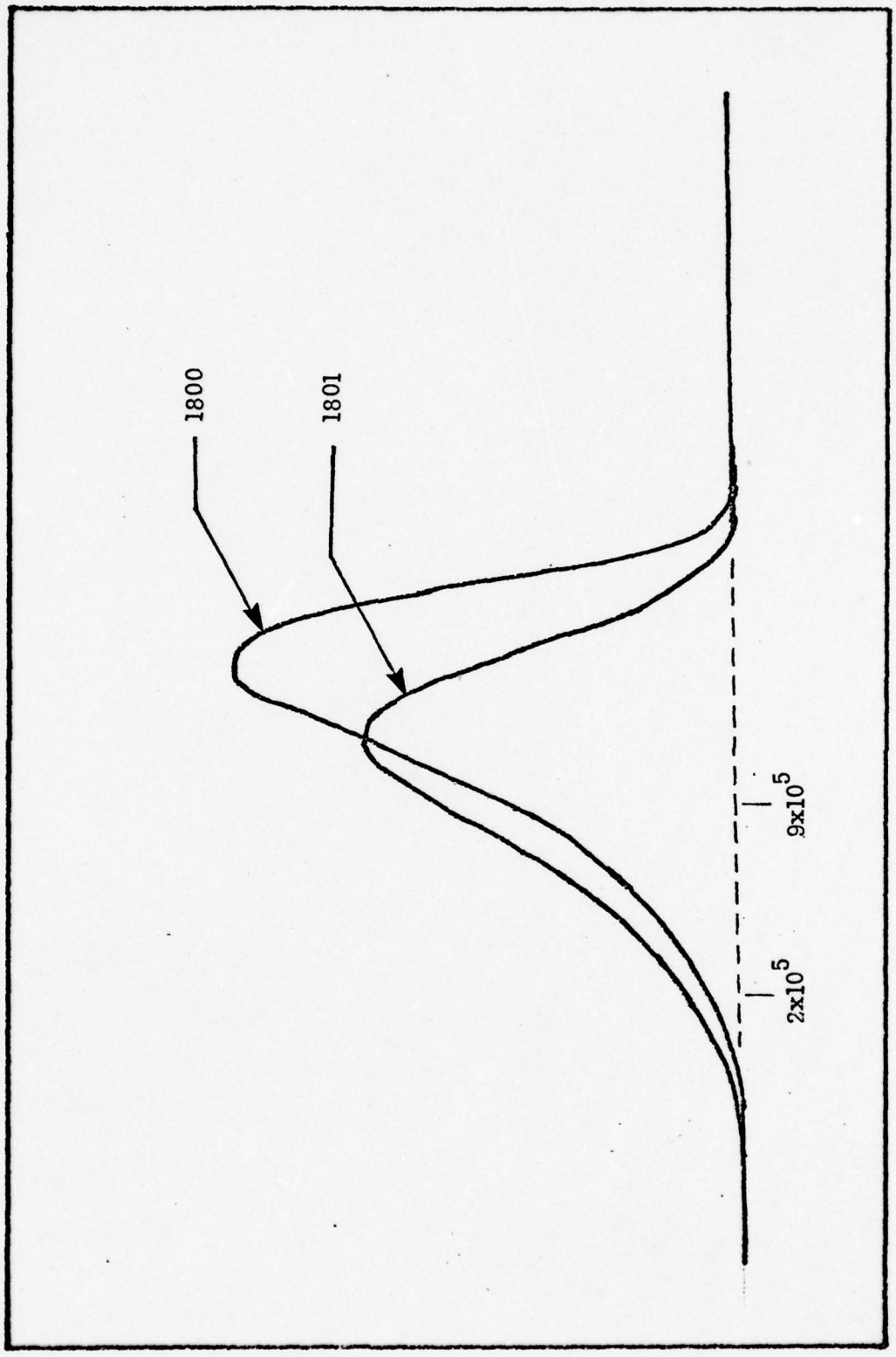

Figure III-4. Trace of Chromatographs of Solutions 1800 and 1801.

TABLE III-2

Intrinsic Viscosity of Solution 1800

Conc. (g/dl)	t (s)	$\frac{n_{sp}}{C}$(dl/g)	$\frac{\ln n_r}{C}$(dl/g)
0.195	143.9	5.19	3.58
0.130	116.2	4.85	3.76
0.0974	103.6	4.62	3.82
0.0731	95.0	4.52	3.90
Solvent	71.5		

(n) = 4.1 (from Figure III-5)

$\bar{M}_v$ = 2,070,000

TABLE III-3

Intrinsic Viscosity of Solution 1801 $\bar{V}$ orifice = 9,620

Conc. (g/dl)	t (s)	$\frac{n_{sp}}{C}$(dl/g)	$\frac{\ln n_r}{C}$(dl/g)
0.195	111.1	2.85	2.27
0.130	96.8	2.73	2.34
0.0974	90.1	2.68	2.38
0.0731	85.2	2.63	2.41
Solvent	71.5		

(n) = 2.5 (from Figure III-5)

$\bar{M}_v$ = 1,070,000

These results were verified by GPC, where the number average molecular weight was also reduced by about a factor of two, from 1,960,000 to 1,130,000 (see Figure III-4).

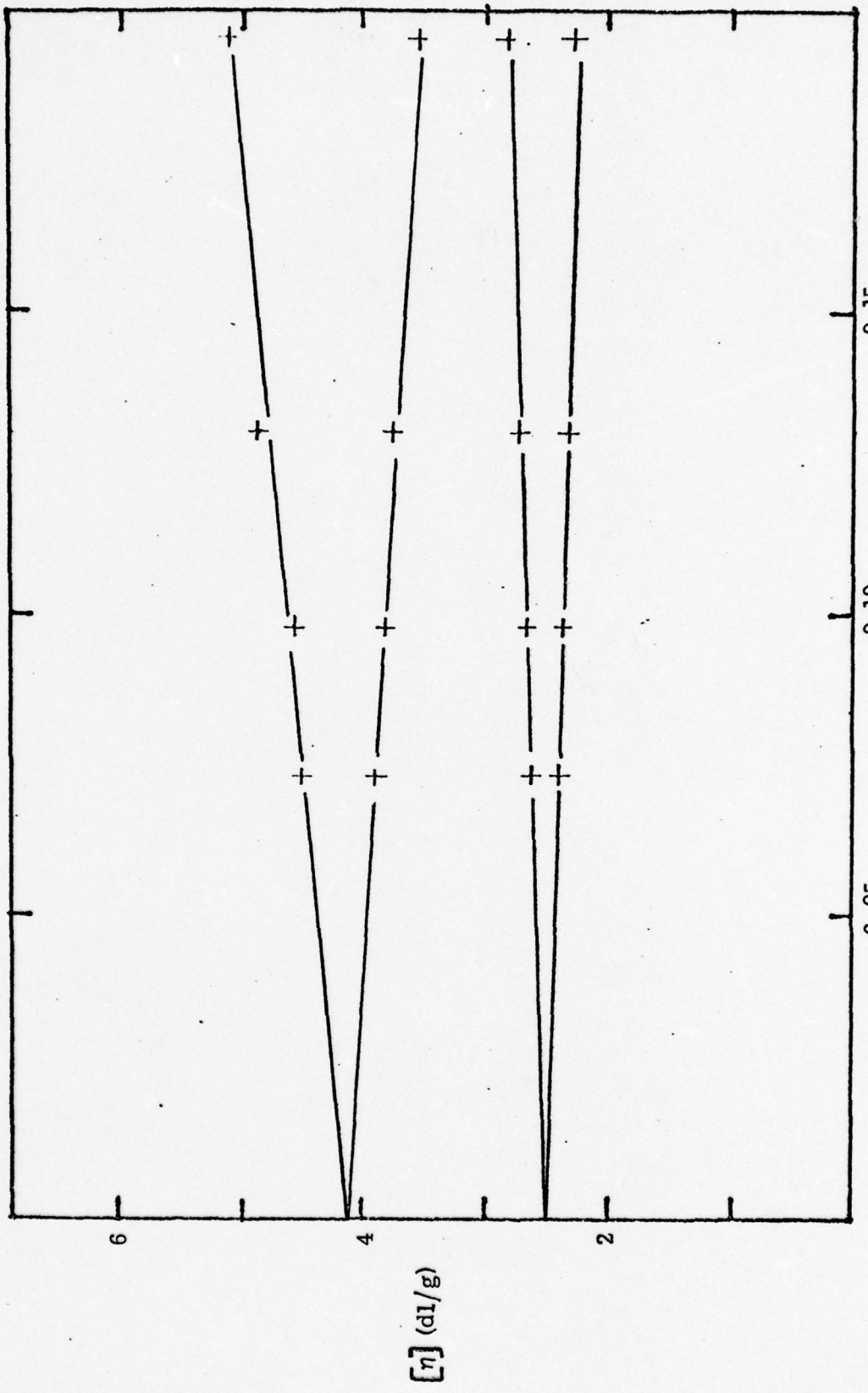

Figure III-5. Intrinsic Viscosity Results of Solutions 1800 (above) and 1801.

B. Polyethylene Oxide

J. Moore (17) observed the degradation of PEO in dichloromethane in extensional flow. His results were duplicated, monitoring the degradation of PEO by intrinsic viscosity.

TABLE III-4

Intrinsic Viscosity of Solution 2000

Conc. (g/dl)	t (s)	$\frac{n_{sp}}{c}$(dl/g)	$\frac{\ln n_r}{c}$(dl/g)
0.0499	62.9	12.5	9.69
0.0333	54.5	12.2	10.20
0.0250	50.2	11.9	10.50
0.0187	47.5	11.9	10.80
Solvent	38.8		

(n) = 11.5 (from Figure III-6)

TABLE III-5

Intrinsic Viscosity of Solution 2003 $\overline{V}_{orifice}$ = 12,500

Conc. (g/dl)	t (s)	$\frac{n_{sp}}{c}$(dl/g)	$\frac{\ln n_r}{c}$(dl/g)
0.4999	49.1	5.35	4.74
0.0333	45.6	5.27	4.86
0.0250	43.7	5.12	4.81
0.0187	42.3	4.89	4.68
Solvent	38.8		

(n) = 4.8 (from Figure III-6)

B. Polyethylene Oxide

J. Moore (17) observed the degradation of PEO in dichloromethane in extensional flow. His results were duplicated, monitoring the degradation of PEO by intrinsic viscosity.

TABLE III-4

Intrinsic Viscosity of Solution 2000

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0.0499	62.9	12.5	9.69
0.0333	54.5	12.2	10.20
0.0250	50.2	11.9	10.50
0.0187	47.5	11.9	10.80
Solvent	38.8		

(n) = 11.5 (from Figure III-6)

TABLE III-5

Intrinsic Viscosity of Solution 2003 $\overline{V}_{orifice}$ = 12,500

Conc. (g/dl)	t (s)	$\frac{n_{sp}}{C}$(dl/g)	$\frac{\ln n_r}{C}$(dl/g)
0.4999	49.1	5.35	4.74
0.0333	45.6	5.27	4.86
0.0250	43.7	5.12	4.81
0.0187	42.3	4.89	4.68
Solvent	38.8		

(n) = 4.8 (from Figure III-6)

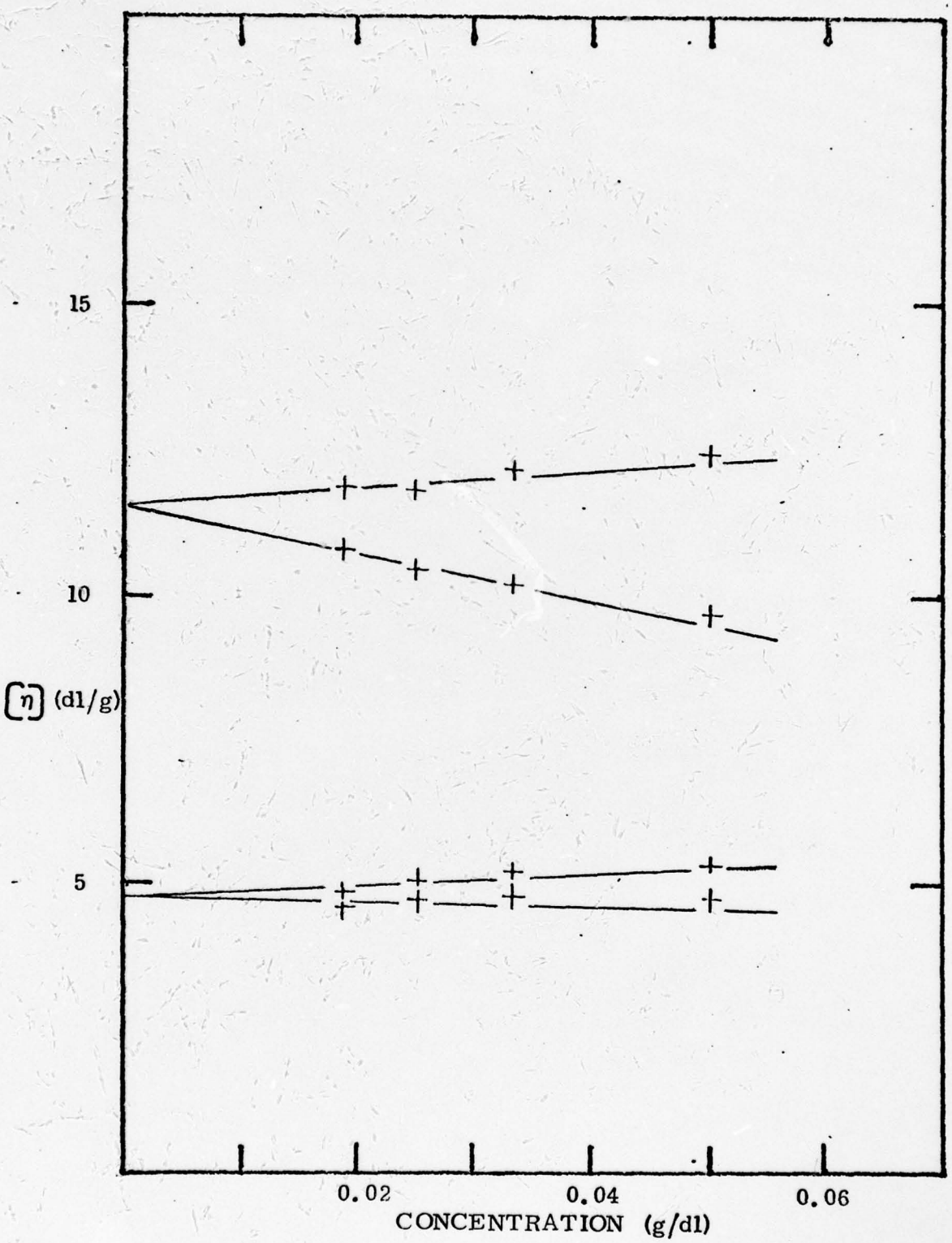

Figure III-6. Intrinsic Viscosity Results of Solutions 2000 (above) and 2003.

IV. DISCUSSION OF RESULTS

A. Effect of Orifice

Using the same apparatus as P. Leopairat, with a slightly modified orifice, no degradation was observed at high strain rates. Different orifice configurations were used, but no degradation of polystyrene in dilute solutions could be induced, as shown by GPC chromatographs. The degradation which Leopairat observed may have been due to an artifact of Leopairat's apparatus, which no longer exists.

Careful examination of Leopairat's kymographs reveals a discontinuity in the slope (see Figures IV-1 and IV-2) not present in the kymographs produced during this study. This discontinuity indicates a sudden and large increase in $\overline{V}_{orifice}$. This last 1 1/2 mm of the curve corresponds to about one-half milliliter (about 5%) of the solution originally in the high pressure cylinder. If it is the case that the last one-half milliliter of solution was forced through the orifice at this higher velocity, this last one-half milliliter of solution underwent tremendous shear as it flowed between the rising piston and the orifice plate.

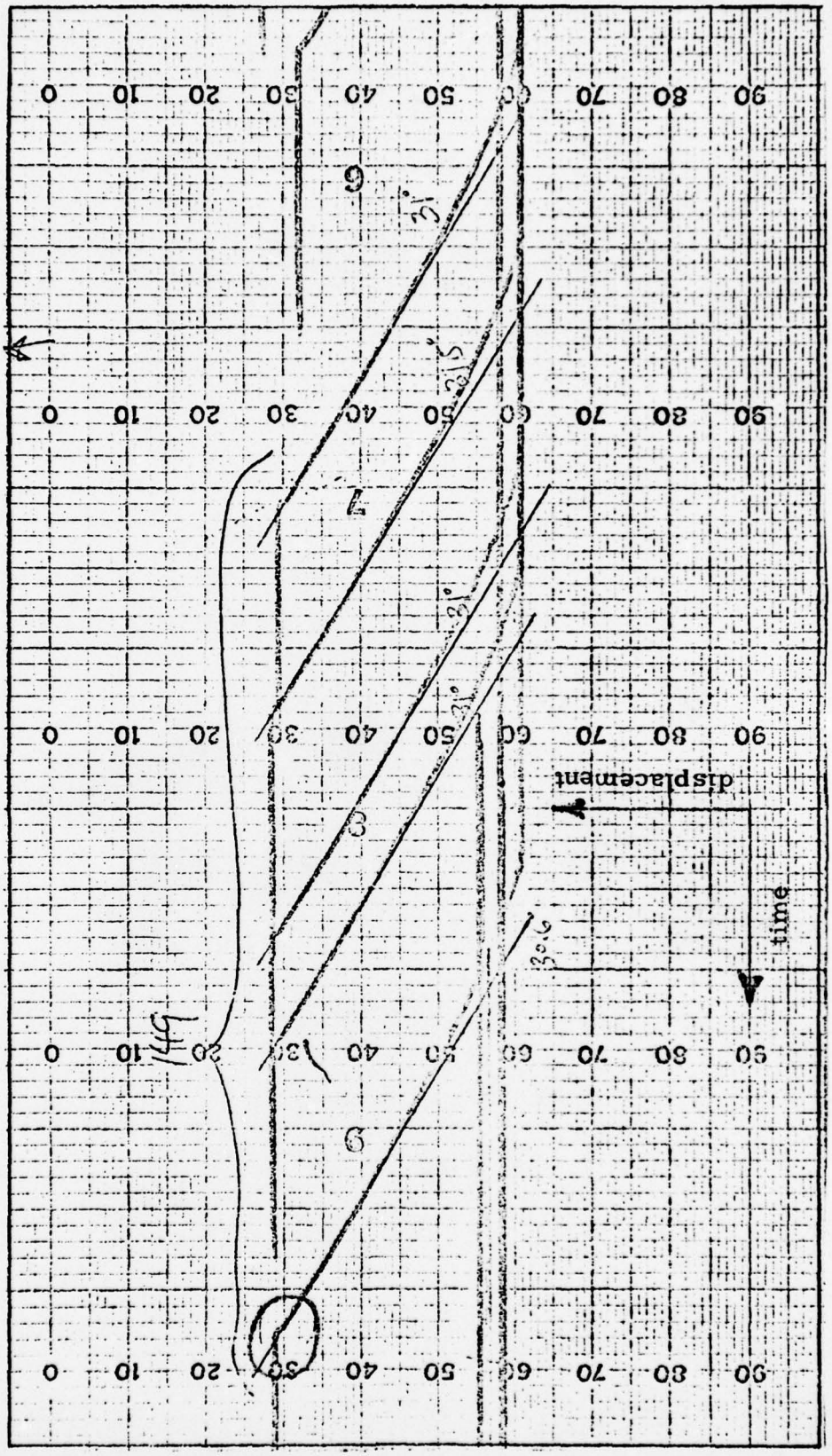

Figure IV-1. Copy of Leopairat's kymographs showing discontinuity.

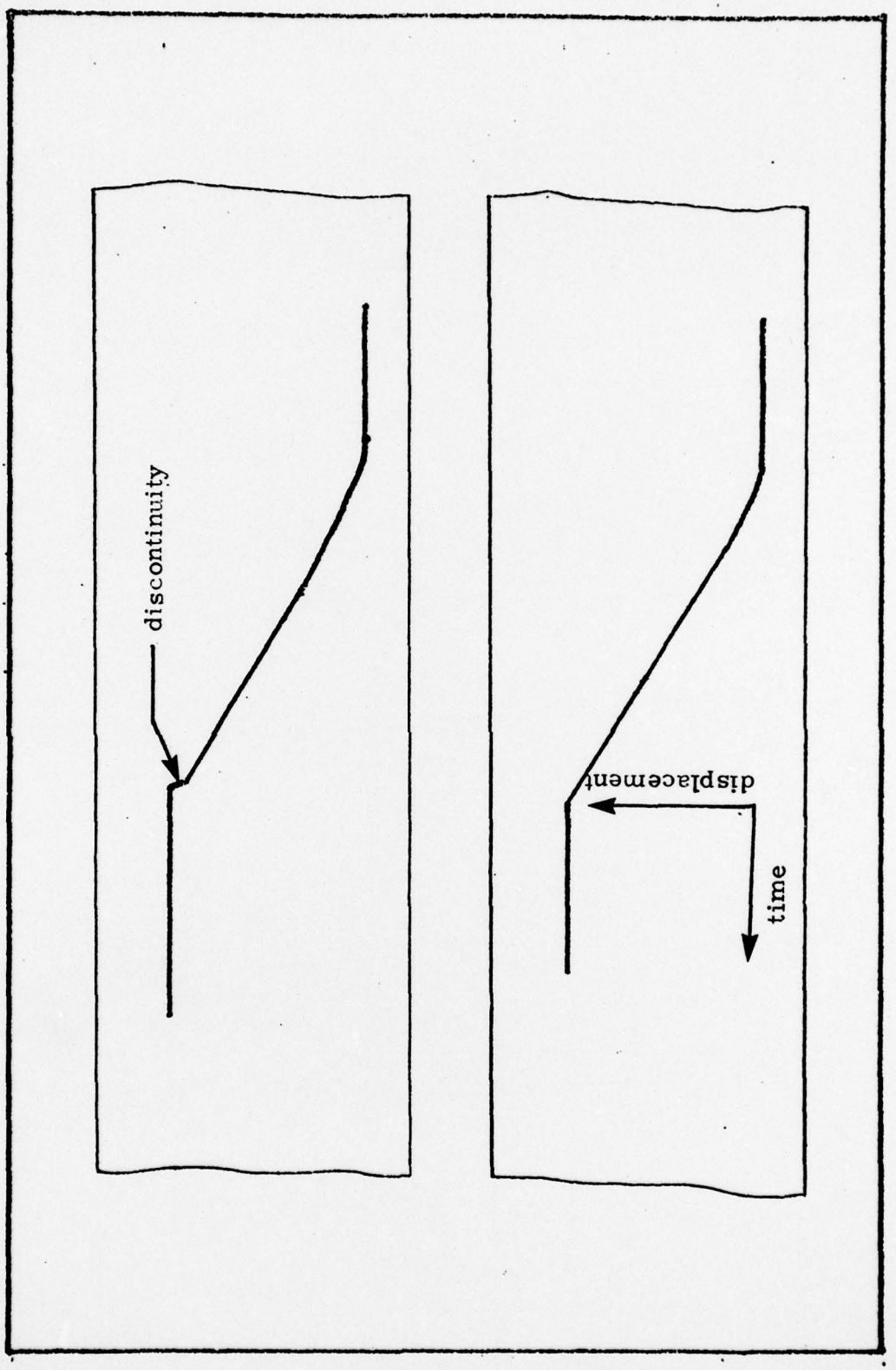

Figure IV-2. Kymograph of Leopairat (above) compared with that of author.

Mr. Ed Lane of Draper Laboratory (who helped Leopairat with his apparatus) attributed this discontinuity to small amounts of air which may have been trapped in the high-pressure cylinder and did not escape until the piston forced them through the orifice. These bubbles of air would have been highly compressed as the piston rose under pressures of about 1000 psi. After passing through the orifice to the low-pressure cylinder, these bubbles would have violently expanded, resulting in high shear rates in the polymer solution surrounding the bubbles and the degradation Leopairat documented.

B. Effect of Concentration

Using concentrations in excess of the critical concentration, polystyrene degraded in extensional flow, as indicated by both GPC and intrinsic viscosity. The reduction in molecular weight was probably due to intermolecular entanglements of the polymer chains. It is doubtful that the degradation Leopairat observed was due to intermolecular entanglements, as the signal to noise ratio and peak areas on the chromatographs he produced suggested he used the same concentrations as he indicated.

Working with PEO, J. Moore observed degradation using concentrations slightly above the critical concentration. His work was verified using intrinsic viscosity.

V. CONCLUSIONS

1. Polystyrene in dilute solutions does not degrade under high rates of strain, contrary to the findings of Leopairat. The source of the discrepancy has yet to be determined, but comparison of kymograph traces suggests that in Leopairat's experiment, there was an abrupt increase of the piston velocity just prior to the end of the stroke, not present in this work. This abrupt change could have resulted either in a much greater strain rate on the last element of liquid expelled through the orifice, or, if air was entrapped, the air expelled through the orifice would drastically and violently expand beyond the throat. This would result in huge local strain rates in the polymer solution surrounding the bubbles.

2. At concentrations above the critical concentration, polystyrene suffers a loss in molecular weight when subjected to similar rates of strain.

3. As observed by Moore, PEO at concentrations above the critical concentration degrades under similar rates of strain.

VI. RECOMMENDATIONS FOR FURTHER STUDY

Further attempts should be made to determine the source of the degradation Leopairat observed. A study to determine the concentrations at which intermolecular entanglements become important would be of use. It is also recommended that polymers with a lower characteristic ratio in dilute solutions be studied. A lower characteristic ratio may well lead to enough intramolecular entanglements to produce degradation in dilute solutions.

APPENDIX A

Calculation of $V_{orifice}$

Velocity of Rotating Drum	=	0.20 cycle/sec
The Drum's Circumference	=	25 inches
Velocity at Circumference	=	12.7 cm/sec
Slope of Straight Line Generated in Kymograph	=	θ
Velocity of Holding Piston	=	12.7 tan θ cm/sec
Diameter of Orifice	=	Y inches
Diameter of Pressurized Chamber	=	0.75 inches
Therefore, $V_{orifice}$	=	$12.7 \tan \theta \frac{(0.75)^2}{Y^2}$
	=	$\frac{7.144}{Y^2} \tan \theta$

APPENDIX B

Calculation of $(\bar{r}^2)^{1/2}$ and Critical Concentrations

Mark-Houwink-Sakurada Equation: $[\eta] = k M^a$

Flory-Fox Equation: $[\eta] = \frac{\Phi (\bar{r}^2)^{3/2}}{M}$

thus: $(\bar{r}^2)^{1/2} = \left[\frac{k M^{a+1}}{\Phi}\right]^{1/3}$

Where for polystyrene in tolune (18):

$\Phi = 2.1 \times 10^{21}$ dl/g-mole cm^3

$k = 7.5 \times 10^{-5}$ dl/g

$a = 0.75$

Critical Contration: $\frac{M}{(\bar{r}^2)^{3/2} N_{avo.}}$ g/cc

TABLE B-1

Polymer	MW	$(\bar{r}_{nm}^2)^{1/2}$	Critical Contraction (wt.%)
PSt	390,000	60.1	0.30
PSt	2,000,000	156.0	0.088
PEO	1,200,000	167.0 (13)	0.043

APPENDIX C

Sources of Polymers Used

Polymer	MW	Description
PSt	390,000	Monodispersed polystyrene purchased from Pressure Chemical Company
PSt	2,000,000	Monodispersed polystyrene purchased from Pressure Chemical Company
PEO	1,200,000	Polyox$_{TM}$ WSR301 from Union Carbide Corporation

APPENDIX D

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Polymer Degradation
Polymers in Dilute Solutions

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Dilute solutions (0.025 to 0.05 wt.%) of polystyrene in toluene were placed in an extensional flow field. The molecular weight distribution of the polymer was studied before and after being placed in the flow field by gel permeation chromatography. Monodispersed polystyrene showed no change in molecular weight distribution after passing through the flow field. These results are contrary to those of P. Leopairat (MIT PhD Thesis; 1977). It is suggested that the degradation Leopairat observed was due

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to an artifact in the apparatus he used.