VISCOSITY DETERMINATION DURING POLYMERIZATION

By

ELMER D. JONES

Submitted in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE

in Chemical Engineering

in the

Graduate Division

at the

Newark College of Engineering

May 15, 1954

ACKNOWLEDGEMENTS

The author extends his sincere appreciation and gratitude to Dr. Saul I. Kreps of Newark College of Engineering for his guidance as research supervisor and to Dr. G. A. Nesty, Messrs. H.E. Gronich, P. Papero, and J.S. Shrensel of Allied Chemical and Dye Corporation for their cooperation and advice, and for making available laboratory facilities and materials.

TABLE OF CONTENTS

ABSTRACT

This project was undertaken for the purpose of designing, constructing, and operating a viscometer which could be employed for measuring viscosities in the range of 200 to 700 poises at temperatures up to 300°C. Such an instrument was built and used to study the viscosity of Type EV polymer during polymerization.

The new viscometer is based on the principle of concentric rotating cylinders. It is unique in that it can be suspended directly in a polymer batch and will operate under temperature and viscosity conditions as outlined above. Polymerization curves for batches studied show that the instrument gives viscosity values which are reproducible to the extent of ± 3 percent of the value at 330 to 640 poises.

INTRODUCTION

Batch polymerizations of Type EV polymer have been controlled solely by arbitrarily timing the various stages of the process. Polymers produced under supposedly similar conditions were found to vary considerably from batch to batch with respect to flow characteristics when the polymer was remelted and extruded. It was postulated that viscosity measurements might provide a superior method for determining the desired degree of polymerization.

Since the molten polymer is oxidized upon exposure to air and its properties are altered by heating and cooling, it is not feasible to remove samples during the polymerization for viscosity measurement. It is therefore desireable to install a viscometer in the reactor which can indicate viscosity changes as polymerization progresses. The reaction can thus be terminated at any desired viscosity without regard to polymerization time. Efforts made to locate a viscometer which could be put to such use revealed that no commercial instruments were available which would operate within the reactor at temperatures of 200° to 300°C in material whose viscosity is 200 to 700 poises.

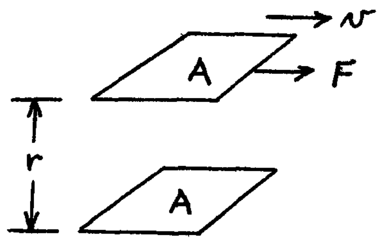
Green[2*] recommends the use of a rotational viscometer for determining viscosities up to 1000 poises. His design, however, is for a laboratory bench model not suitable for use at high temperatures or for sealing into a closed reactor.

* Note: Superscripts refer to articles listed in The Bibliography, page 57.

THEORY OF OPERATION AND EXPERIMENTAL APPARATUS

(1) Theory of the Rotational Viscometer:

Newton defined the coefficient of viscosity (η) as the tangential shearing force per unit area that will produce a unit rate of shear.[5] For two plates, each of unit area, A, separated by distance, r, in the fluid, one of which is moving parallel to the other at velocity, v, by force, F, the coefficient of viscosity is expressed as follows:



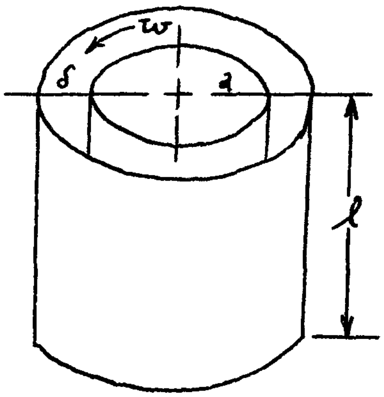
$$\eta = \frac{F/A}{dv/dr} = \frac{\text{Force per Unit Area}}{\text{Rate of shear}}$$

Newton's concept may be adapted to co-axial cylinders:[4]

$$F/A = \frac{T}{2a\pi l a}$$

$$dv/dr = \frac{\omega a}{\delta}$$

$$\eta = F/A \Big/ \frac{dv}{dr} = \frac{T\delta}{2\pi a^3 l \omega}$$



Where: T = torque

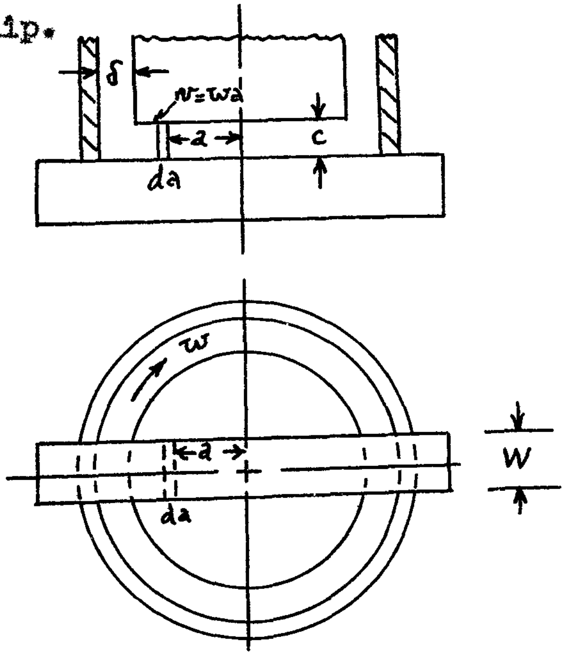
l = length of the cylinders

ω = angular velocity of inner cylinder

a = radius of inner cylinder

δ = clearance between cylinders

However the presence of the keeper bars necessary to hold the hollow outer cylinder in position in the viscometer makes it necessary to incorporate an end correction factor in the above relationship.



Consider an increment of volume which is being placed under shear between the moving bob and the stationary keeper bar. The dimensions of this increment are: da x W x c.

Where: a = radius

W = width of keeper bar

c = distance between bottom of bob and keeper bar

η = viscosity of the fluid

R = rate of shear = $\frac{dv}{dc} = \frac{\omega a}{c}$

λ = shearing stress = $\eta \cdot R = \eta \frac{\omega a}{c}$

T_T = total torque registered by the viscometer = $4T_c + T_N$

T_c = torque due to the effect of one end of one keeper bar

T_N = net torque due to the resistance of sidewalls

$$= \frac{2\pi \eta a^3 l \omega}{\delta}$$

$$dA = W\,da$$

$$dT_e = \lambda\, dA\, a$$

$$dT_e = \eta \frac{\omega a}{c} \cdot a \cdot dA = \frac{\eta \omega}{c} a^2\, dA = \frac{\eta \omega}{c} a^2 W\, da$$

$$\int_0^{T_e} dT_e = \frac{\eta W \omega}{c} \int_{a=0}^{a=a} a^2\, da$$

$$T_e = \frac{\eta W \omega a^3}{3c}$$

$$T_T = 4T_e + T_N = \frac{4\eta W \omega a^3}{3c} + \frac{2\pi \eta a^3 l \omega}{\delta}$$

$$\eta = \frac{T_T}{2\omega a^3 \left(\frac{2W}{3c} + \frac{\pi l}{\delta} \right)}$$

(viscometer equation corrected for end effect)

Using the measured values for constants,

a = radius of viscometer bob = 1.871 cm.

W = width of keeper bars = 1.905 cm.

c = clearance between bottom of bob and keeper bar = .051 cm.

l = length of bob = 4.000 cm.

δ = clearance between bob and outer cylinder = .359 cm.

the above equation may be reduced for the present viscometer design to:

$$\eta = \frac{T_T}{2\omega (1.871)^3 \left(\frac{2 \times 1.905}{3 \times .051} + \frac{3.142 \times 4.000}{.359} \right)}$$

$$\eta = \frac{T_T}{\omega} \times 1.243 \quad \text{(Equation 1)}$$

(Where T_T is expressed in dyne-centimeters and ω in radians/sec, η is in poises.)

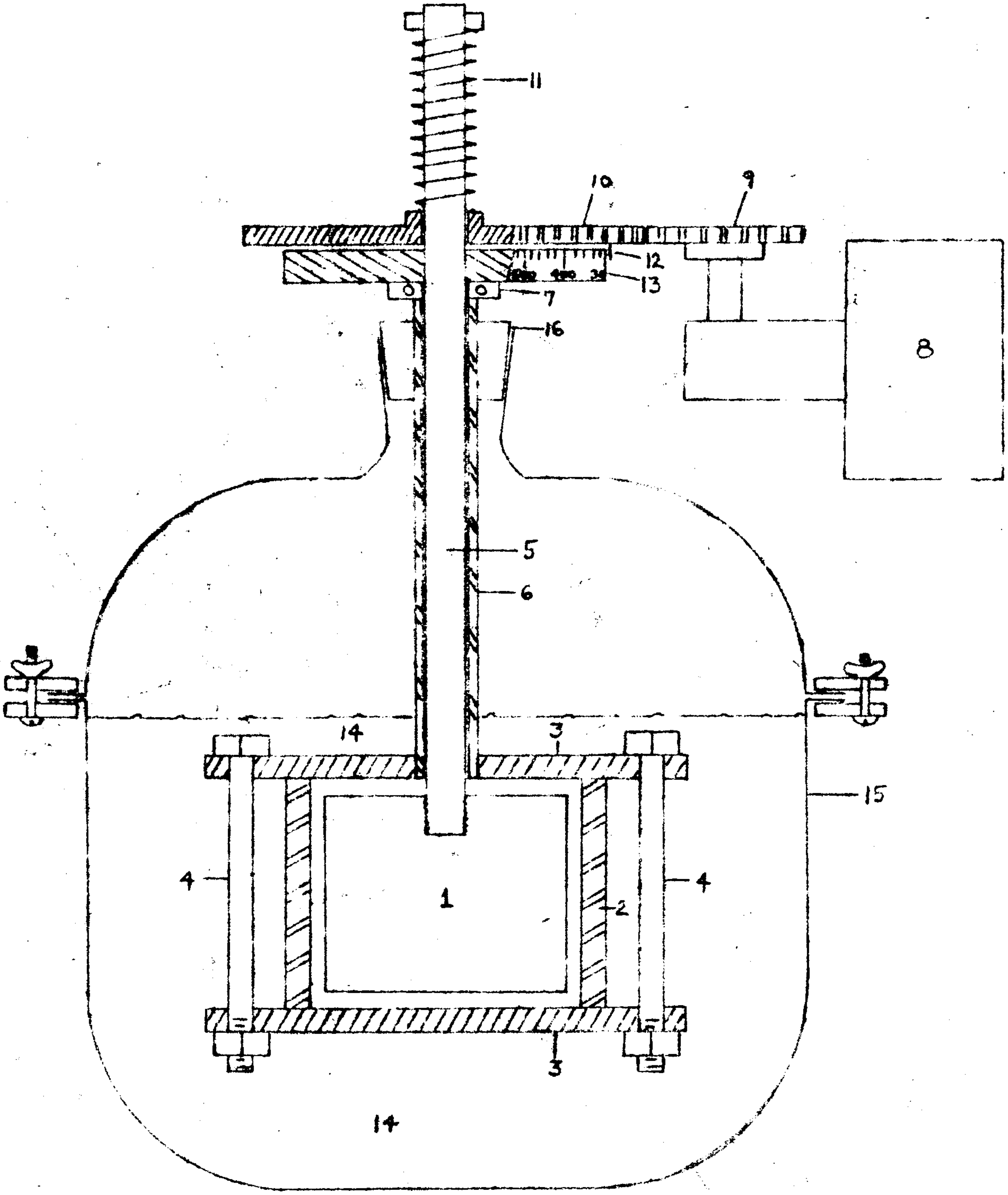
(2) Construction of the Rotational Viscometer:

A schematic cross sectional view of the rotational viscometer used is shown in Figure 1. The apparatus consists of an inner cylinder or bob (1) which is suspended coaxially inside a hollow cylinder (2). Keeper bars(3) and bolts (4) hold the hollow cylinder in place. The bob is suspended and rotated by the shaft (5) which is held in place by the shaft-housing (6) and thrust-bearing (7). A gear-in-head variable speed motor (8) with driving gear (9) is used to drive the viscometer at the desired speed (from 5 to 35 r.p.m.). The driven gear (10) transmits the torque required to drive the bob through the helical spring (11) to the shaft (5). Since the liquid whose viscosity is to be measured (14) will produce a retarding force on the bob (1) proportional to the viscosity of the liquid, the spring (11) will deflect an amount indicated by the pointer (12) on the fixed scale (13) which is calibrated in gram-centimeters (torque). The details and critical dimensions of the rotating bob assembly are shown in Figure 2. A detailed list of specifications for all parts used in the rotational viscometer is shown on page 41 .

All data reported here were obtained in a 1000 ml. resin flask (15), heated by an electric mantle (not shown). The bob and surrounding members of the rotational viscometer were immersed in the low polymer (14) and the instrument was supported by the tapered plug (16) in the neck of the flask.

ROTATIONAL VISCOMETER

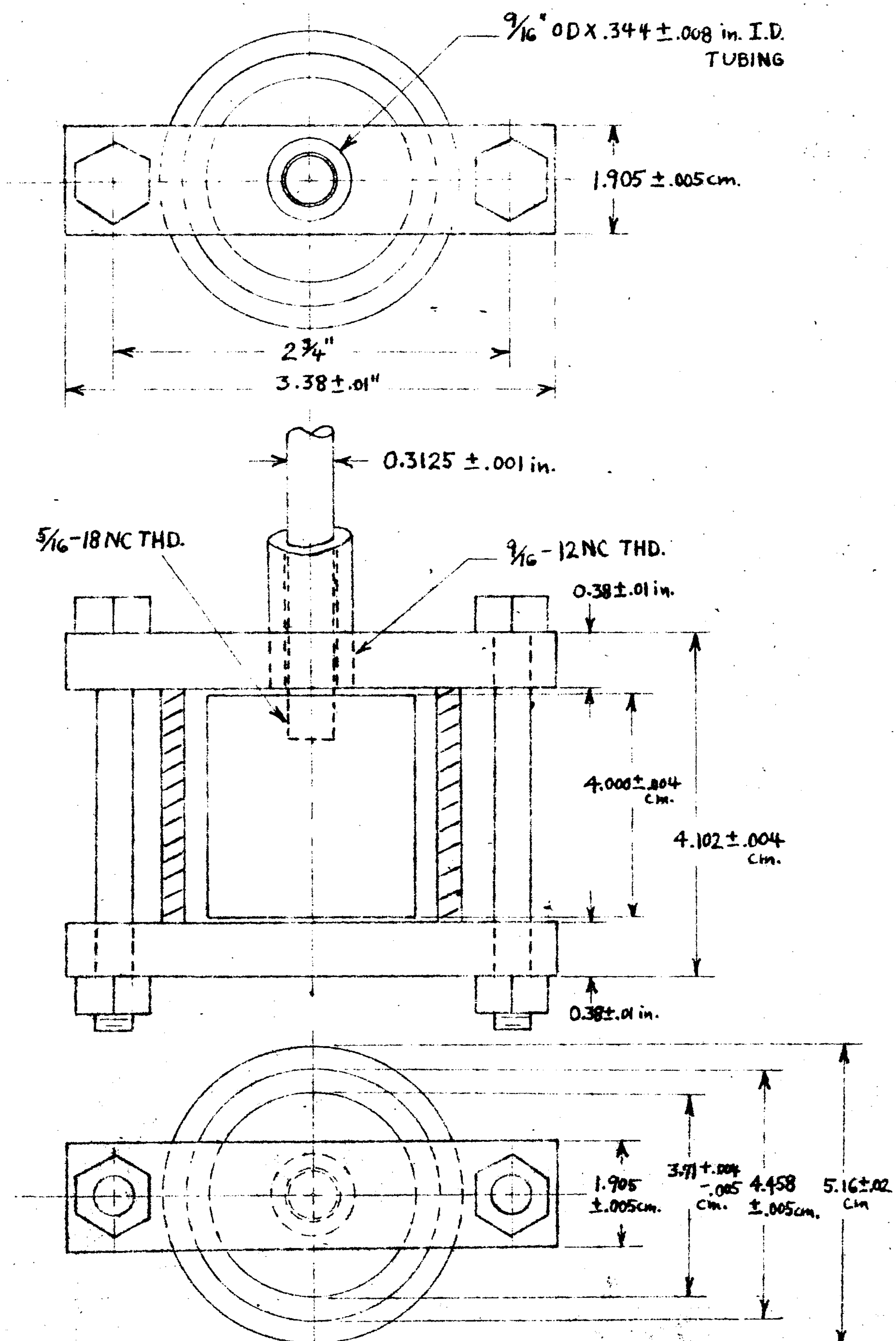
Figure 1



E.D. Jones
1-30-1954

DETAIL OF ROTATING BOB ASSEMBLY

Figure 2



SCALE: 1 CM. = 1 CM.

C. A. Jones 3-13-54

The bob (1) was rotated at essentially constant speed (approximately 20 r.p.m.) and the amount of torque registered on the scale (13) was recorded. The viscosity of the polymer was calculated from the torque and the speed of the instrument by use of Equation 1.

(3) Calibration of the Viscometer:

The helical spring used on the viscometer (Figure 1, No. 11) was wound from .032 inch diameter steel music wire and consisted of twelve one-half inch-diameter turns spread 3/16 inch apart. This spring was calibrated on the viscometer by locking the bob at the point of zero deflection and marking the deflection produced on the scale (Figure 1, No. 13) by application of known torques.

The viscosity of a sample of honey was determined by measuring the time required for 10 cc to flow through a large capillary (0.147 inches in diameter and 5.625 inches long) and relating it to the time required for the same quantity of glycerine of known viscosity to flow through the same tube. Alcohol-in-glass thermometers (range: -10 to + 50°C) were used to determine the temperatures of the glycerine and the honey during the measurement of their viscosities. All materials were in thermal equilibrium with the closed room in which the work was done and their temperatures remained at 23.8°C. throughout the determinations. The viscosity of the honey was calculated by the relationship:

$$\eta_H = \frac{\eta_G \times D_H \times t_H}{D_G \times t_G}$$

Where: η = viscosity in poises

D = density, gms./cc

t = time to flow through tube, seconds

SubH = honey

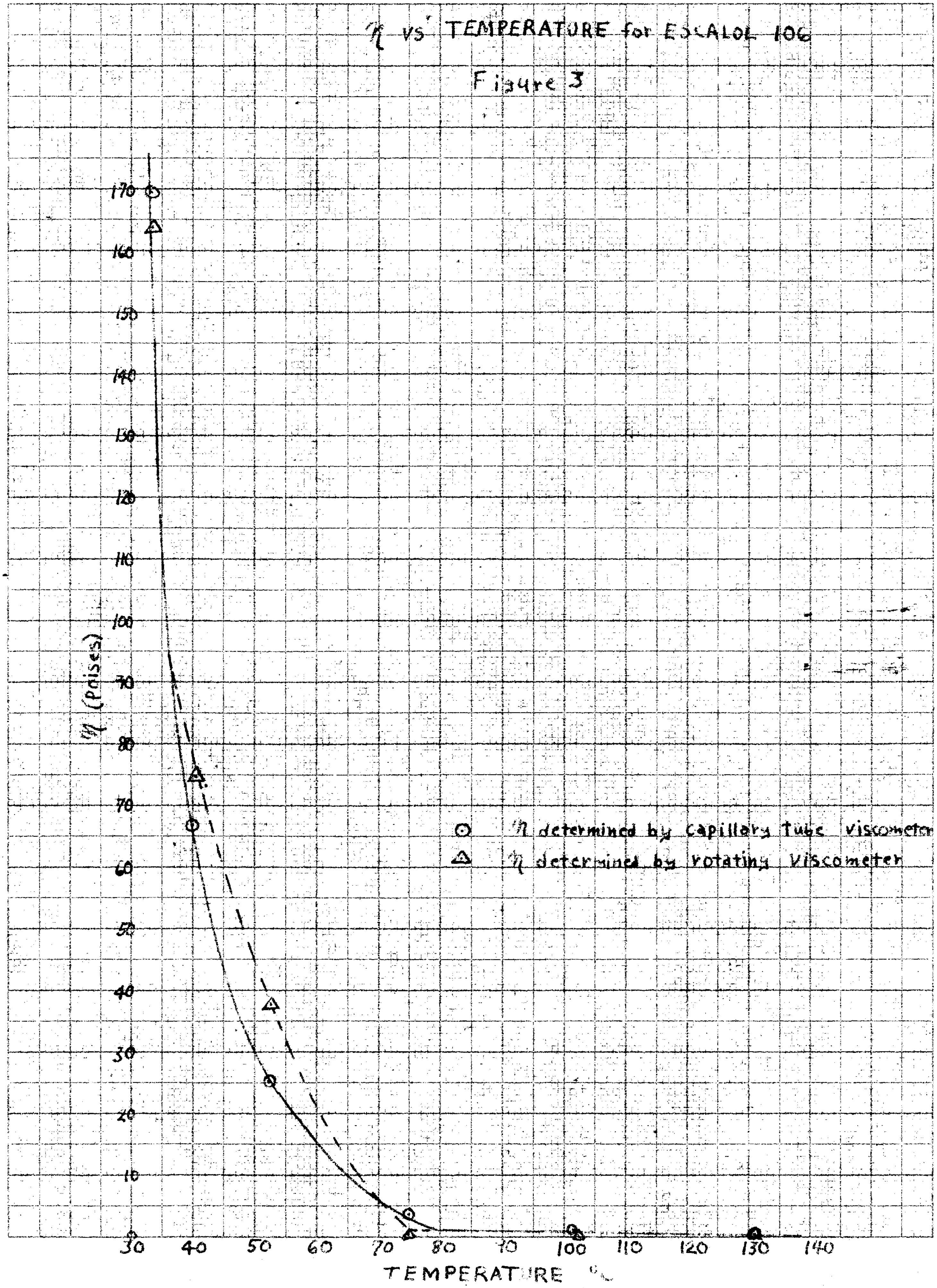
SubG = glycerine

The data used for calculating the viscosity of the honey are shown in the table below:

Determination No.	Vol. of Flow cc	Time of Flow Sec.	Density g/cc	$\eta_{23.8°C}$ Poises
Glycerine				
1	10	37.4		
2	10	36.9		
3	10	38.0		
4	10	37.4		
5	10	36.8		
Average		37.3	1.250	10.5
Honey				
1	10	1122.8		
2	10	1119.3		
3	10	1126.7		
4	10	1112.4		
5	10	1125.3		
Average		1121.3	1.438	382

Page 54 of The Appendix contains the calibration data which were determined with a sample of Escalol 106 (Glyceryl p-Aminobenzoate, U.S. Patent 2,327,899). The viscosity of the Escalol 106 was determined at various temperatures with a capillary tube viscometer in a manner similar to that employed with the honey. Figure 3 shows the effect of temperature upon the viscosity of the Escalol 106. Since the variation in the viscosity as determined by the rotating viscometer and the capillary tube viscometer did not change significantly with increasing temperature (page 54), the effect of temperature upon the accuracy of the instrument in the range of 25 to 130 °C is negligible compared to other sources of error. This temperature effect is analyzed mathematically on page 14 where it is again shown to be negligible at a temperature of 265°C.

The honey and Escalol 106 were employed to check the accuracy of Equation 1: $\eta = \frac{T_T}{\omega} \times 1.243$ as applied to the rotational viscometer. When ω = 2.10 radians/second in the honey a torque of 640 gm-cm. or 627,000 dyne-cm. was indicated by the instrument. This corresponds to a viscosity of 375 poises, calculated by Equation 1. Assuming that the viscosity of the honey determined by the capillary tube method (η_H = 382 poises) is true viscosity, the value obtained with the rotational viscometer and Equation 1 is in error by only 1.8%.



η vs TEMPERATURE for ESCALOL 106
Figure 3
η (Poises)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
30 40 50 60 70 80 90 100 110 120 130 140
TEMPERATURE °C
⊙ η determined by capillary tube viscometer
△ η determined by rotating viscometer

The same procedure with the Escalol 106 gives an average error for the various temperatures of about 7.5%. The maximum error obtained was 48.8% or 12.4 poises at 52°C where the viscosity of the Escalol 106 was only 25.4 poises. The error of 12.4 poises at full scale (1200 gm-cm. or 710 poises) however, amounts to only 1.75%. The Escalol 106 also did not appear to exhibit a sharp melting point but changed from an amorphous solid to an oily liquid in the range of 30 to 50°C upon standing.

The rotational viscometer was calibrated at approximately 25°C and was operated in Type EV polymer at various temperatures from 80 to 265°C. The linear expansion co-efficient of the soft steel of the instrument is 0.0000110 cm. per cm. per °C. The table below shows the critical dimensions of the instrument as measured at 25°C and as calculated at 265°C.

	At 25°C	At 265°C
Diameter of bob (2a)	3.741 cm	3.753 cm.
Diameter of outer cylinder	4.458 cm.	4.470.cm
Clearance between cylinders(δ)	0.359 cm.	0.359 cm.

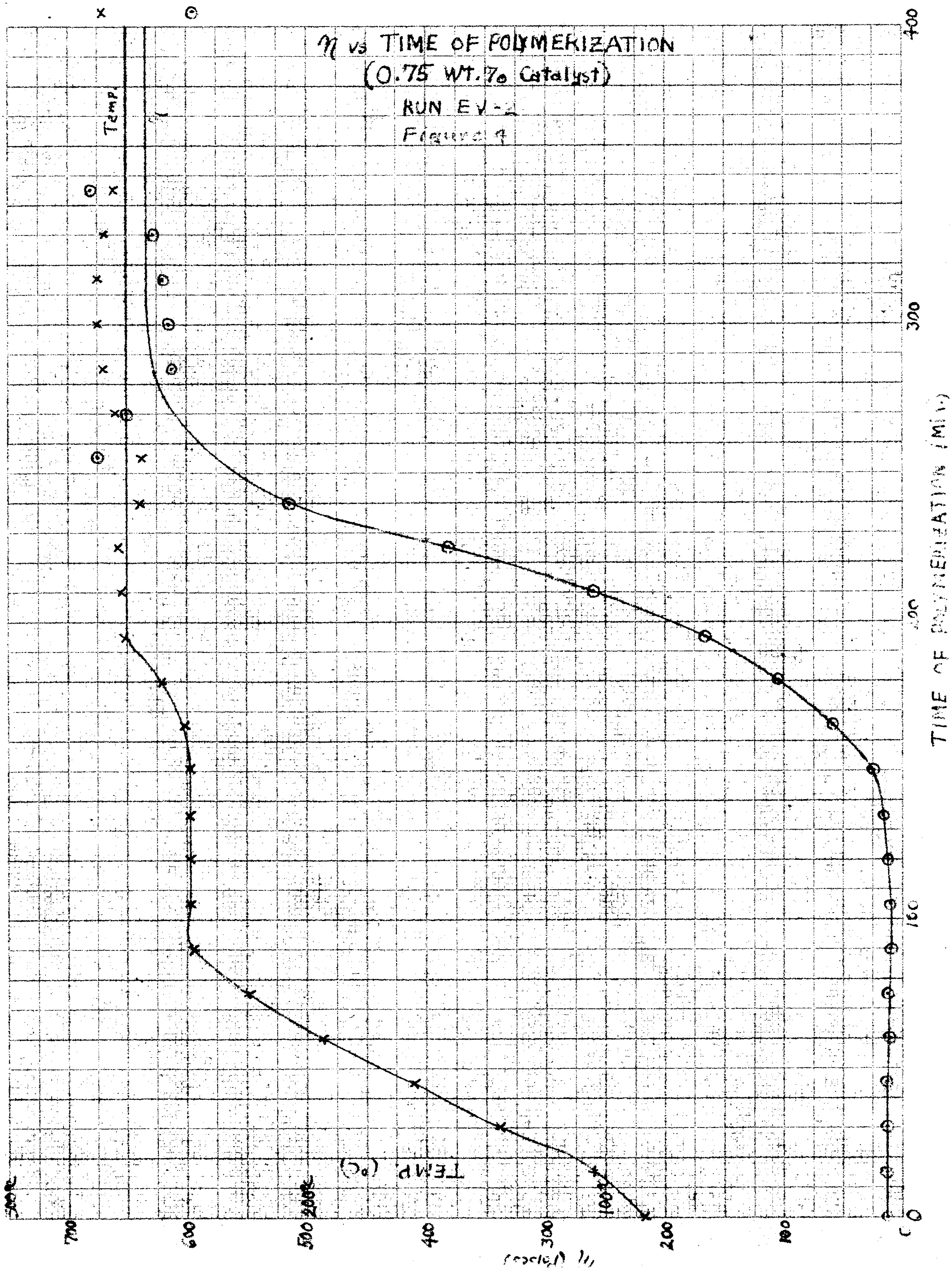
Since there is no significant difference in the amount of clearance between the cylinders due to the temperature changes encountered, it is not necessary to correct the viscometer equation (Equation 1) for the temperature changes which occurred during the polymerization cycles.

DISCUSSION OF EXPERIMENTAL RESULTS

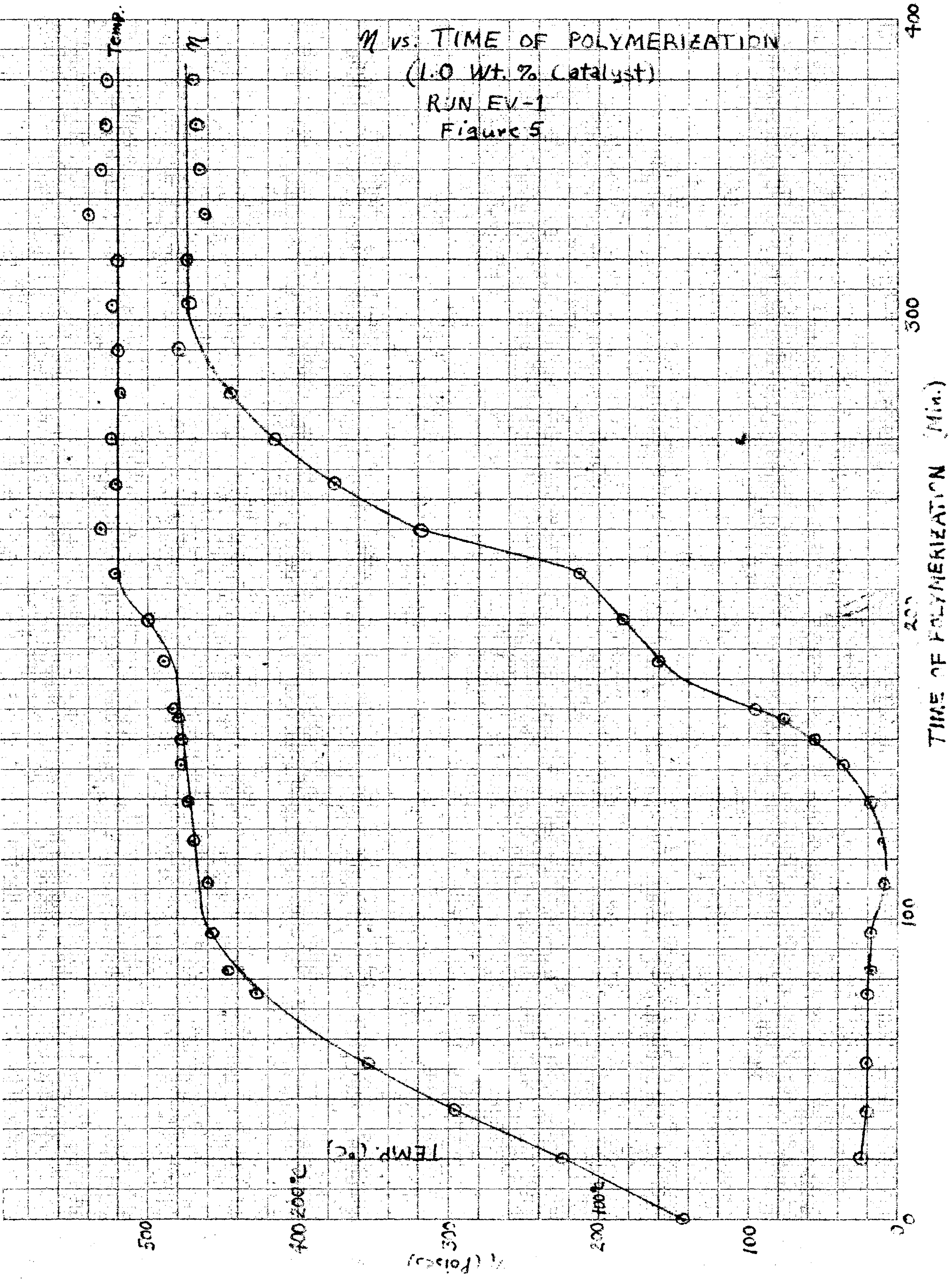
(1) Relationship between Viscosity and Time of Polymerization:

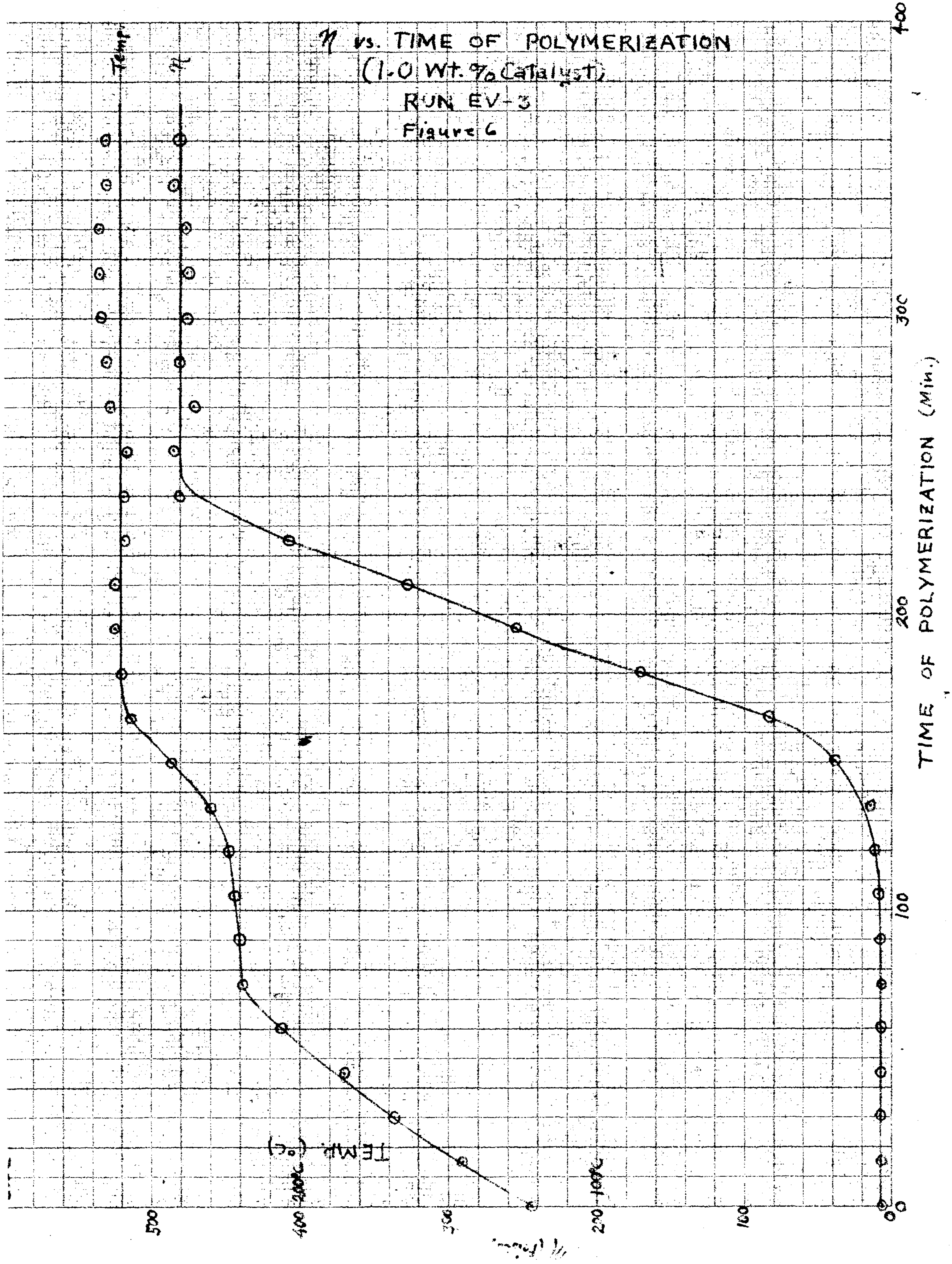
Batches of Type EV polymer, approximately 750 gms. in size, were polymerized in a 1000 ml. resin flask and the melt viscosity was measured at approximately fifteen minute intervals throughout each run. The ultimate degree of polymerization obtained was dependent upon the amount of catalyst used. As shown in Figures 4 through 11 and in pages 42 through 49 of the appendix batches were studied which contained 0, 0.75, 1.00, and 1.25 percent by weight catalyst. In all cases, except where no catalyst was present and thus no polymerization occurred (Fig. 11) a plot of melt viscosity vs. time of polymerization resulted in an S-shaped curve. These curves were all very similar in contour although considerable variation occurred between the center sections as can be seen in Figures 12, 13, and 14. This variation is due to differences in the rate of heating which in turn is dependent upon the amount of moisture initially present in the raw material.

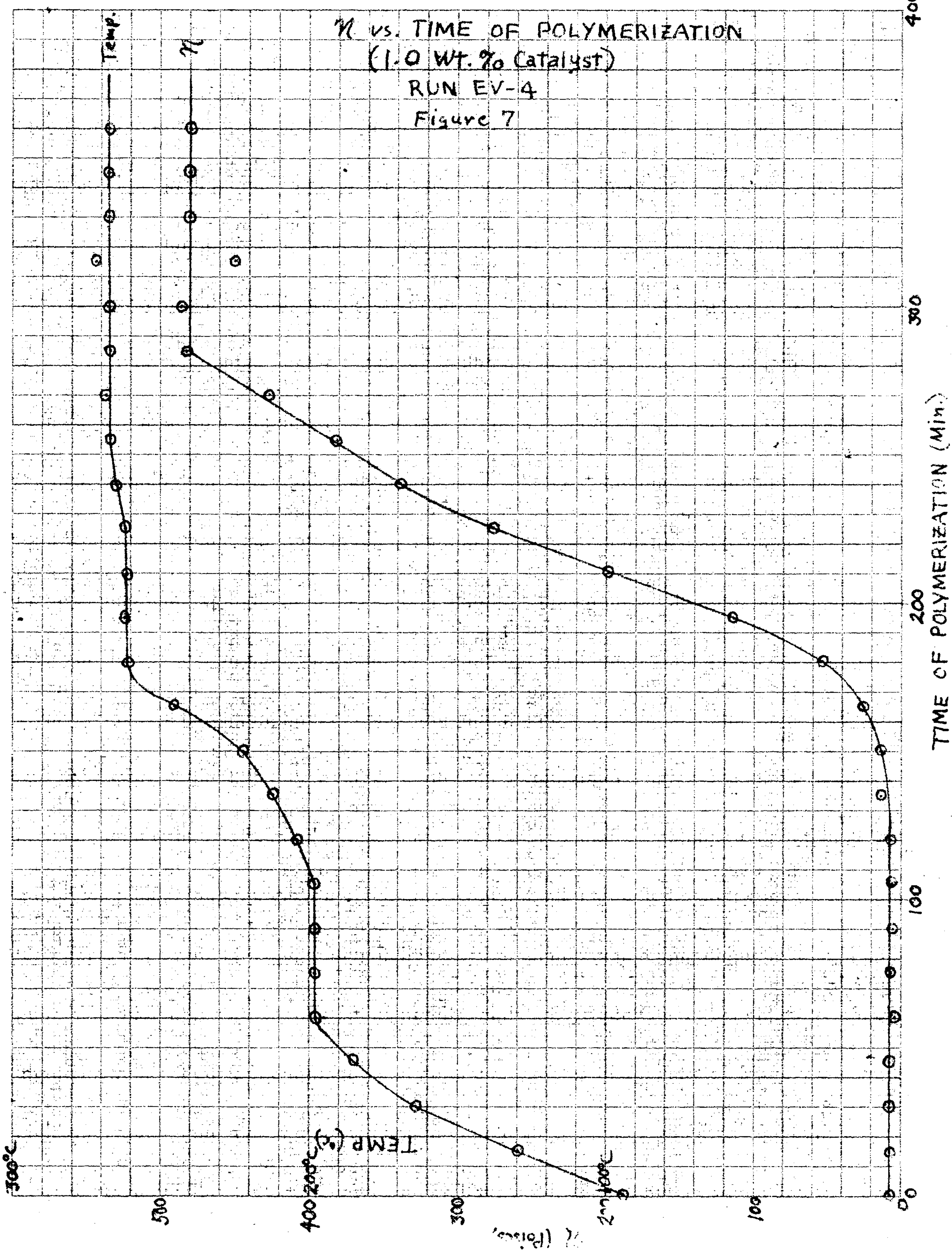
The most important section of the curve with respect to this particular investigation is the final plateau which represents the time range of 250 to 400 minutes. During this time the viscosity of batches containing the same quantity of catalyst is relatively constant and represents the final viscosity of the polymer. Since these viscosities are in good agreement from batch to batch as shown below, the accuracy of the rotational

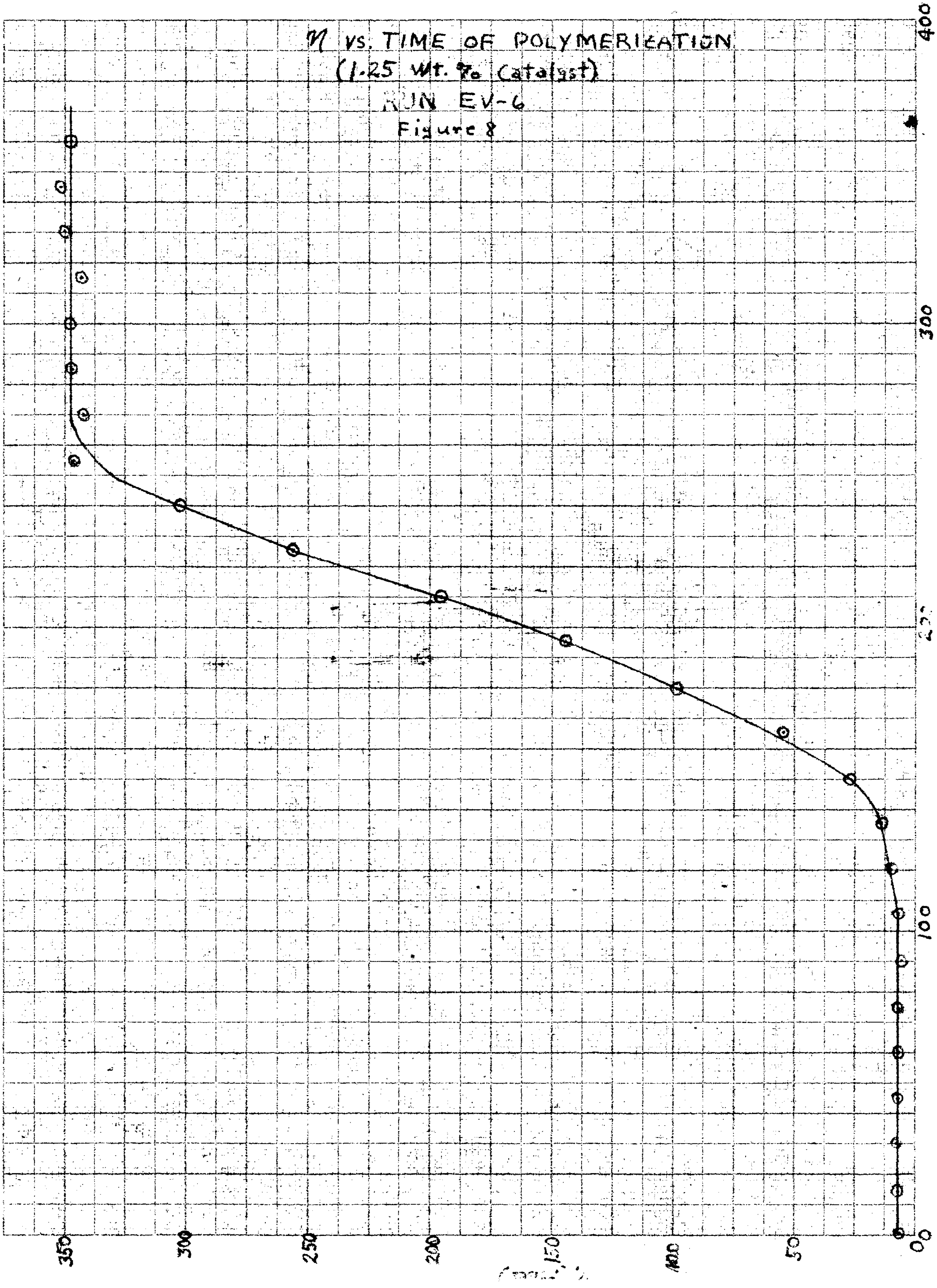


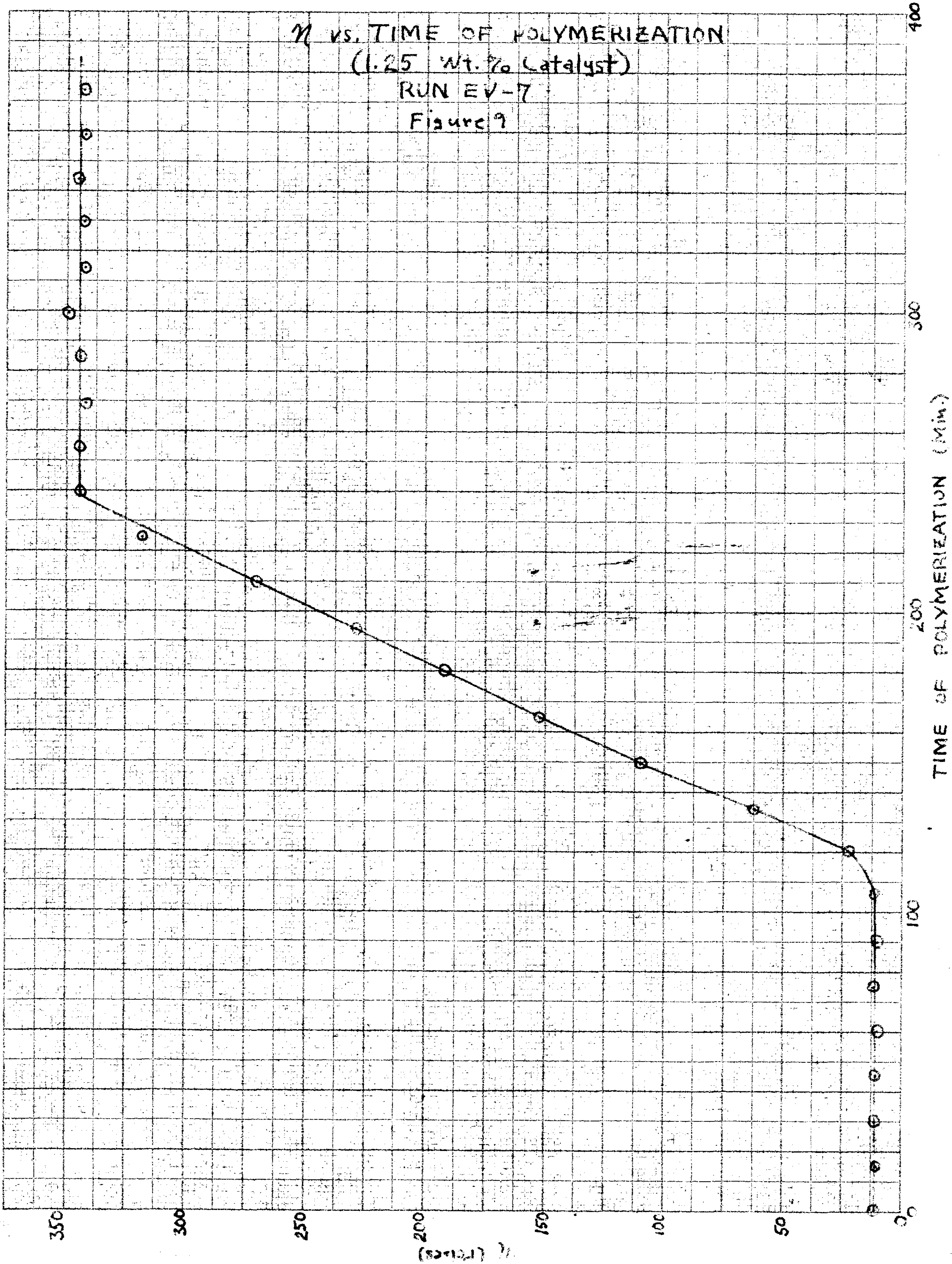
η vs TIME OF POLYMERIZATION
(0.75 Wt.% Catalyst)
RUN EV-2
Temp.
η
TIME OF POLYMERIZATION (MIN.)
TEMP. (°C)
0
100
200
300
400
0
100
200
300
400
500
600
700
100
200
300

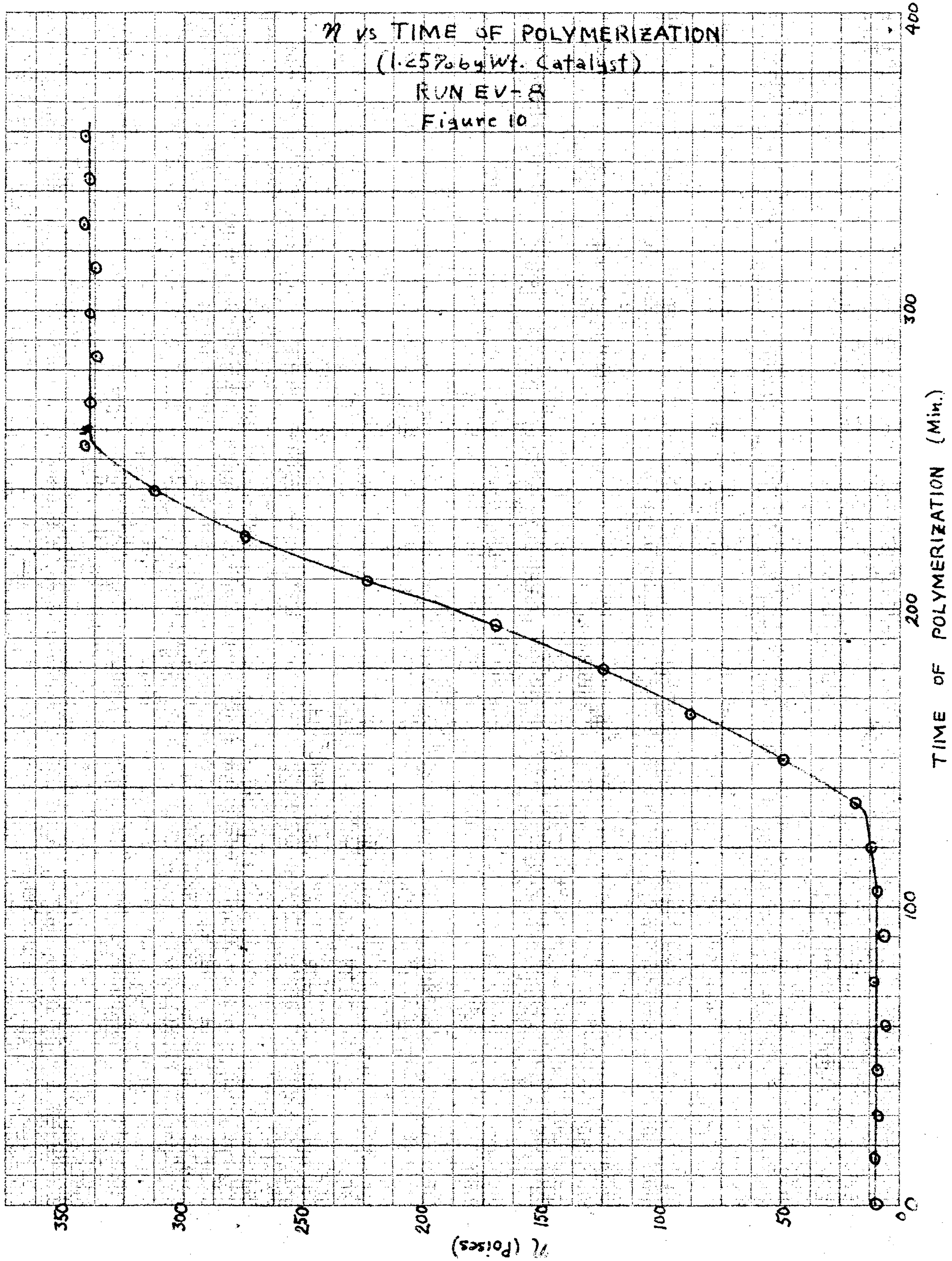

η vs. TIME OF POLYMERIZATION
(1.0 Wt. % Catalyst)
RUN EV-1
Figure 5
Temp.
η
TIME OF POLYMERIZATION (Min.)
0
100
200
300
400
TEMP. (°C)
η (Poises)
500
400
300
200
100
200°C
100°C

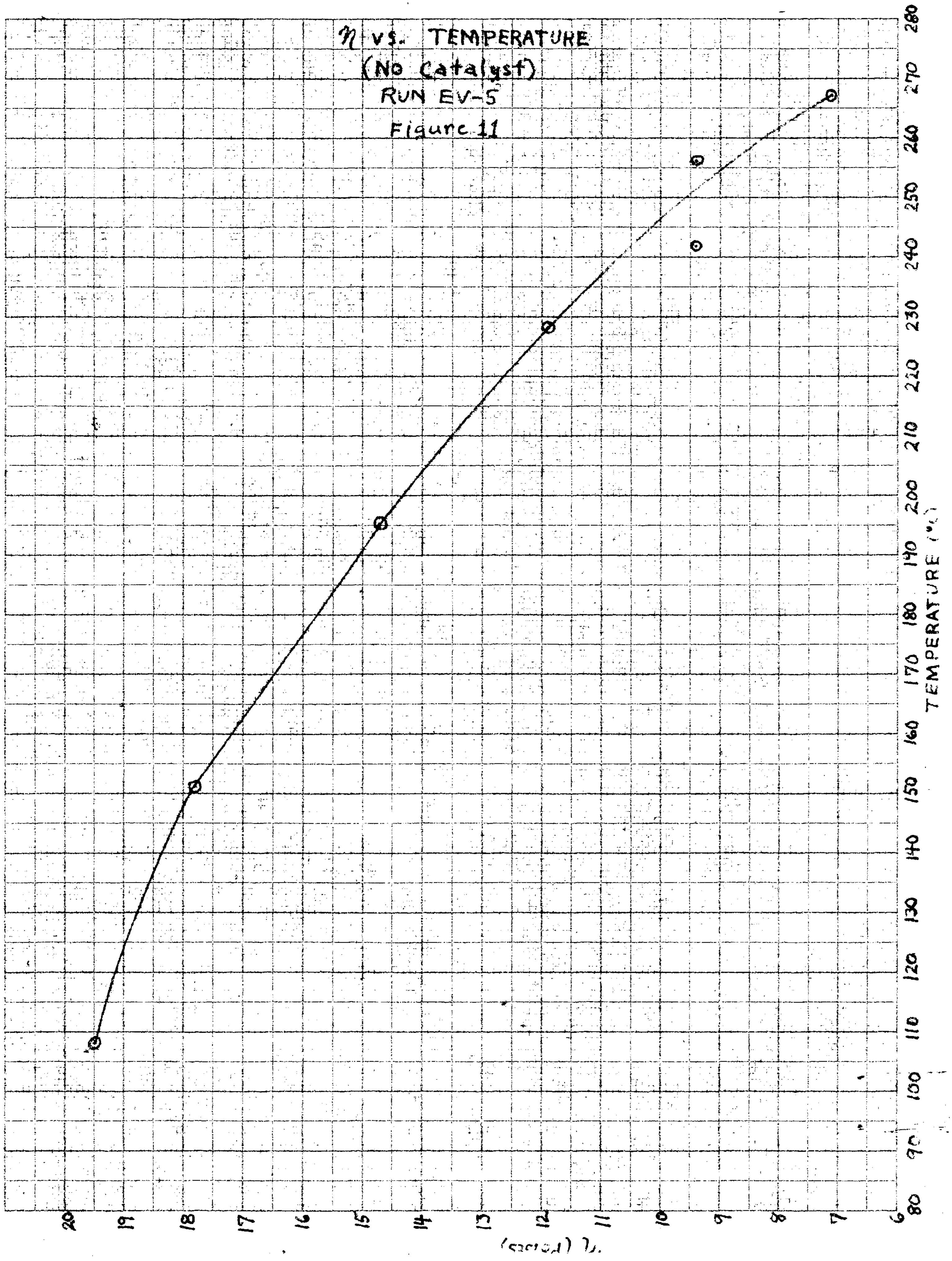

η vs. TIME OF POLYMERIZATION
(1.0 Wt. % Catalyst)
RUN EV-3
Figure 6
Temp.
η
TIME OF POLYMERIZATION (Min.)
TEMP. (°C)
0
100
200
300
400
100
200
300
400
500
100°C
200°C


η vs. TIME OF POLYMERIZATION
(1.0 Wt. % Catalyst)
RUN EV-4
Figure 7
Temp.
η
TIME OF POLYMERIZATION (Min.)
0
100
200
300
400
TEMP (°C)
300°C
400
200°C
100°C
500
300
200
100
0
η (Poises)


η VS. TIME OF POLYMERIZATION
(1.25 Wt. % Catalyst)
RUN EV-6
Figure 8
TIME OF POLYMERIZATION Min.
0
100
300
400
0
50
100
150
200
250
300
350


η vs. TIME OF POLYMERIZATION
(1.25 Wt.% Catalyst)
RUN EV-7
Figure 9
TIME OF POLYMERIZATION (Min.)
0
100
200
300
400
350
300
250
200
150
100
50
0


η vs TIME OF POLYMERIZATION
(1.25% by Wt. Catalyst)
RUN EV-8
Figure 10
TIME OF POLYMERIZATION (Min.)
η (Poises)
0
100
200
300
400
0
50
100
150
200
250
300
350


η vs. TEMPERATURE
(No Catalyst)
RUN EV-5
Figure 11
TEMPERATURE
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
260
270
280
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6

viscometer is firmly established.

Batch No.	Wt. % Catalyst	Final Avg. η	% Deviation
EV-5	0.00	7.1	--
EV-2	0.75	639	--
EV-1	1.00	470	-1.1
EV-3	1.00	480	1.1
EV-4	1.00	476	0.2
EV-6	1.25	347	1.8
EV-7	1.25	338	-0.9
EV-8	1.25	337	-1.2

The original objective of this particular rotating viscometer was to provide a method of determining the point at which to stop polymerization of various batches of Type EV polymer in order to obtain a uniform batch-to-batch viscosity. The work described herein shows that time of polymerization, beyond a minimum time of approximately 250 minutes, is not an important variable in the ultimate viscosity.

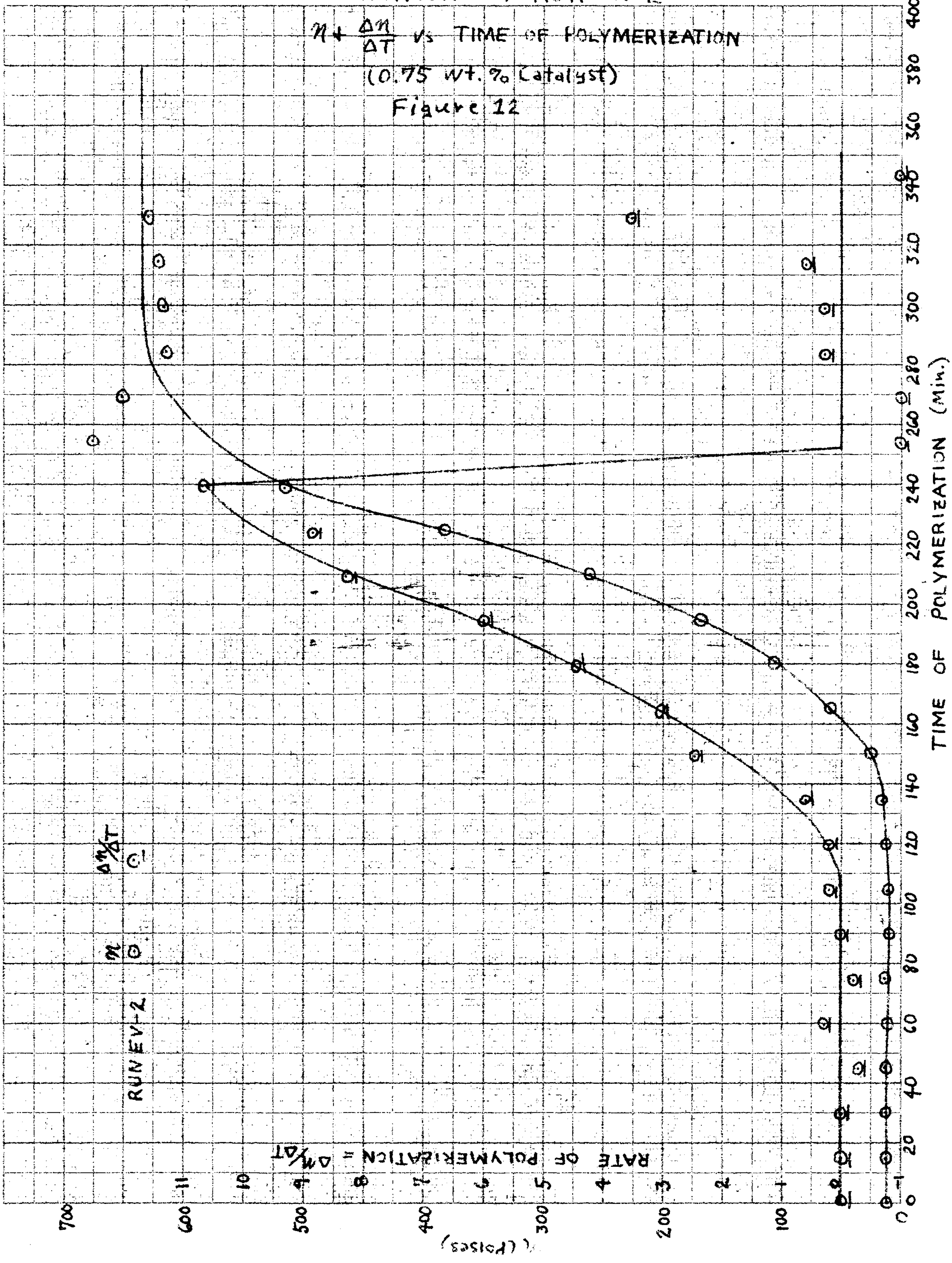
When the first derivative of the melt viscosity with respect to time (rate of polymerization) is plotted against the time of polymerization, curves such as those shown in Figures 12, 13 and 14 are obtained. Although there are some points which do not fall on the curves, a fair correlation exists among the batches that were made with the same amount of catalyst. When

CORRELATION OF RUN EV-2

$\eta + \frac{\Delta\eta}{\Delta T}$ vs TIME OF POLYMERIZATION

(0.75 Wt. % Catalyst)

Figure 12

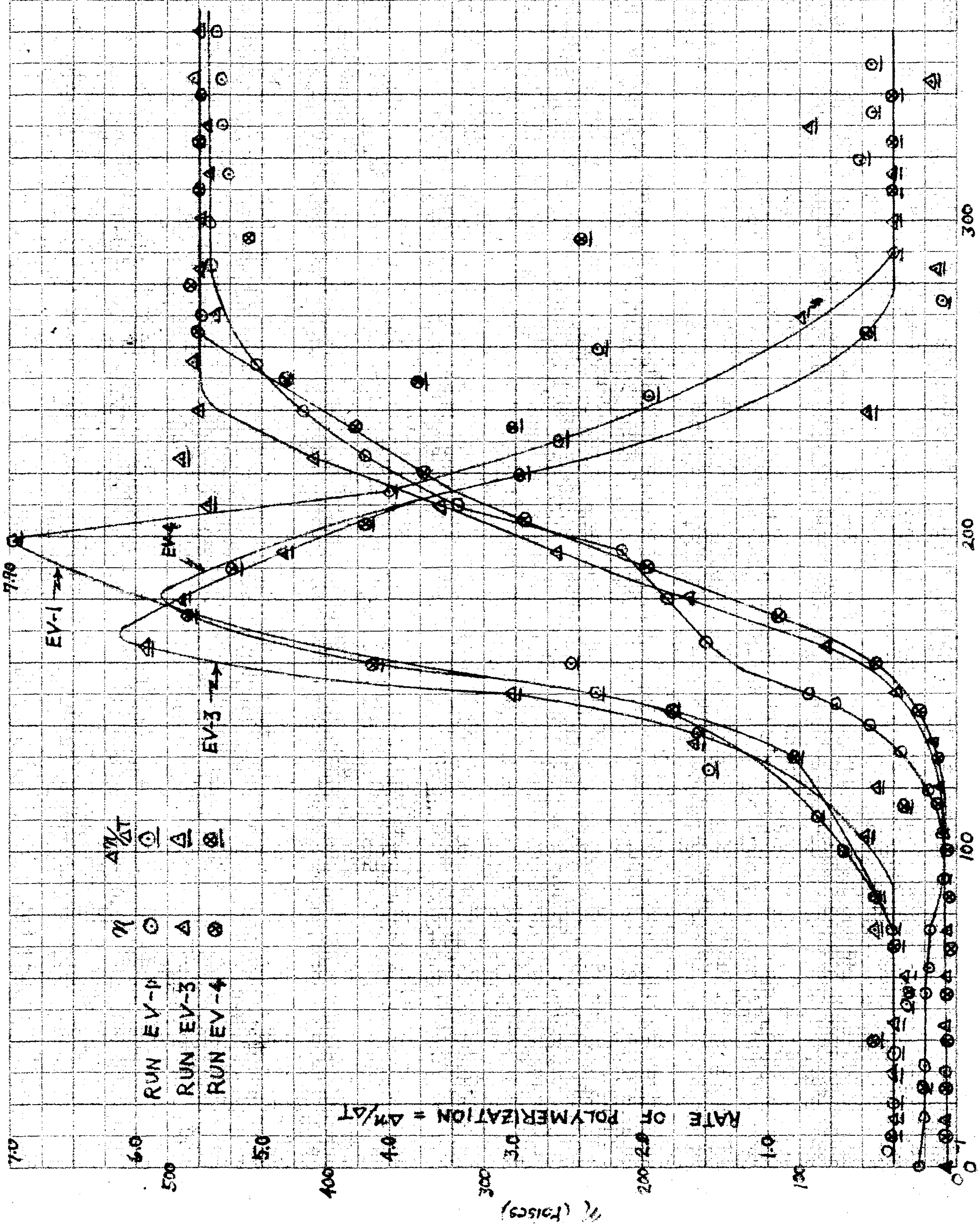


CORRELATION OF RUNS EV-1,3,4

η + $\frac{\Delta \eta}{\Delta T}$ VS. TIME OF POLYMERIZATION

(1.0 Wt. % Catalyst)

Figure 13

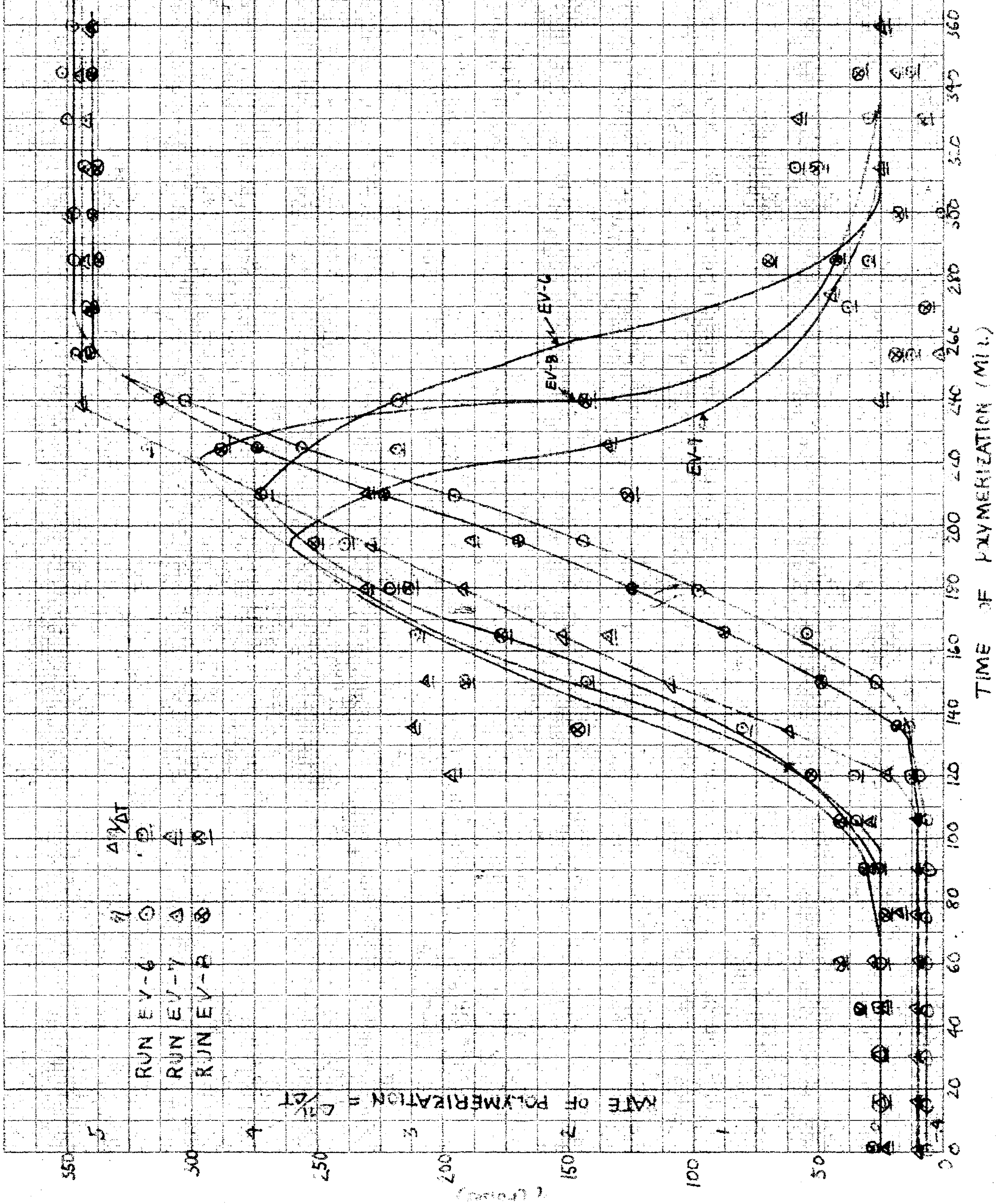


CORRELATION OF RUNS EV-6,7,8

$\eta + \frac{\Delta\eta}{\Delta T}$ vs. TIME OF POLYMERIZATION

(1.25 Wt. % Catalyst)

Figure 14



the rate of polymerization is plotted against temperature (Figure 15), it is apparent that the rate of polymerization increases with temperature until equilibrium is reached, then falls directly to zero. The maximum rate of polymerization occurs very near the point of inflection in the S-shaped plots of viscosity vs. time of polymerization. This is shown in Figures 12, 13 and 14 where the rate of polymerization vs time curves are superimposed upon the viscosity vs. time curves.

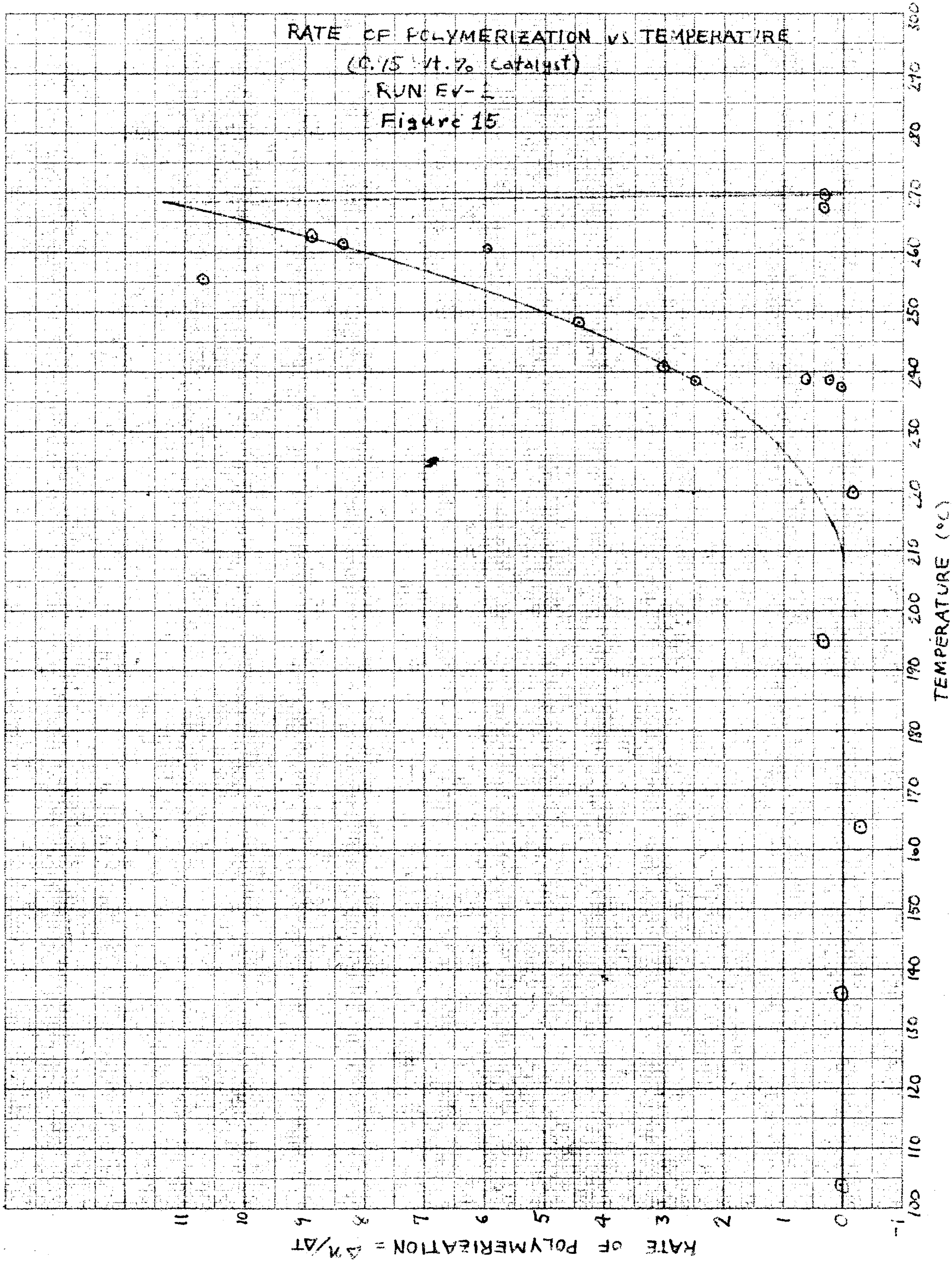
Attempts were made to plot the second derivative of viscosity with respect to temperature (rate of change in rate of polymerization) against both the time of polymerization and the rate of polymerization but no continuous curves could be drawn through these points.

(2) Analysis of Data by the Davis Method:

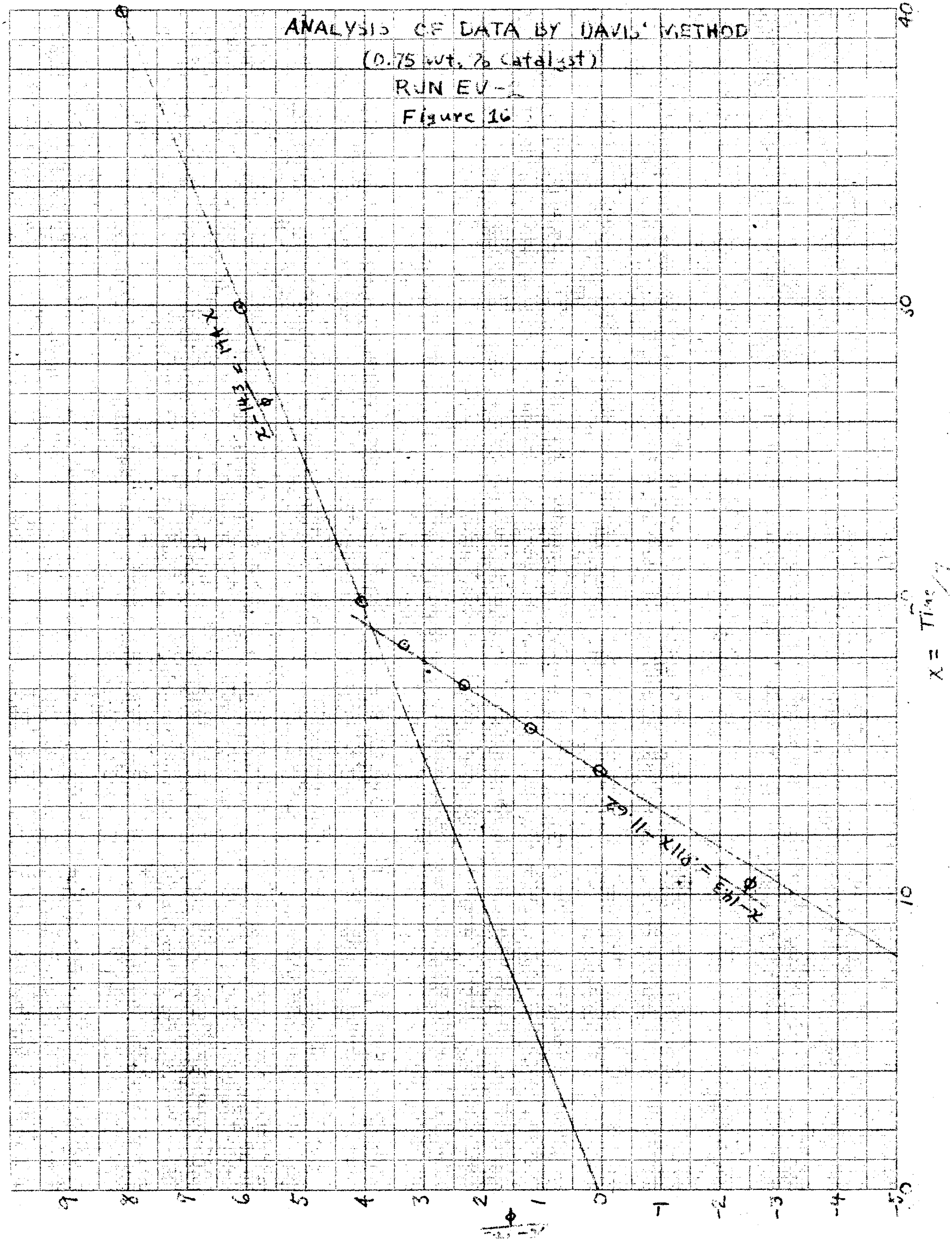
D.S. Davis [1.] states that an equation of the form:

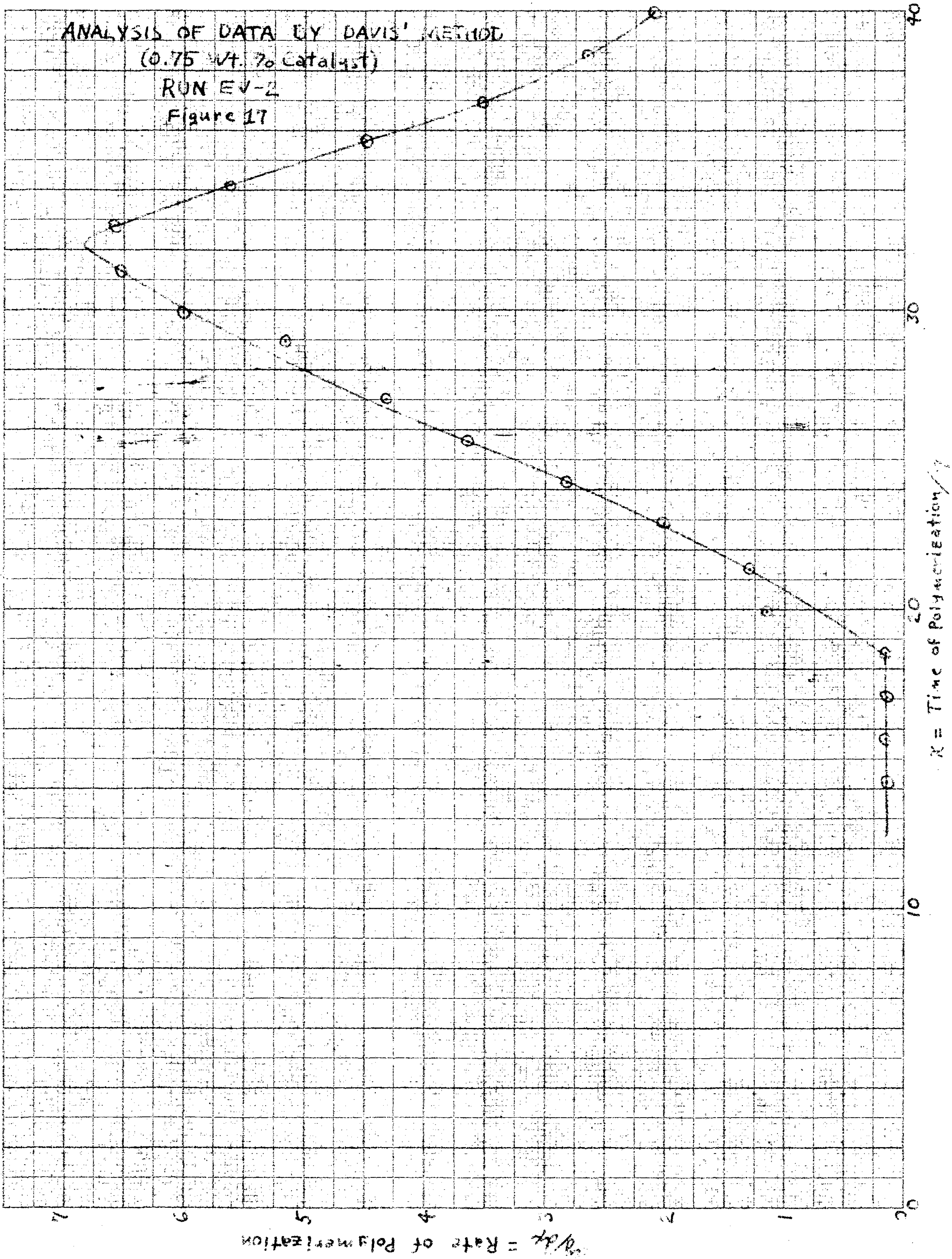
$$\phi = \frac{x - x_1}{a + bx} = \log \left[\frac{20y}{\log (100 - y)} \right]$$

fits numerous S-shaped curves. The method described for fitting data to the above equation was applied to the data obtained in Run EV-2 (page 53 and Figures 16 and 17). Although a fair agreement exists for plots of rate of polymerization vs. time of polymerization between Davis' method of determining the derivative (Figure 17) and the method of differentiating from point to point (Figure 12), Davis' method cannot be applied to the straight sections at



RATE OF POLYMERIZATION vs TEMPERATURE
(0.15 wt.% catalyst)
RUN EV-1
Figure 15


ANALYSIS OF DATA BY DAVIS' METHOD
(0.75 wt. % catalyst)
RUN EV-1
Figure 16
x - 14.3 / φ = 14.4
x - 14.3 / φ = 0.11x - 11.62
x = Time
φ
40
30
10
0
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5



ANALYSIS OF DATA BY DAVIS' METHOD
(0.75 Wt. % Catalyst)
RUN EV-2
Figure 17

each end of the S-curve. Therefore the above equation for the S-shaped curves obtained in polymerization of Type EV polymer holds only for the center portion of the curves (Figure 4) and is least applicable at the top of the curve where equilibrium is reached very abruptly.

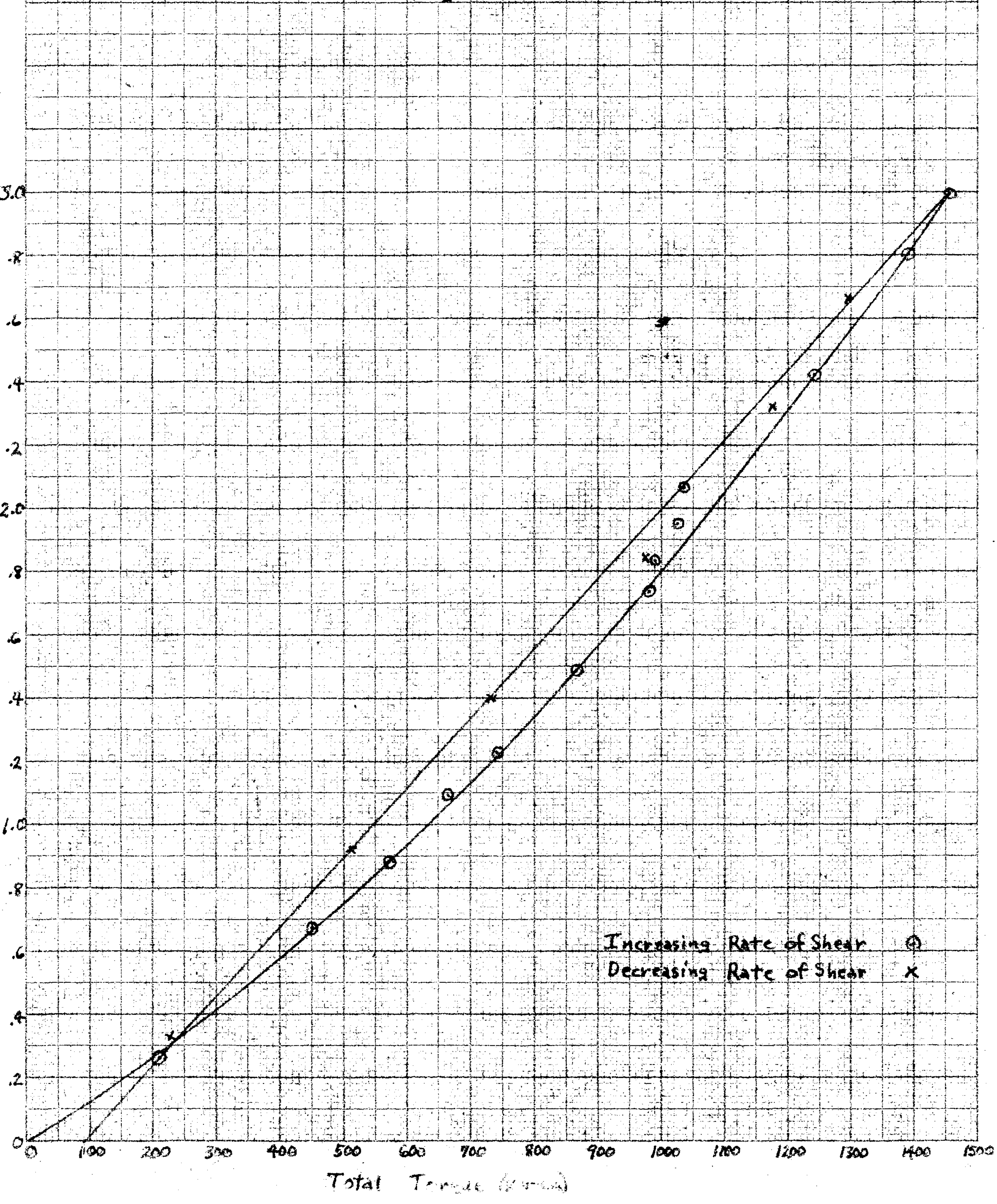
(3) Rheological Characteristics of Type EV Polymer:

The thixotropic nature of liquids can be studied readily by means of the rotational viscometer. Thixotropy is defined as changing the structure of a material by doing work upon it. This break-down which is evidenced by a lower apparent viscosity is a function of time as well as the rate of shear. The structure can rebuild itself, if not prevented from doing so by externally applied forces. No explanation of this phenomenon has been fully accepted.[2,3]

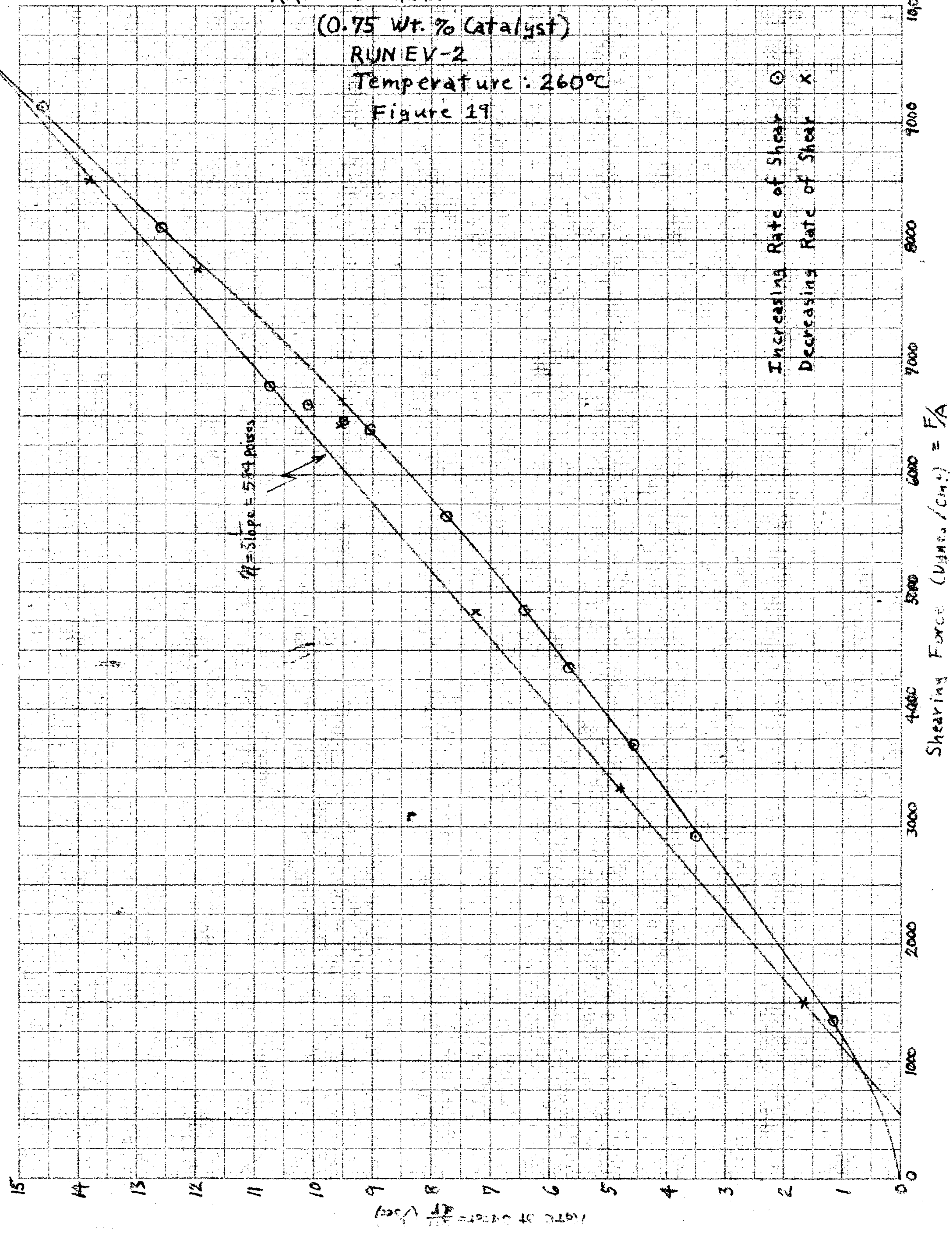
The curves that are shown in Figures 18 through 23 inclusive demonstrate the thixotropic nature of Type EV polymer. When rate of shear (or angular velocity of the viscometer bob) is plotted against shearing force (or the torque registered by the viscometer) a curve which opens upward is obtained at the rate of shear increases. As the rate of shear is decreased a relatively straight line is obtained. Although there are no units for thixotropy, such curves represent a relatively small amount of thixotropic break-down.

The curves obtained with increasing rate of shear in Figures 18 through 23 inclusive also show that Type EV polymer is somewhat pseudoplastic in character, that is the rate of shear increases faster than linearly as shearing stress is increased. Such observations are useful in predicting and explaining the behavior of Type EV polymer in flow through pumps, pipes, and etc.

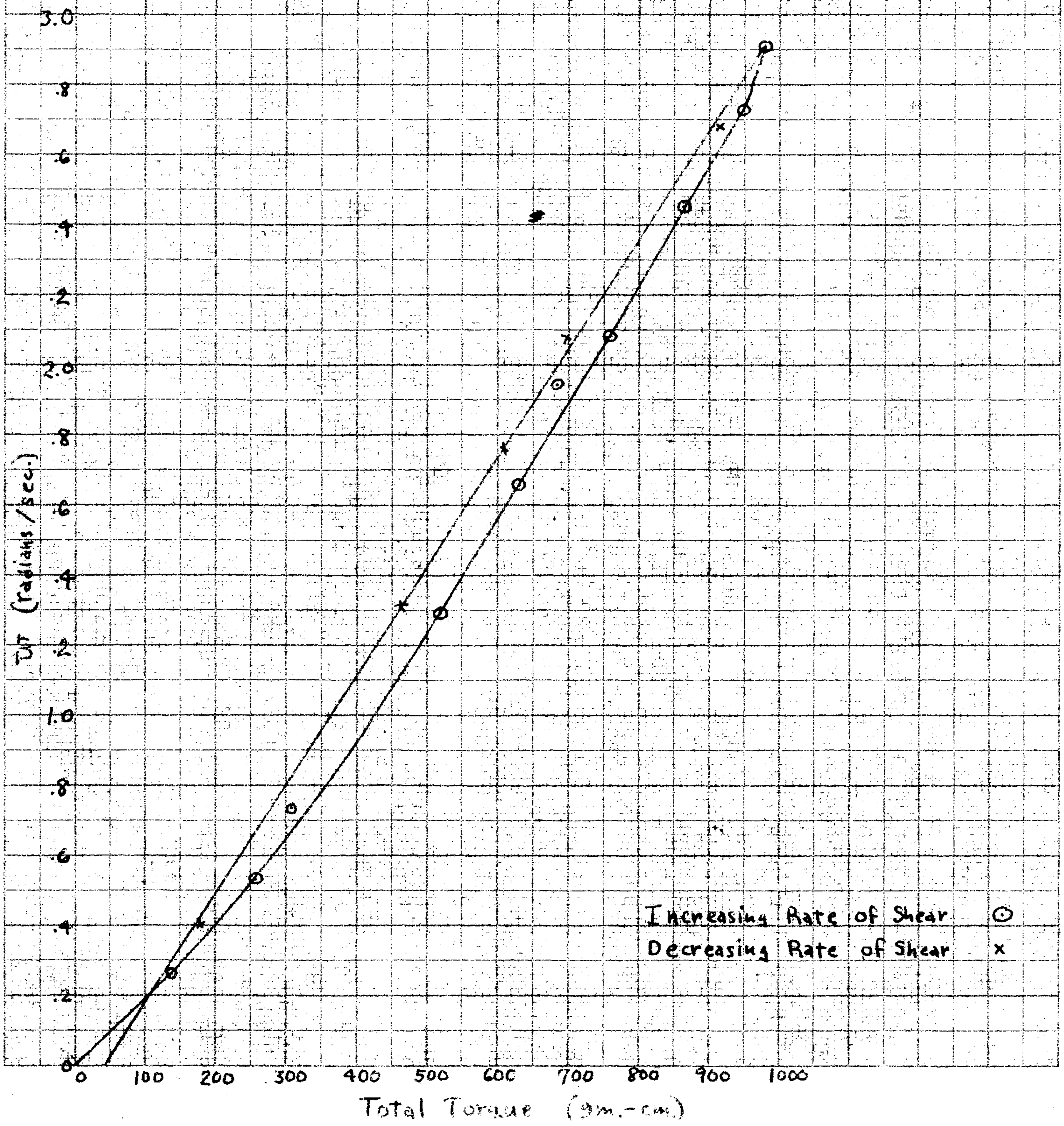
ANGULAR VELOCITY vs. TORQUE
(0.75 Wt.% Catalyst)
RUN EV-2
Temperature: 260°C
Figure 18

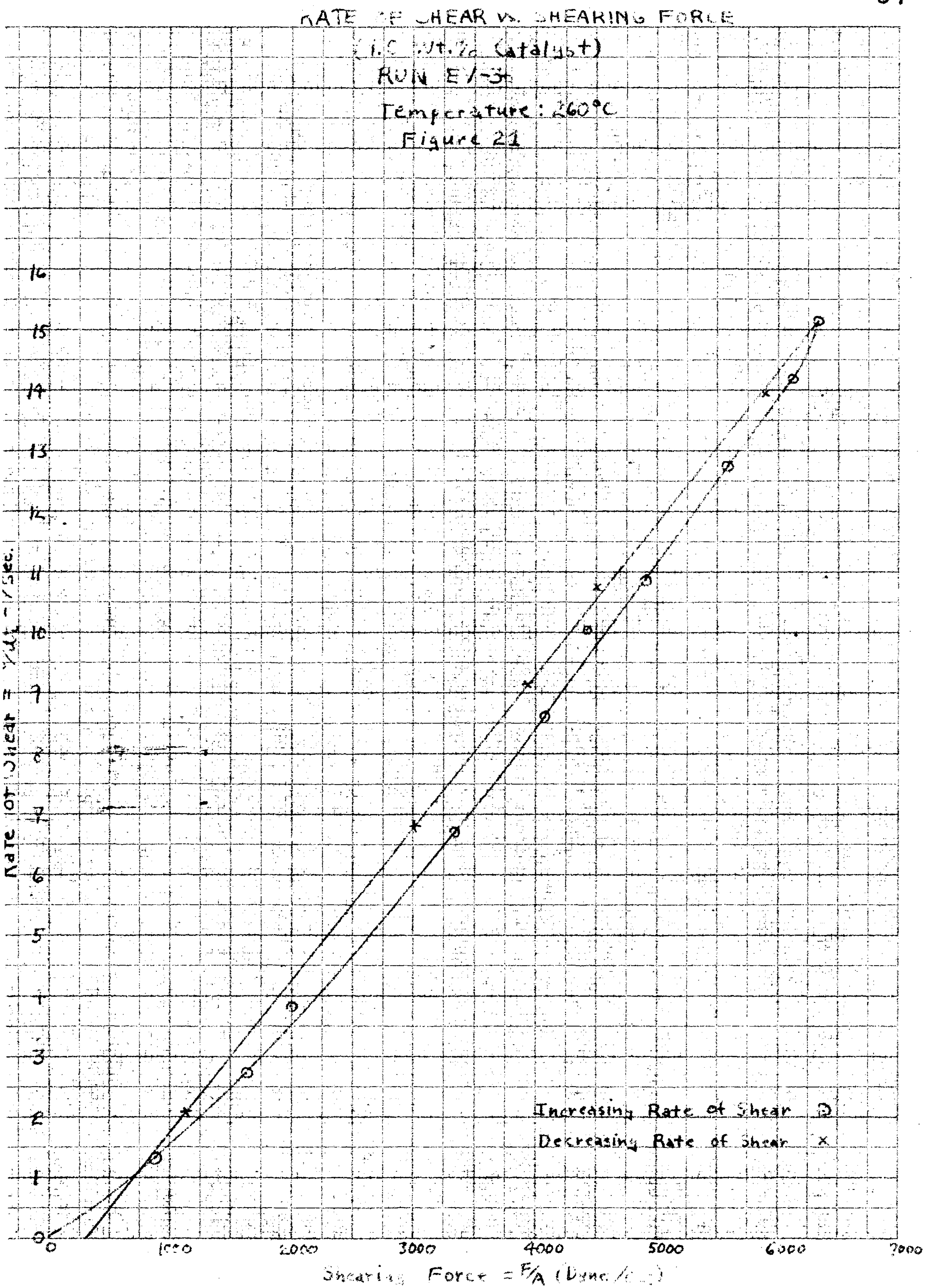


RATE OF SHEAR VS. SHEARING FORCE



ANGULAR VELOCITY vs. TORQUE
(1.0 Wt. % Catalyst)
RUN EV-3
Temperature 260°C
Figure 20




RATE OF SHEAR vs. SHEARING FORCE
(1.0 Wt.% Catalyst)
RUN EY-3
Temperature: 260°C
Figure 21
Rate of Shear
Shearing Force = F/A (Dyne/
Increasing Rate of Shear
Decreasing Rate of Shear
0
1000
2000
3000
4000
5000
6000
7000
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

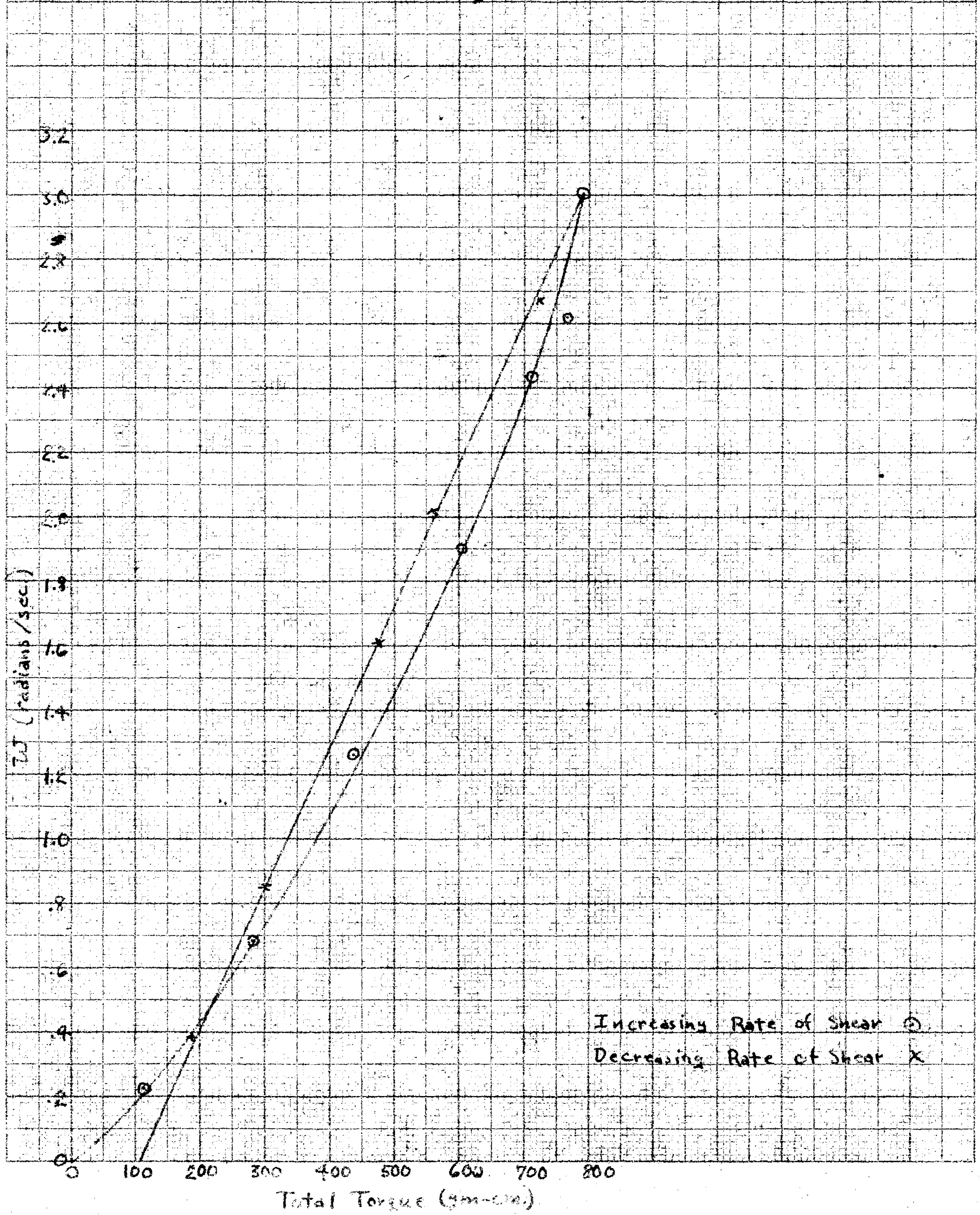
ANGULAR VELOCITY vs. TORQUE

(1.25 Wt. % Catalyst)

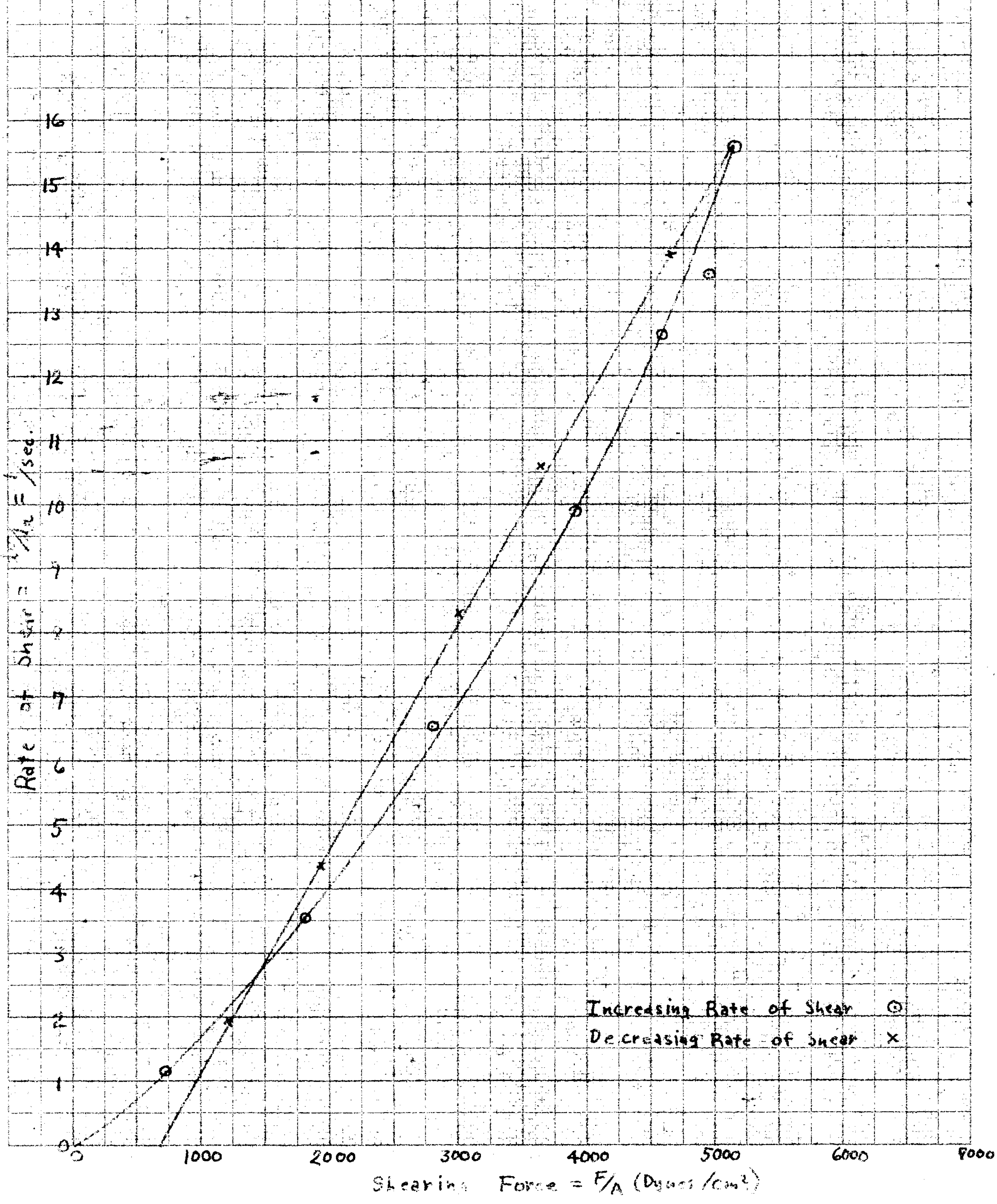
RUN EV-8

Temperature: 260°C

Figure 22



RATE OF SHEAR vs. SHEARING FORCE
(1.25 Wt. % Catalyst)
RUN EV-8
Temperature: 260°C
Figure 23



CONCLUSIONS

The rotational viscometer designed and used in this work is satisfactory for determining melt viscosities up to 700 poises at temperatures up to 265°C. It is also useful for checking the rate and extent of polymerization and for studying the rheological character of finished polymers. Its operating characteristics are not obtainable in any instruments previously described.

Although this work has shown that it is not necessary to control polymerization with a viscometer in the case of Type EV polymer, the instrument nevertheless is valuable for checking the uniformity of production batches and for predicting the flow characteristics of experimental batches of Type EV polymer.

APPENDIX

Specifications for Individual Parts of the Rotational Viscometer

(1) Bob: Diameter: 3.741 cm. + .004 -.005, Length: 4.000 cm + .004, Material: soft carbon steel. Finish: medium polish.

(2) Hollow Cylinder: Inside Diameter: 4.458 cm. ± .005, Wall thickness: 0.35 cm. + .01, Length: 4.102 cm. ± .004 cm. , Material: soft carbon steel, Finish: medium polish.

(3) Keeper Bars: Width: 1.095 cm. ± .005 cm., Thickness: 0.375 inch± .01, Length: 3.375 inch ± .01, Material: soft carbon steel, Finish: medium polish.

(4) Bolts: 1/4-20 NC x 2 3/4 inchs long, soft carbon steel.

(5) Shaft: Length 15½ inches, Material: 5/16 inch diam. ± .001 inch annealed drill rod.

(6) Shaft Housing: Length: 7½ inches, I.D: 11/32 inch ± .01 in. O.D.: 9/16 inches.

(7) Thrust Bearing: 5/16 inch Nice radial-thrust bearing with 11- 3/16 in. diam. balls.

(8) Gear-in-Head-Motor: G.K. Heller Co.- Type NSH-334, speed range 20-200 rpm. with Type 6T60 motor controller.

(9) Driving Gear: Pitch Diam: 2 inches, No. of teeth: 32 Face: 1/8 inch.

(10) Driven Gear: Pitch Diam: 3 inches, No. of teeth 48 Face: 1/8 inch.

(11) Helical Spring: No. Turns: 12, Diam: 1/2 inch, Spacing of turns: 3/16 inch, Material: .032 inch diam. steel music wire.

(12) Pointer: Material: Black steel banding strap, attached to the driven gear with a machine screw.

(13) Fixed Scale: Diameter: 2.0 inches, Thickness: 1/2 inch, Material: soft carbon steel faced with glass tape which is calibrated from 0 to 1200 gm-cm torque.

RUN EV-5 (No Catalyst Present)

Time (min.)	Temp. (°C)	RPM of Bob	ω (radians/sec.)	Torque (gm-cm)	η (Poises)
0	108	20.1	2.10	33	19.5
10	151	20.1	2.10	30	17.8
20	195	20.2	2.12	25	14.7
30	228	20.1	2.10	20	11.9
40	242	20.2	2.12	16	9.4
50	256	20.2	2.12	16	9.4
60	267	20.2	2.12	12	7.1

RUN EV-2 (0.75 wt. % catalyst)

Time (min.)	Temp. (°C)	RPM of Bob	ω (radians/sec.)	Torque (gm-cm)	η (poises)	ΔTime (min.)	Δη (poises)	$\frac{\Delta\eta}{\Delta T}$
0	87	19.9	2.08	20	12.0	15	0	0
15	104	19.9	2.08	20	12.0	15	-.10	-.01
30	136	20.1	2.10	20	11.9	15	0	0
45	164	20.1	2.10	20	11.9	15	-4.9	-.33
60	195	20.3	2.13	12	7.0	15	4.6	.31
75	220	20.5	2.15	20	11.6	15	-3.4	-.23
90	238	20.4	2.14	14	8.2	15	0	0
105	239	20.4	2.14	14	8.2	15	3.3	.22
120	239	20.6	2.16	20	11.5	15	3.0	.20
135	239	20.4	2.14	25	14.5	15	8.7	.58
150	239	20.4	2.14	40	23.2	15	35.3	2.45
165	241	20.3	2.13	100	58.5	15	44.5	2.97
180	249	20.3	2.13	176	103	15	66.0	4.40
195	261	20.3	2.13	290	169	15	89	5.93
210	262	20.2	2.12	440	258	15	124	8.26
225	263	20.2	2.12	650	382	15	132	8.80
240	256	20.2	2.12	875	514	15	159	10.60
255	255	20.1	2.11	1141	673	15	-24	-1.60
270	264	20.1	2.11	1100	649	15	-39	-2.60
285	268	20.1	2.11	1035	610	15	4	.27
300	270	20.1	2.10	1035	614	15	5	.33
315	270	20.1	2.11	1050	619	15	9	.60
330	268	20.0	2.10	1060	628	15	53	3.53
345	265	20.1	2.11	1155	681	60	-95	-1.58
405	269	19.9	2.08	980	586			

RUN EV-1 (1.0 wt. % Catalyst)

Time (min.)	Temp. (°C)	RPM of Bob	ω (radians/sec)	Torque (gm-cm.)	η (poises)	Δ Time (min.)	$\Delta\eta$ (poises)	$\frac{\Delta\eta}{\Delta T}$
0	112	21.1	2.21	45	25.4	20	-4.5	-.23
20	148	21.1	2.21	37	20.8	16	0	0
36	177	21.1	2.21	37	20.8	16	0	0
52	214	21.1	2.21	37	20.8	23	-2.2	-.10
75	224	21.1	2.21	33	18.6	8	0	0
83	229	21.1	2.21	33	18.6	12	-10.2	-.85
95	230	21.1	2.21	15	8.4	16	1.1	.07
111	235	21.1	2.21	17	9.6	15	9.0	.60
126	237	21.1	2.21	33	18.6	13	19.0	1.46
139	239	20.5	2.15	65	37.6	12	18.7	1.56
151	239	21.1	2.21	100	56.3	9	21.2	2.36
160	240	21.0	2.20	137	77.5	7	17.7	2.53
167	242	20.8	2.18	167	95.2	3	66.1	22.3
170	245	21.0	2.20	285	161	16	23.7	1.48
186	250	21.0	2.20	325	184	14	29.0	2.07
200	261	20.9	2.19	375	213	15	105.0	7.00
215	266	20.9	2.19	560	318	15	59.5	3.97
230	261	20.6	2.16	655	378	15	39.5	2.63
245	262	20.8	2.18	730	416	15	29.0	1.93
260	259	20.8	2.18	780	445	15	35.0	2.34
275	260	20.8	2.18	840	480	15	-6.0	-.40
290	262	20.8	2.18	830	474	15	0	0
305	260	20.8	2.18	830	474	15	-13.0	-.87
320	270	20.7	2.17	805	461	15	4.0	.27
335	266	20.7	2.17	810	465	15	2.5	.17
350	264	20.7	2.17	815	468	15	2.5	.17
365	264	20.6	2.16	815	470			

RUN EV-3 (1.0% by wt. Catalyst)

Time (min.)	Temp. (°C.)	RPM of Bob	ω (radians /sec)	Torque (gm-cm)	η (poises)	Δ Time (min.)	Δη (poises)	$\frac{\Delta\eta}{\Delta T}$
0	122	21.6	2.26	12	6.6	15	.3	.02
15	145	20.6	2.16	12	6.9	15	0	0
30	168	20.6	2.16	12	6.9	15	0	0
45	185	20.7	2.17	12	6.9	15	0	0
60	206	20.7	2.17	12	6.9	15	-1.2	-.08
75	219	20.8	2.18	10	5.7	15	2.2	.15
90	220	21.0	2.20	14	7.9	15	.3	.02
105	222	20.3	2.13	14	8.2	15	3.5	.23
120	224	20.2	2.12	20	11.7	15	2.1	.14
135	230	20.6	2.16	24	13.8	15	23.5	1.57
150	243	20.7	2.17	65	37.3	15	45.4	3.03
165	257	20.5	2.15	143	82.7	15	88.3	5.89
180	260	20.6	2.16	295	170	15	84	5.60
195	262	20.6	2.16	440	254	15	72	4.80
210	262	20.5	2.15	563	326	15	81	5.40
225	259	20.4	2.14	700	407	15	84	5.60
240	259	20.3	2.13	840	491	15	3	.20
255	258	20.4	2.14	850	494	15	-25	-1.67
270	264	20.4	2.14	805	469	15	11	.73
285	265	20.4	2.14	825	480	15	-5	-.33
300	267	20.2	2.12	810	475	15	0	0
315	267	20.2	2.12	810	475	15	0	0
330	267	20.2	2.12	810	475	15	10	.67
345	265	20.2	2.12	825	485	15	-5	-.33
360	265	20.1	2.10	810	480			

RUN EV-4 (1.0% by wt. Catalyst)

Time (min.)	Temp. (°C)	RPM of Bob	ω (radians /sec.)	Torque (gm-cm)	η (poises)	Δ Time (min.)	Δη (poises)	$\frac{\Delta\eta}{\Delta T}$
0	130	20.9	2.19	15	8.5	10	.1	.01
10	164	20.6	2.16	15	8.6	15	0	0
25	185	20.7	2.17	15	8.6	15	-4.0	-.27
40	198	20.8	2.18	8	4.6	15	2.2	.15
55	198	20.3	2.13	15	8.8	15	-1.8	-.12
70	198	20.2	2.12	12	7.0	15	0	0
85	198	20.2	2.12	12	7.0	15	1.9	.13
100	204	20.1	2.10	15	8.9	15	5.8	.39
115	212	20.2	2.12	25	14.7	15	-.1	-.07
130	222	20.3	2.13	25	14.6	15	11.8	.79
145	245	20.2	2.12	45	26.4	15	26.4	1.76
160	261	20.2	2.12	90	52.8	15	61.7	4.11
175	262	20.2	2.12	195	114.5	15	83.5	5.56
190	261	20.1	2.10	335	198	15	78	5.20
205	268	20.1	2.10	[illegible]	276	15	62	4.14
220	265	20.1	2.10	570	338	15	44	2.93
235	267	20.1	2.10	645	382	15	45	3.00
250	268	20.1	2.10	720	427	15	56	3.74
265	267	20.1	2.10	815	483	15	3	.20
280	268	20.1	2.10	820	486	15	-42	-2.80
295	272	20.2	2.12	755	444	15	36	2.40
310	267	20.2	2.12	817	480	15	0	0
325	267	20.2	2.12	817	480	15	0	0
340	267	20.2	2.12	817	480	15	0	0
355	267	20.2	2.12	817	480			

Run EV-6 (1.25% Catalyst)

Time (min.)	Temp. (^{o}C)	RPM of Bob	ω (radians /sec)	Torque (gm-cm)	η (poises)	Δ Time (min)	$\Delta\eta$ (Poises)	$\frac{\Delta\eta}{\Delta T}$
0	118	20.6	2.16	15	8.7	15	0	0
15	131	20.6	2.16	15	8.7	15	-.4	-.03
30	158	20.6	2.16	14	8.3	15	0	0
45	183	20.7	2.17	14	8.3	15	0	0
60	206	20.6	2.16	14	8.3	15	0	0
75	225	20.6	2.16	14	8.3	15	.6	.04
90	225	20.3	2.13	15	8.9	15	0	0
105	227	20.3	2.13	15	8.9	15	2.1	.14
120	230	20.3	2.13	19	11.0	15	2.4	.16
135	237	20.4	2.14	23	13.4	15	13.1	.87
150	245	20.3	2.13	45	26.5	15	27.6	1.84
165	256	20.2	2.12	92	54.1	15	44.1	2.94
180	261	20.3	2.13	168	98.2	15	46.8	3.12
195	262	20.3	2.13	248	145	15	51.0	3.40
210	263	20.2	2.12	334	196	15	59.0	3.94
225	261	20.4	2.14	439	255	15	46.0	3.07
240	261	20.2	2.12	513	301	15	46.0	3.07
255	260	20.2	2.12	591	347	15	-3.0	-.20
270	259	20.2	2.12	586	344	15	3.0	.20
285	262	20.2	2.12	591	347	15	1.0	.07
300	265	20.3	2.13	596	348	15	-6.0	-.40
315	263	20.2	2.12	583	342	15	8.0	.53
330	263	20.2	2.12	595	350	15	1.0	.07
345	264	20.2	2.12	597	351	15	-3.0	-.20
360	263	20.2	2.12	592	348			

Run EV-7 (1.25 wt. % Catalyst)

Time (min.)	Temp. (°C)	RPM of Bob	ω (radians/sec.)	Torque (gm-cm)	η (poises)	Δ Time (min)	$\Delta\eta$ (poises)	$\frac{\Delta\eta}{\Delta T}$
0	115	20.5	2.15	17	9.7	15	-.3	-.02
15	124	20.5	2.15	16	9.4	15	.3	.02
30	156	20.5	2.15	17	9.7	15	0	0
45	199	20.3	2.13	17	9.7	15	-.3	-.02
60	208	20.5	2.15	16	9.4	15	2.6	.17
75	208	20.2	2.12	20	12.0	15	-2.6	-.17
90	208	20.2	2.12	16	9.4	15	1.8	.12
105	210	20.2	2.12	19	11.2	15	11.6	.77
120	222	20.2	2.12	39	22.8	15	40.7	2.72
135	231	20.2	2.12	108	63.5	15	44.5	2.97
150	247	20.2	2.12	184	108	15	43	2.87
165	258	20.2	2.12	257	151	15	26	1.73
180	262	20.1	2.10	298	177	15	49	3.27
195	262	20.2	2.12	385	226	15	39	2.60
210	262	20.2	2.12	451	265	15	49	3.27
225	262	20.2	2.12	535	314	15	26	1.73
240	262	20.2	2.12	579	340	15	0	0
255	263	20.2	2.12	579	340	15	-8	-.53
270	260	20.2	2.12	565	332	15	5	.33
285	260	20.2	2.12	574	337	15	11	.73
300	259	20.2	2.12	593	348	15	-15	-1.0
315	264	20.2	2.12	567	333	15	0	0
330	263	20.2	2.12	567	333	15	8	.53
345	263	20.2	2.12	581	341	15	-2	-.13
360	263	20.2	2.12	578	339	15	-1	-.07
375	263	20.2	2.12	575	338			

Run EV-8 (1.25% wt. catalyst)

Time (Min.)	Temp. (°C)	RPM of Bob	ω (radians/sec)	Torque (gm-cm)	η (poises)	Δ Time (min.)	$\Delta\eta$ (poises)	$\frac{\Delta\eta}{\Delta T}$
0	103	20.1	2.10	15	9.0	15	.2	.01
15	124	20.1	2.10	16	9.2	15	-.6	-.04
30	156	20.1	2.10	14	8.6	15	.4	.03
45	180	20.1	2.10	15	9.0	15	-2.6	.17
60	201	20.1	2.10	11	6.4	15	4.1	.27
75	221	20.1	2.10	18	10.5	15	-2.0	-.13
90	221	20.1	2.10	14	8.5	15	1.0	.07
105	221	20.1	2.10	16	9.5	15	3.5	.23
120	223	20.1	2.10	22	13.0	15	6.3	.42
135	231	20.1	2.10	33	19.3	15	29.3	1.95
150	244	20.1	2.10	82	48.6	15	39.5	2.64
165	253	20.1	2.10	149	88.1	15	35.9	2.40
180	261	20.2	2.12	209	124	15	45	3.00
195	263	20.2	2.12	288	169	15	54	3.60
210	263	20.1	2.10	376	223	15	24	1.60
225	265	20.1	2.10	416	247	15	63	4.20
240	264	20.1	2.10	523	310	15	28	1.87
255	262	20.1	2.10	571	339	15	-2	-.13
270	262	20.1	2.10	568	337	15	-5	-.33
285	262	20.1	2.10	560	332	15	4	.27
300	262	20.1	2.10	567	336	15	-2	-.13
315	263	20.1	2.10	564	334	15	6	.40
330	262	20.1	2.10	573	340	15	-4	-.27
345	262	20.1	2.10	567	336	15	2	.13
360	261	20.1	2.10	570	338			

Effect of Rate of Shear on Viscosity

Run EV-2 (0.75 wt. % Catalyst)

RPM of Bob	ω (radians/sec)	Total Torque (gm-cm)	$\eta_{260°C}$ (poises)	Rate of Shear $\frac{dv}{dr}$ (1/sec.)	Net Torque (dyne-cm)	Shearing Force F/A (dynes/cm.^{2})
2.44	.255	210	1027	1.33	119,600	1,360
6.44	.674	450	835	3.50	256,000	2,920
8.39	.877	570	815	4.56	326,000	3,710
10.4	1.090	665	766	5.66	381,000	4,340
11.7	1.234	740	751	6.41	426,000	4,850
14.2	1.490	865	730	7.74	497,000	5,650
16.6	1.740	980	706	9.04	561,000	6,380
17.5	1.830	990	680	9.50	567,000	6,460
18.6	1.945	1025	661	10.11	586,000	6,600
19.75	2.065	1035	629	10.73	592,000	6,740
23.2	2.425	1240	643	12.61	712,000	8,110
26.8	2.805	1390	626	14.60	802,000	9,130
28.6	2.995	1455	615	15.58	840,000	9,550
25.4	2.660	1295	615	13.82	746,000	8,500
22.2	2.320	1175	642	11.98	680,000	7,740
17.6	1.840	975	673	9.56	565,000	6,420
13.4	1.402	730	663	7.28	425,000	4,830
8.8	0.921	510	695	4.79	292,000	3,320
3.1	0.324	225	879	1.68	130,000	1,480

Effect of Rate of Shear on Viscosity

Run EV-3 (1.00 Wt. % Catalyst)

RPM of Bob	ω (radians/sec)	Total Torque (gm-cm)	$\eta_{260°C}$ (poises)	Rate of Shear $\frac{dv}{dr}$ (1/sec)	Net Torque (dyne-cm)	Shearing Force F/A (dynes/cm²)
2.50	0.262	134	637	1.36	76,100	866
5.05	0.528	252	594	2.74	143,300	1,630
7.06	0.739	301	506	3.84	171,000	1,940
12.35	1.292	513	494	6.72	291,500	3,315
15.90	1.663	626	468	8.64	356,000	4,050
18.60	1.945	680	435	10.11	386,000	4,390
20.00	2.095	754	448	10.89	428,000	4,870
23.55	2.460	860	435	12.80	488,000	5,550
26.20	2.740	945	429	14.23	536,000	6,100
27.90	2.920	975	416	15.20	554,000	6,300
25.70	2.690	910	421	13.98	516,000	5,880
19.90	2.080	695	416	10.80	395,000	4,490
16.90	1.770	605	425	9.20	343,000	3,900
12.60	1.320	460	434	6.85	262,000	2,980
3.82	0.400	175	544	2.08	99,400	1,130

Effect of Rate of Shear on Viscosity

Run EV-8 (1.25 Wt. % Catalyst)

RPM of Bob	ω (radians /sec)	Total Torque (gm-cm)	$\eta_{260°C}$ (poises)	Rate of Shear $\frac{dv}{dr}$ (1/sec)	Net Torque (dyne-cm)	Shearing Force F/A (dynes/cm²)
2.14	0.224	110	610	1.16	62,400	710
6.55	0.685	278	505	3.56	157,800	1,795
12.10	1.265	434	426	6.57	245,500	2,790
18.20	1.904	603	394	9.89	342,000	3,890
23.35	2.441	712	362	12.70	403,000	4,585
25.12	2.630	765	362	13.55	435,000	4,950
28.80	3.018	789	329	15.68	452,000	5,140
25.60	2.681	722	335	13.95	410,000	4,660
19.35	2.024	561	344	10.63	320,000	3,645
15.39	1.610	465	360	8.36	264,500	3,010
8.11	0.849	299	438	4.41	169,700	1,930
3.65.	0.382	187	609	1.98	106,200	1,210

Analysis of Data by Davis' Method

Run EV-2 (0.75 wt. % catalyst)

η observed	$y=\eta/7$	Time (min)	$x=T/7$	ϕ	$x-\frac{100}{7}$	$\frac{x-\frac{100}{7}}{\phi}$	Calc. $\frac{x-14.3}{\phi}$	Calc. ϕ	Calc. y	Deviation	S	$\frac{dy}{dx}$
10	1.4	100	14.3	1.160	0	0	-.02	0	1.4	0	.320	.152
11	1.6	110	15.7	1.200	1.4	1.17	1.11	1.26	1.7	.1	.280	.157
12	1.7	120	17.1	1.235	2.8	2.27	2.26	1.240	1.7	0	.260	.153
15	2.1	130	18.6	1.323	4.3	3.25	3.48	1.235	1.7	-.4	.210	.173
19	2.7	140	20.0	1.430	5.7	3.99	3.88	1.470	2.9	.2	.150	1.145
25	3.6	150	21.4	1.557	7.1	4.56	4.15	1.713	5.0	1.4	.121	1.290
45	6.4	160	22.9	1.819	8.6	4.73	4.44	1.938	8.5	2.1	.067	1.990
73	10.4	170	24.3	2.030	10.0	4.92	4.71	2.125	13.0	2.6	.043	2.810
105	15.0	180	25.7	2.191	11.4	5.20	4.98	2.285	18.5	3.5	.0301	3.610
142	20.3	190	27.1	2.330	12.8	5.49	5.25	2.440	26.0	5.7	.0227	4.285
194	27.7	200	28.6	2.475	14.3	5.78	5.55	2.575	34.0	6.3	.0171	5.110
260	37.1	210	30.0	2.615	15.7	6.01	5.81	2.700	44.0	6.9	.0133	5.980
335	47.9	220	31.4	2.746	17.1	6.22	6.09	2.805	53.5	5.4	.0112	6.470
425	60.7	230	32.9	2.882	18.6	6.45	6.38	2.915	64.0	3.3	.01016	6.515
513	73.3	240	34.3	3.012	20.0	6.64	6.65	3.010	73.1	-.2	.01089	5.580
558	79.7	250	35.7	3.085	21.4	6.93	6.92	3.090	80.0	.3	.0126	4.460
588	84.0	260	37.1	3.144	22.8	7.24	7.19	3.170	85.5	1.5	.0150	3.470
610	87.1	270	38.6	3.195	24.3	7.61	7.48	3.250	89.8	2.7	.0182	2.630
623	89.0	280	40.0	3.233	25.7	7.95	7.75	3.320	92.4	3.4	.0214	2.085
629	89.9	290	41.4	3.250	27.1	8.34	8.03	3.380	93.9	4.0	.0236	1.765
632	90.3	300	42.9	3.262	28.6	8.75	8.32	3.440	95.1	4.8	.0242	1.605

Calibration of Viscometer with Escalol 106

Rotating Viscometer					Capillary Tube Viscometer				%
Temp. °C.	RPM	ω (rad/sec)	Torque (gm-cm)	η_E poises	Temp °C.	t_E	D_E	poises* η_E	Variation
33.3	20.0	2.10	276	164	33.3	111.70	1.287	169.5	-3.2
39.5	20.0	2.10	126	74.5	39.5	45.00	1.257	66.7	+11.7
52	20.0	2.10	64	37.8	52	17.60	1.224	25.4	+48.8
74	20.0	2.10	0	0	74	2.61	1.203	3.71	--
101.5	20.0	2.10	0	0	101.5	0.42	1.186	0.6	--
130	20.0	2.10	0	0	130	0	1.172	0	--

$$* \quad N_E = \frac{N_G \times D_E \times t_E}{D_G \times t_G}$$

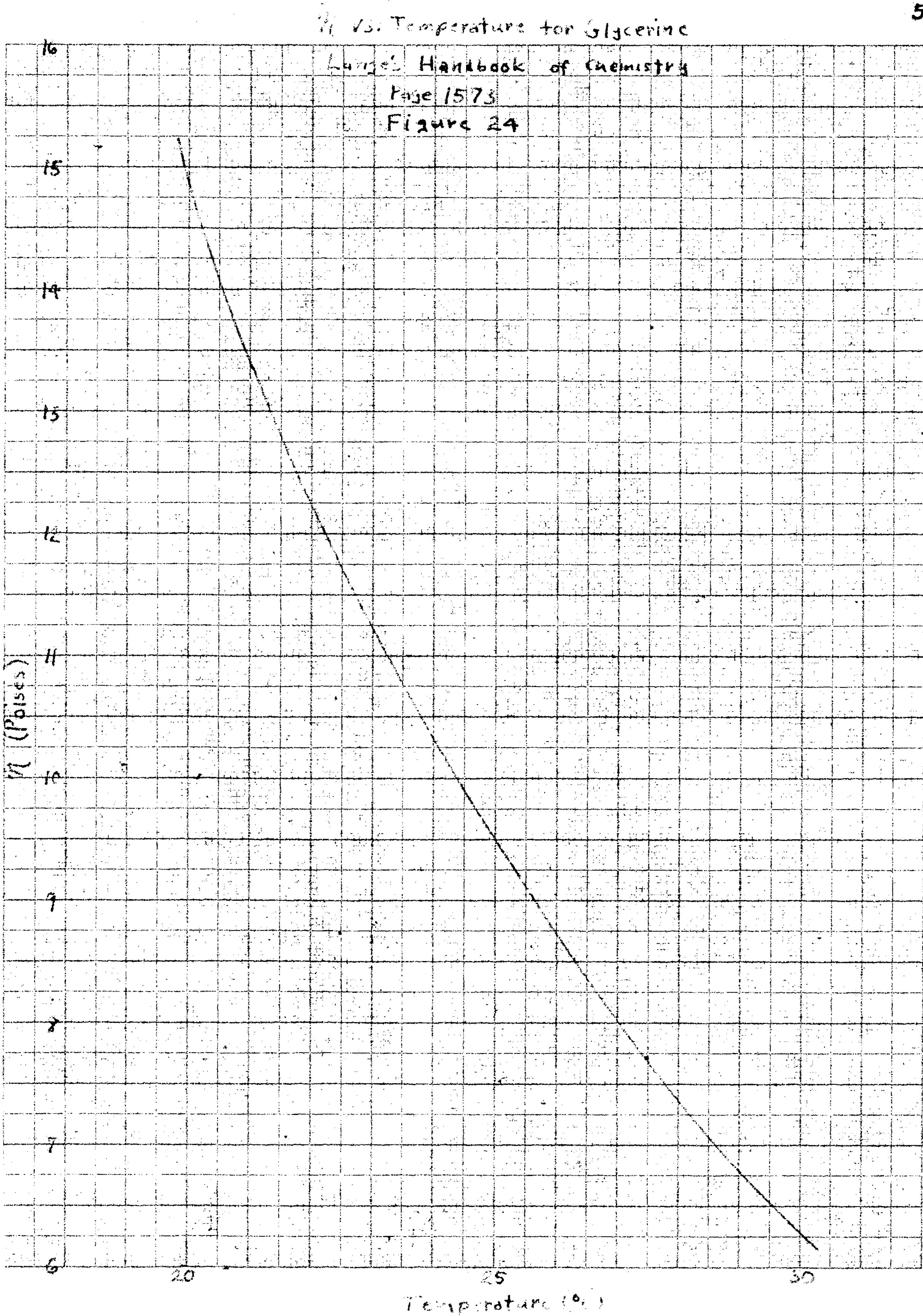
Where: N_G = 8.1 poises @ 26.9°C (Viscosity)

D_G = 1.248 g/cc @ 26.9°C (Density)

t_G = 5.50 seconds (Time)

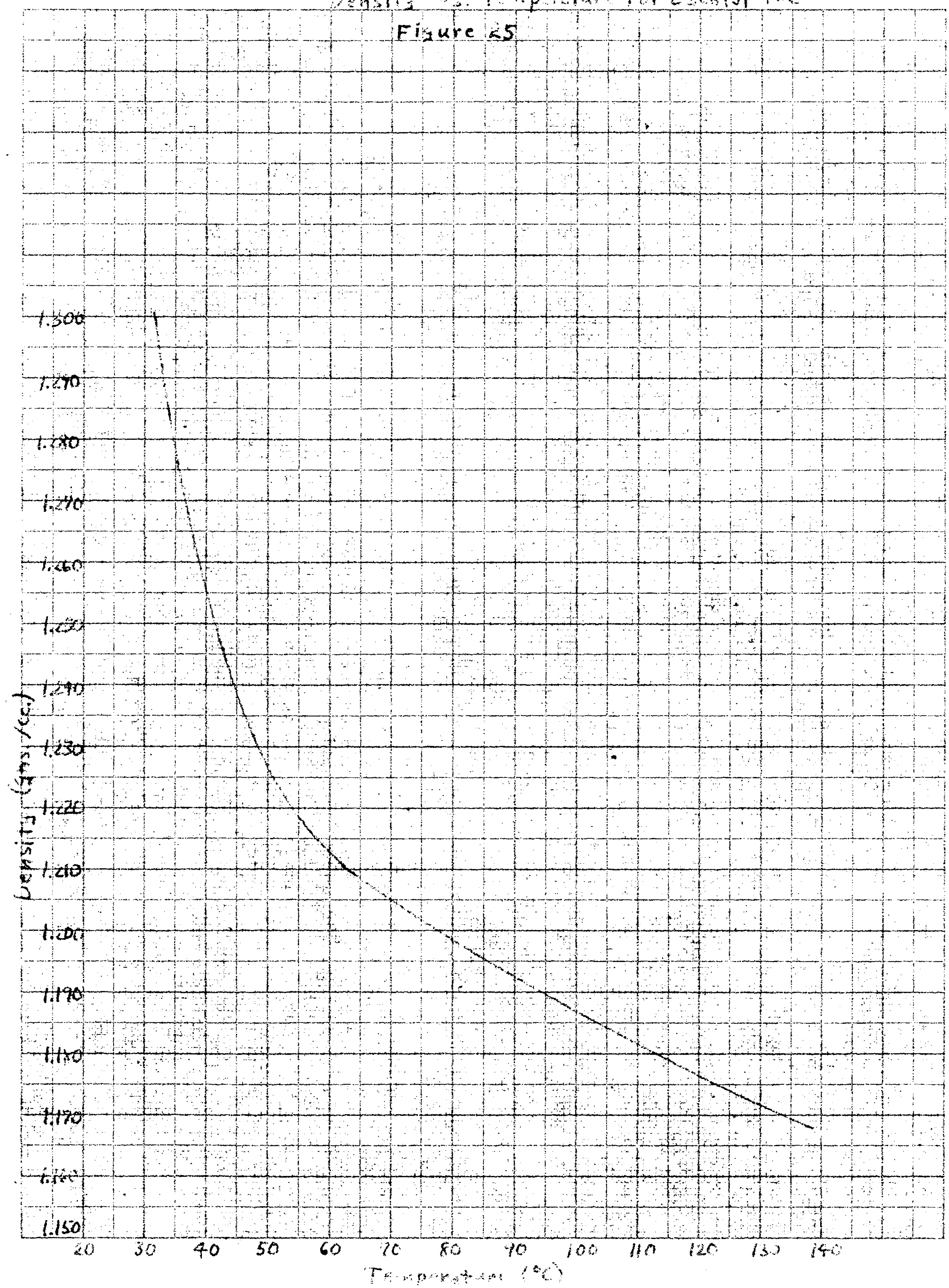
sub G = glycerine

sub E = Escalol 106 (Commercial glyceryl -p-aminobenzoate)


η vs. Temperature for Glycerine
Lange's Handbook of Chemistry
Page 1573
Figure 24
η (Poises)
16
15
14
13
12
11
10
9
8
7
6
20
25
30
Temperature (°C)

Density vs. Temperature for Escalol 106

Figure 25



BIBLIOGRAPHY

1. Davis, D.S., "A New Equation for S-Shaped Curves," Chemical Processing, Dec., 1953, pages 65a-65c.

2. Green, Henry, Industrial Rheology and Rheological Structures, John Wiley and Sons, Inc., New York, 1949, 297 pages.

3. Lapple, C.E., Fluid and Particle Mechanics, Edwards Bros. Inc., Ann Arbor, Michigan, 1951, pages 115-133.

4. Mark, H. and Tobolsky, A.V., Physical Chemistry of High Polymeric Systems, Interscience Publishers Inc., New York, 1950, Second Edition, pages 274-295.