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The Cationic Copolymerization of B-Pinene and Styrene

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THE CATIONIC COPOLYMERIZATION OF B-PINENE AND STYRENE

by

William D. ^{avid}McIver, U.C. 1973
" "

Senior Thesis Submitted
in Partial Fulfillment
of the Requirements for Graduation

DEPARTMENT OF CHEMISTRY

UNION COLLEGE

June, 1973



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ABSTRACT

The cationic polymerization process is least well known of the polymerization mechanisms. Copolymerization by cationic initiation is not well understood. Charles Snyder began investigating the copolymerization of B-pinene and styrene in the fall of 1971, and found some interesting things. He reported, however, that the project was incomplete.

This project was based on the work that Snyder began. The products he made, in addition to several others, were completely analyzed in an effort to obtain information about the cationic polymerization process. DSC, GPC and solvent studies, along with VPO, were the methods of analysis.

This thesis is dedicated to Gregory Olson, Union, Class of 1967.

It was he who encouraged my interest in both chemistry and Union College.

This Thesis

Submitted by

William David McIver
William David McIver

to the

Department of Chemistry of Union College

in partial fulfillment of the requirements of the degree of

Bachelor of Science with a Major in Chemistry

is approved by

Howard E. Sheffer

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INTRODUCTION

It has been reported that the cationic copolymerization of B-pinene and styrene in methylene dichloride has given a product of two homopolymers.¹ Also it has been found that a one to one molar ratio in m-xylene yielded some copolymer.² Finally it was shown that the amount of copolymer obtained in the methylene dichloride depends upon the molar ratio of the B-pinene to styrene, with one to one giving little, and one to four giving considerable copolymer.³ Since all three papers may have some validity, this project was begun in the fall of 1971 by Charles Snyder⁴ to investigate the polymerization of B-pinene and styrene.

Snyder prepared both homopolymers and copolymers of styrene and B-pinene using aluminum trichloride as the catalyst. The catalyst concentrations were 0.5 mole percent, one mole percent, and five mole percent. Polymerations were conducted at 30° C and -78° C, dry-ice acetone temperature. Methylene dichloride and m-xylene were used as solvents. The molar ratio of solvent to monomer was kept constant at three to one. Two different molar ratios of B-pinene to styrene were used: one to one, and one to four. Table 1 shows the reaction variables, a yield of products and the solubilities of those products. Having prepared 20 batches of homopolymers and copolymers, Snyder tried to characterize his products. His first method of analysis was by extraction of products with either acetone or hexane. Acetone will dissolve only polystyrene homopolymer, and hexane will dissolve only polyB-pinene homopolymer. His second method of characterization was to determine molecular weights by Vapor Phase Osmometry. Thirdly, a one meter gel permeation chromatography column packed with Sephadex LH-20 in chloroform was used to obtain separation of homopolymers based on molecular weight. Next, a Waters Gel Permeation

Chromatograph was used to obtain separation, also by molecular weight. Lastly, Snyder used NMR analysis to determine mole percent styrene in each product. Snyder reported that more work needed to be done.

TABLE 1

POLYMERIZATION VARIABLES USED BY C. SNYDER⁴

RUN	SOLVENT	TEMP(°C)	FEED RATIO	[AlCl ₃]	YIELD (WT%)	WT% INSOLUBLE IN ACETONE	WT% INSOLUBLE IN HEXANE
3	CH ₂ Cl ₂	30°	1:1	0.5	66	100	0
4	"	"	1:1	1.0	82	84	1
6	"	"	styrene	1.0	100		
7	"	"	1:1	5.0	97	64	2
8	"	"	1:1	0.5			
9	"	"	B-pinene	1.0	62		
10	"	"	1:4	1.0	85	68	83
11	"	"	1:4	5.0			
12	CH ₂ Cl ₂	-78°	1:1	1.0	0		
13	"	"	1:1	5.0	94	100	2
14	"	"	1:1	1.0	0		
15	"	"	1:4	5.0	100	98	98
16	"	"	B-pinene	5.0	23		
17	"	"	styrene	5.0	100		
18	"	"	1:4	1.0	93	99	100
19	"	"	B-pinene	5.0	33		
23	m-xylene	-78°	1:4	5.0	59	0	0
24	"	"	1:1	5.0	71	0	0
25	"	"	B-pinene	5.0	84		
26	"	"	styrene	5.0	79		
27	"	"	1:4	1.0	LOW	31	66
28	"	"	1:1	1.0	LOW	3	7

BACKGROUND

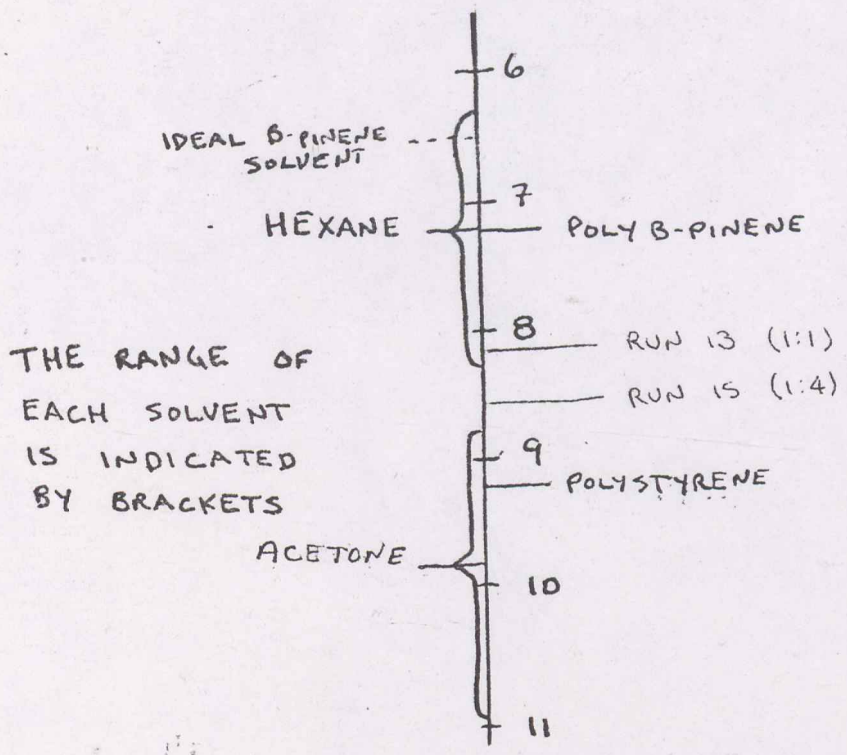
The first method of characterization used by Snyder was solubility studies. Polymers, and the solvents which will dissolve those polymers, are given a number called the solubility parameter. Solubility parameters are both calculable and experimentally derived. The calculation is based on a summation of molar attraction constants of the solvent (or repeating unit), times its density, divided by the molecular weight. Solubility of a polymer in a given solvent can be expected within 1.1 solubility parameter units.⁵

B-pinene and hexane have equal solubility parameters, 7.2, whereas polystyrene is 9.2 and acetone is 9.8. Thus B-pinene dissolves in hexane but not in acetone, 2.6 units away. Polystyrene still dissolves in acetone, 0.6 units away, but not in hexane, with a difference of 2.0 units. This information can be applied to the copolymer studies. (See Figure 1).

Beginning with a one to one molar ratio feed of B-pinene to styrene a copolymer product may dissolve completely in one, or in the other, or neither solvent depending on its solubility parameter. If two homopolymers form from an equimolar ratio feed, about 56 percent by weight should dissolve in hexane, and 44 percent by weight should dissolve in acetone. (The variation from 50 percent is because B-pinene has a molecular weight of 136 and styrene a molecular weight of 104 - a ratio of 56 to 44). Unfortunately, molecular weight of polymer plays a part in solubility studies.

A method was devised to analyze the copolymer products. NMR was used to determine the mole percent styrene in the portion which was insoluble in acetone. Since acetone will dissolve any polystyrene in a product, the insoluble portion should be polyB-pinene homopolymer, copolymer (very low in styrene content), or a mixture of both. An NMR

FIGURE 1



THE RANGE OF EACH SOLVENT IS INDICATED BY BRACKETS

SOLUBILITY PARAMETERS

is run on an acetone washed portion in deuterated chloroform and the mole percent styrene determined from the integration. Since styrene has five aromatic protons, and B-pinene has none, a simple ratio is used to calculate an approximate mole percent styrene content.

Another method of characterizing the polymer products is by gel permeation chromatography. Gel permeation chromatography is a separation technique based on particle size and shape. The column or columns are packed with a porous gel, crosslinked dextran, containing many holes of different sizes. If a large polymer molecule is placed on the column, it will find very few pores which it can fit into, thus it will flow through and elute quickly. A small molecule, conversely, will fit into many of the holes and be retained for a longer time. Medium sized molecules will spend intermediate lengths of time on the column. Thus, a molecular weight versus retention time graph is recorded, the largest molecules coming out first.⁶

Our work involved three variations on this basic principle. A Waters GPC/ALC 301 Gel Permeation Chromatograph was used to determine molecular weight, dispersity and an approximate mole percent styrene content. The retention time of a peak is determined by calibrating the instrument with known weight samples and plotting elution volume versus molecular weight. The best resolution was found at a high pump speed, 3.74 milliliters per minute (ml/min) using an injection time of six seconds, and samples containing three milligrams per milliliter (3mg/ml). (Figure 2).

The dispersity of a polymer is a measure of how uniform the polymer is. The more dispersed a polymer is, the more varied the chain lengths are. The dispersity is defined as the weight average molecular weight, divided by the number average molecular weight. The number average molecular

GEL PERMEATION CHROMATOGRAPHY CALIBRATION CURVE

7

CURVE MEVER - 4-9-73A

CONDITIONS

SOLVENT TOLUENE

TEMP. ROOM AMBIENT

COLUMNS 5

FLOW 3.74 ml/min p/ft

STANDARDS USED POLYSTYRENE

MICAL 5000

3500

1750

1000

480

UNKNOWN LIQUIDS

390

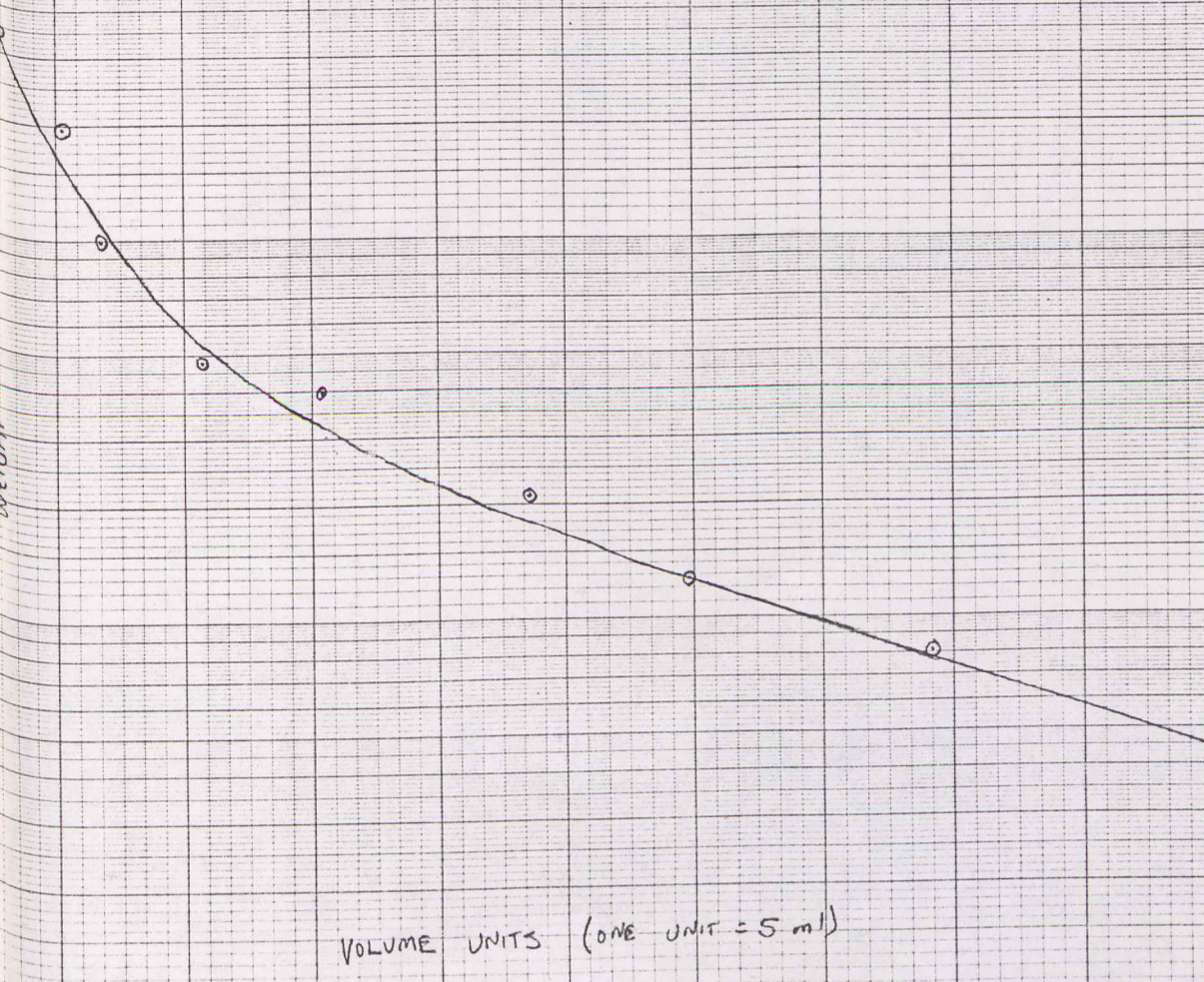
202

122

79

BEZEL

FIGURE 2



VOLUME UNITS (ONE UNIT = 5 ml)

18

19

20

21

22

23

24

25

26 Part No. 27627



weight (\overline{M}_n) is defined as the total weight divided by the total number of molecules present. The weight average molecular weight (\overline{M}_w) is the sum over all chain lengths of the weight of that length (i) times the number of chains of that weight fraction.⁷ It turns out that M_n and M_w are always different (\overline{M}_n is less than \overline{M}_w), except for pure compounds. Thus the dispersity, $\overline{M}_w/\overline{M}_n$ can be calculated using a standard sample. Since the peak width at half the peak height is constant for a given sample, independent of concentration, a ratio can be set up. Let W_c be the peak width at half height for the standard, W_s be the width at half height of the sample, and d_c be the dispersity of the calibration sample. Then d_c is to W_c as d_s is to W_s , where d_s is the dispersity of the unknown sample. The standard polystyrene sample used was 5000/4600; $d_c = 1.06$ and $W_c = 0.66$ centimeters.

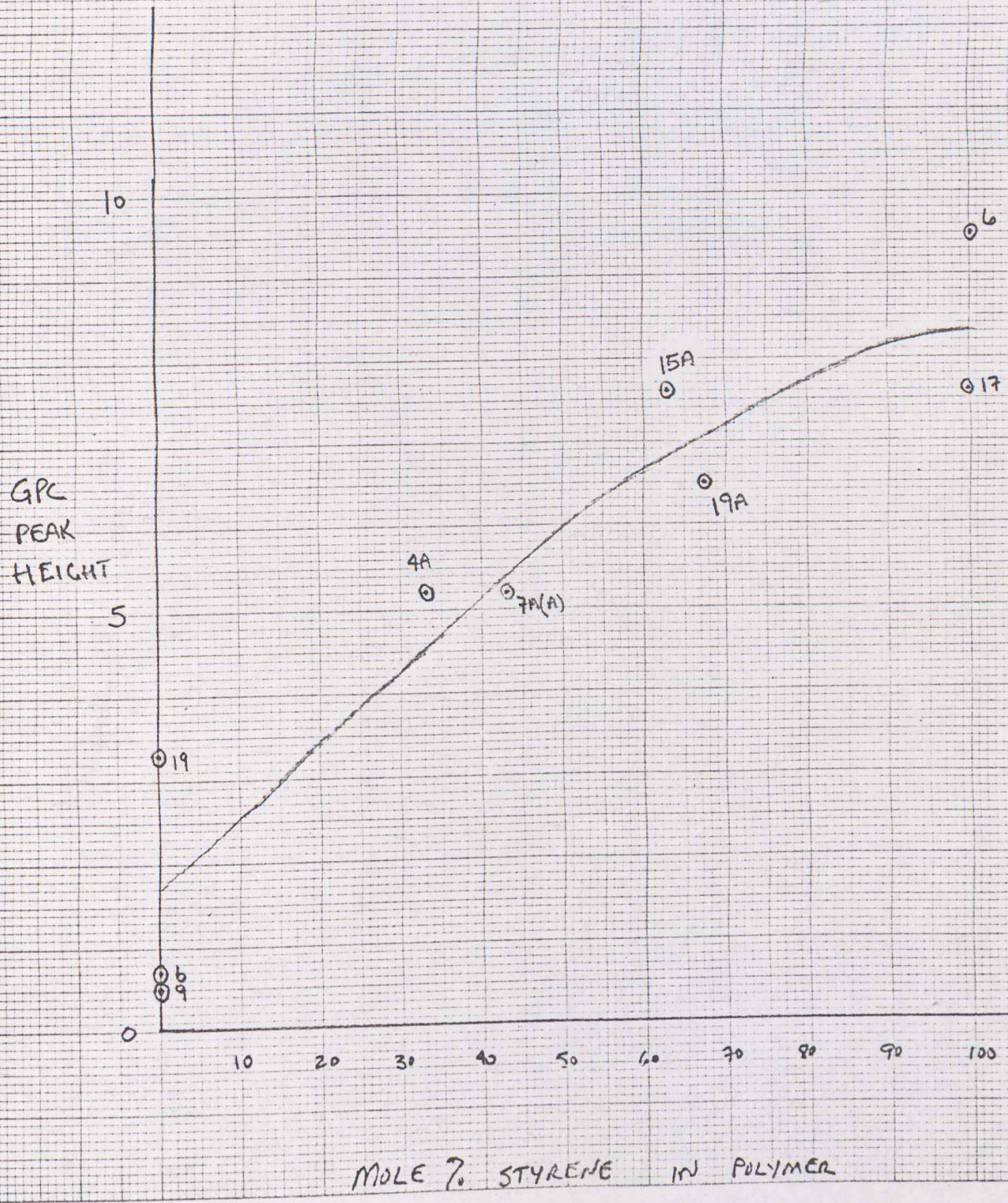
It was observed that polystyrene homopolymer peak heights were very large and the polyB-pinene peak heights were very small. Using the styrene content of samples from NMR analysis, a relationship between peak heights and percent styrene content was observed (Figure 3), which allows a quick estimation of mole percent styrene on the basis of peak heights alone.

Another method of gel permeation chromatography was also tried: a one meter by two centimeter column filled with Sephadex LH-20 in a polar solvent. This method is different than the method used by C. Snyder and H. Sheffer in 1971-1972.⁸

"It is known that Sephadex G-types have an affinity for aromatic and cyclic compounds. Pronounced aromatic adsorption occurs mostly when lower alcohols are used as eluting solvents with Sephadex LH-20."⁹

It was by this method we hoped to separate the aromatic polystyrene and

FIGURE 3



the cyclic polyB-pinene.

A one to one mixture (by weight) of homopolymers was run in a three to one mixture (by volume) of chloroform and isopropanol. (The polymers were insoluble in isopropanol alone.) Two milliliter samples were collected for about five hours in 200 test tubes. The weight difference for each test tube was plotted after the solvent was evaporated and the results showed a wavy line. It is apparent that there is a competition between processes here. High molecular weight polystyrene in pure chloroform should elute first (by molecular weight), but last in pure isopropanol (by adsorption). The lower molecular weight polyB-pinene should elute last in chloroform, and first in isopropanol.

The next method for separation of homopolymers was solubility. If the solubility parameters of a solvent and a polymer are within 1.1 units, solution occurs. Since acetone (solubility parameter = 9.8) and polystyrene (solubility parameter = 9.2) have differing parameters, acetone will remove only polystyrene homopolymers. B-pinene and hexane have equal parameters (7.2) and hexane is able to dissolve both polyB-pinene and copolymer with a high B-pinene content. If we could find a solvent with a solubility parameter of about six, then we could selectively remove polyB-pinene homopolymer and leave behind any copolymer rich in B-pinene, just as acetone removes only polystyrene and leaves behind copolymer. Unfortunately, only fluorinated alkanes were calculated to have solubility parameters of 6.5. The idea was dropped since fluoroalkanes have a cost of nearly one dollar per gram.

Another procedure considered for characterizing copolymer products was differential scanning calorimetry. Differential scanning calorimetry operates on the principle that a phase change requires energy to occur.

For melting, this energy is the heat of fusion. The instrument itself, a Perkin Elmer DSC-1B, has a pair of sample pans, one is empty, the other contains sample. The two pans are heated at the same rate, and the difference in energy needed to keep the sample pan at the same temperature is plotted versus the average temperature.

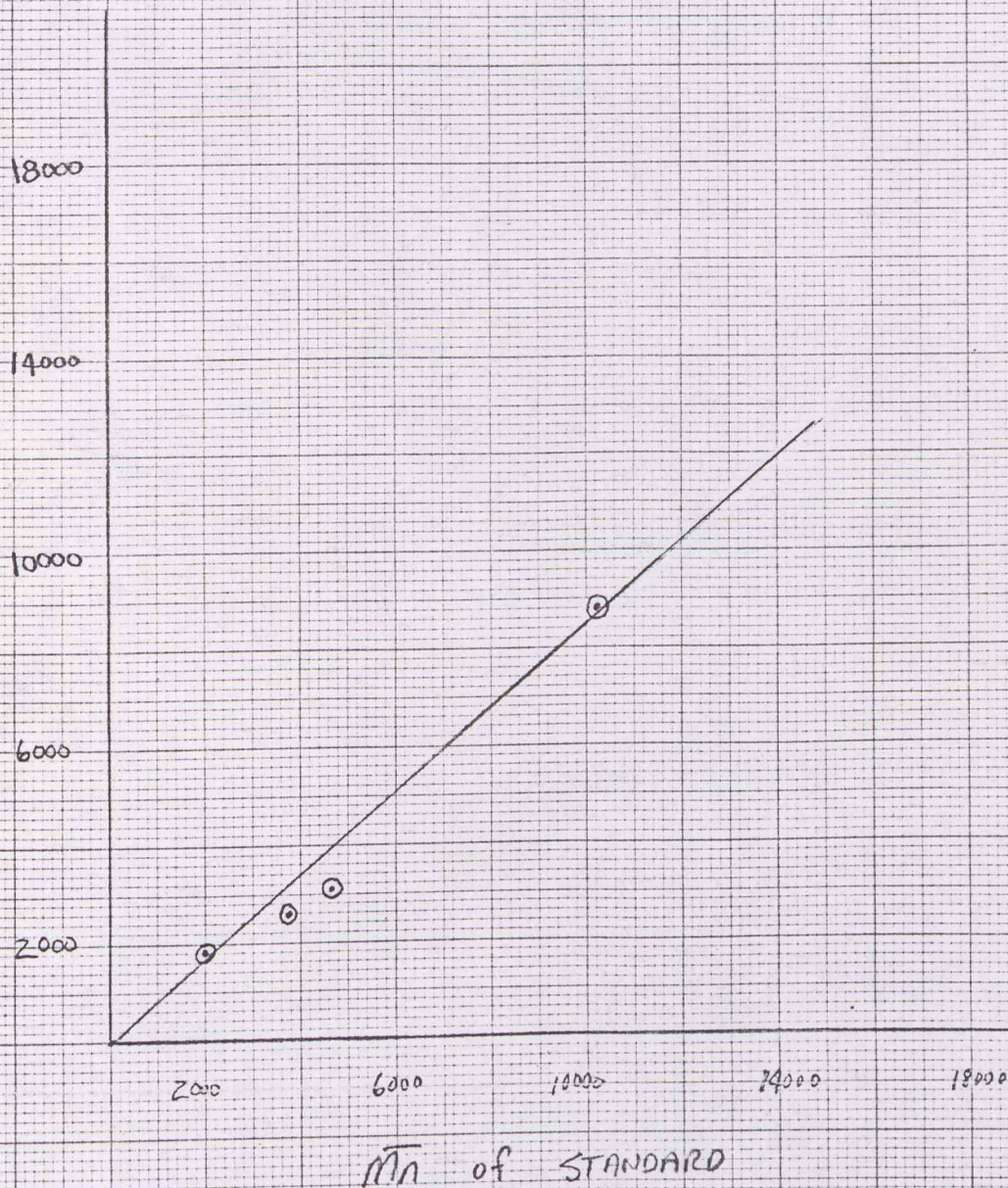
The differential scanning calorimetry plot gives what has been referred to as a fingerprint of the polymer. Our work shows that the history of the polymer, to some extent, determines some of the differential scanning calorimetry curve.

Another method for characterizing the polymers was to determine \overline{M}_n by Vapor Phase Osmometry. The rate of evaporation of a pure solvent will be greater than the rate of evaporation of a solution of known concentration in a saturated atmosphere. The molecular weight is derived by measuring slight temperature differences between solvent and solutions of known concentration. The values obtained on a readout dial are plotted versus concentration, and extrapolated to zero. Having calibrated the instrument with Benzil (molecular weight = 210), a constant is obtained, and the reading at zero concentration is used to calculate \overline{M}_n .

Compared to our samples, Benzil has a much lower molecular weight. High molecular weight substances have fewer particles per unit concentration, introducing a slight error. This error can be eliminated by calibrating with standard samples of known \overline{M}_n . This was done and a graph of \overline{M}_n observed versus \overline{M}_n known is shown in Figure 4. It is essentially a calibration of a calibration.

FIGURE 4

observed
on
PO



The first method used chronologically to characterize the polymer batches was differential scanning calorimetry. The area under the curve of a differential scanning calorimetry plot is a direct measure of the heat of transition from glass to amorphous or amorphous to liquid polymer.¹⁰ The batches were run under constant conditions in a nitrogen atmosphere. Approximately 150 milligrams was used for each sample. The slope was 400 to 430, the sensitivity 16, and the temperature was increased 2.5°C per minute.

The first of the samples to be analyzed was polyB-pinene, RUN #16. (Figure 5). Endothermic disorientation takes place from 62°C to 128°C. Melting begins at 138.2°C and there is a loss of rigidity beginning at 143°C (visible observation), and decomposition (smoke) begins at 148°C. At 165°C there is a second slope in the decomposition and the pattern of heat loss changes to a complex pattern of exotherms and endotherms which we will call spiking.

The second differential scanning calorimetry run is of polystyrene, RUN #17 (Figure 6). Polystyrene was thermally stable to the limit of the instrument, 320° C. (It was liquid, without smoke or discoloration.) The plot was very smooth and yielded some difficulty in obtaining the melting range. The melting point was visually confirmed in an open sample pan at 154° C. The melting range was deduced to be 151° C to 172° C by noting slope changes.

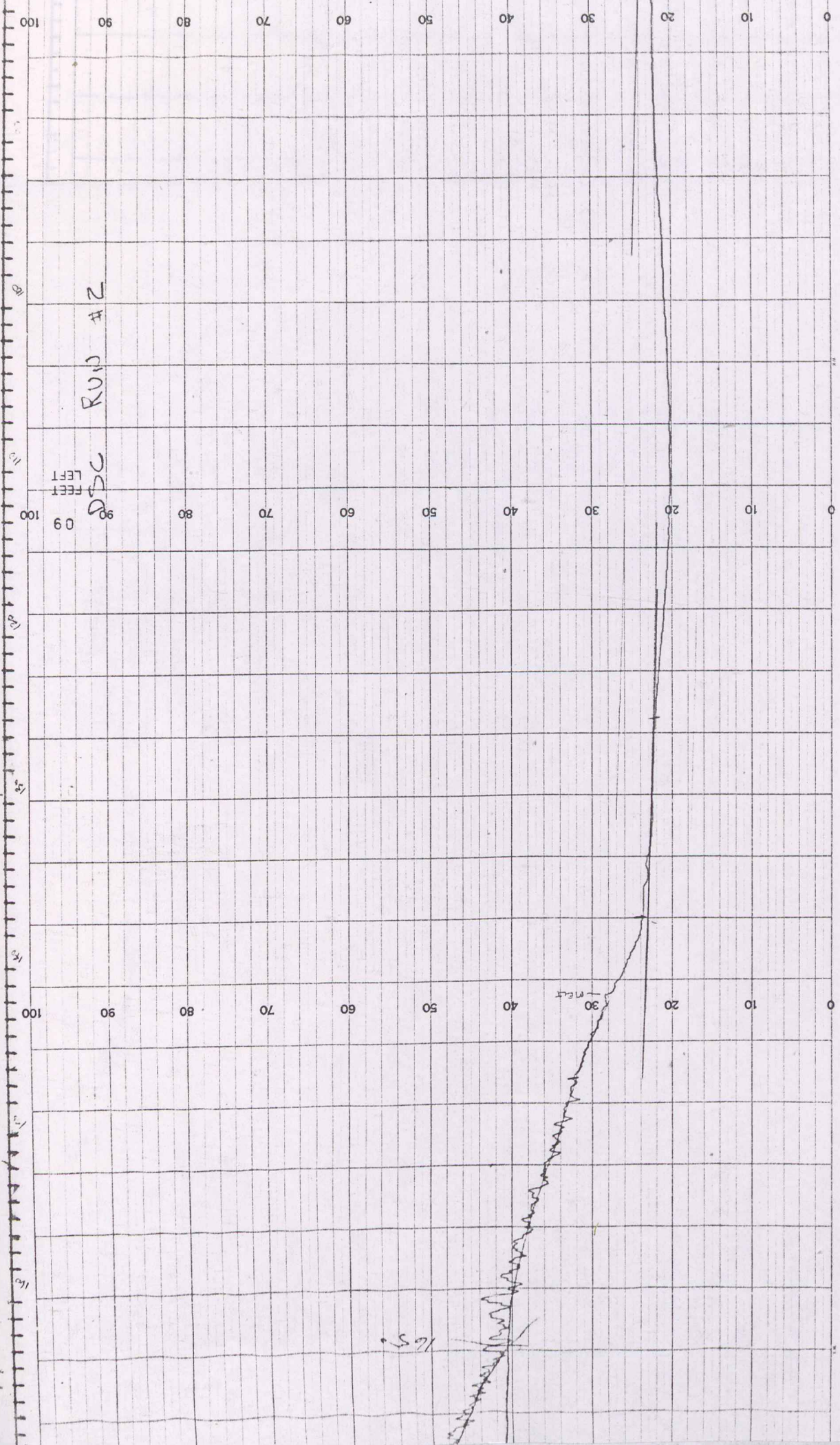
If the results of these first two runs are compared, then a mixture of homopolymers of about one to one by weight should yield the sum of the two graphs. One would expect an endotherm at the beginning, and also melting ranges beginning at 138° C and 151° C to be visible. Spiking from decomposition should occur about 160° C and always be an indication that poly(homo) B-pinene is present.

A one to one by weight mixture of RUN #16 and RUN #17 was done next.

(Figure 7) The plot shows the endothermic disorientation from

14

BATCH # 16 OF OSC 5 32971F



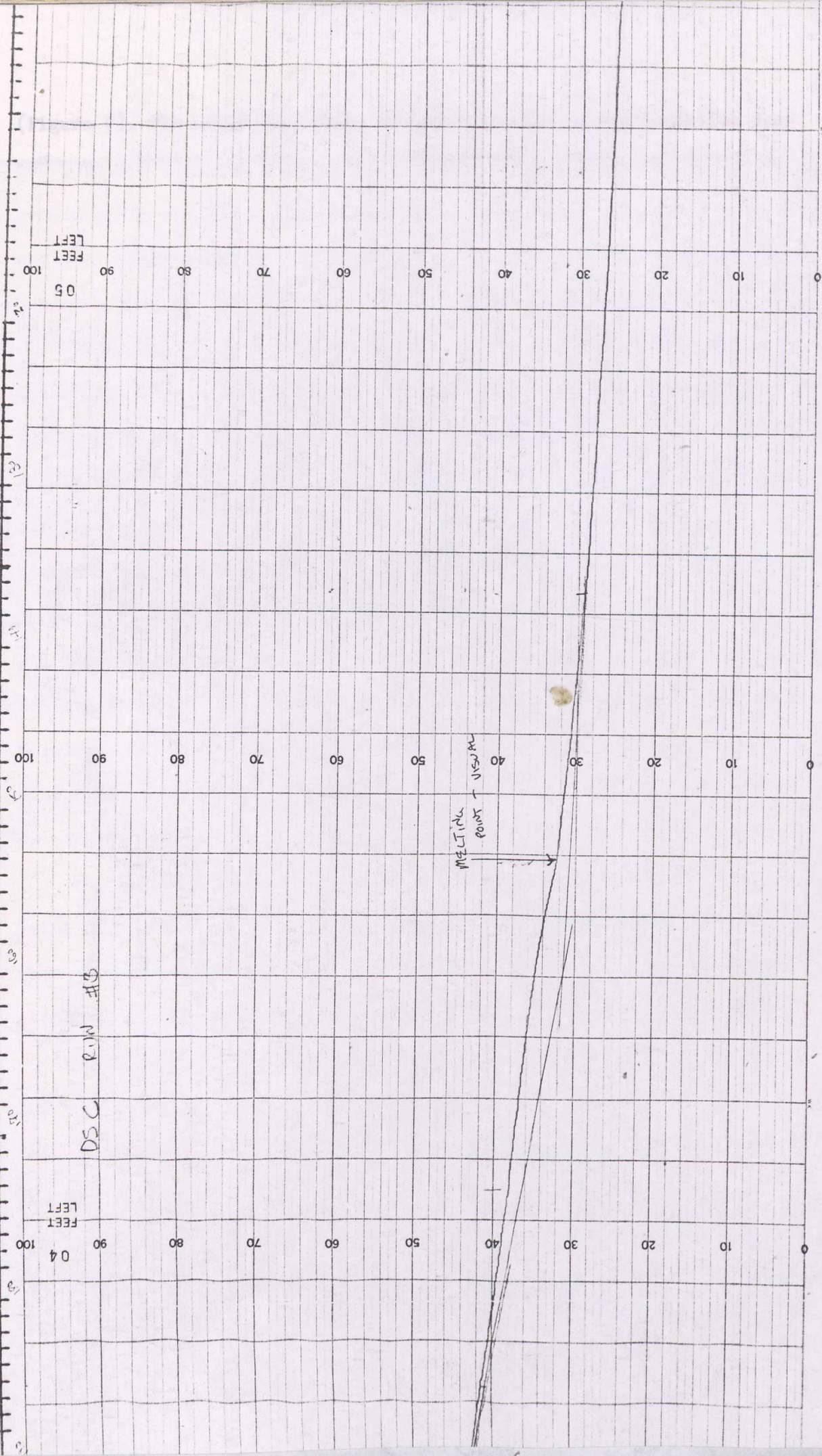
RUN #2

OSC
LEFT

16.5

15

FIGURE 6 DSC OF BATCH #17



(Figure 7). The actual run shows an endotherm due to reorientation from 60° C to 110° C. The first melt begins at 120° C, ending at 134° C. The second melts at 150° C, and at 160° C, a large mess with with several slopes evolves, indicating that polyB-pinene is decomposing. A second trial run produced much the same results with temperatures slightly higher.

Thus, one would conclude that mixing pure homopolymers together causes changes in the melting points of each individual homopolymer, but 1) homopolymeric mixtures may be found by this technique 2) each component which is different enough will add its own characteristics to the plot and 3) polyB-pinene decomposes above 150° C and is easily recognized. Any polyB-pinene homopolymer will cause an endotherm between 138° C and 148° C. Any polystyrene homopolymer will cause an endotherm between 151° C and 172° C. Since the polystyrene is more crystalline than the polyB-pinene, it should have a higher melting point. The copolymer should melt between the ranges of the two homopolymers, as it will have an inbetween crystallinity. Copolymers of a one to four molar ratio should melt higher than one to one molar ratio of B-pinene to styrene because of the higher styrene content.

The next of the differential scanning calorimetry runs was done on Batch #6. This batch is the room temperature polystyrene homopolymer. It shows several endotherms, at 132° , 190° and 198° C. It shows no downward slope, no spiking and was stable to the limit of the instrument. (See Figure 8.)

Next, Batch #9, polyB-pinene synthesized at room temperature, was run. The plot (Figure 9) shows a downward slope, indicating a crystalline reorientation is occurring, from 70° C to 145° C. Above 145° the polymer melts and decomposes.

If one adds together the differential scanning calorimetry plots of these two homopolymer runs, one would expect the following: exotherm beginning at 70° C, melting endotherms at 132° , 145° and decomposition of one portion above

MADE IN U.S.A.

CHART WK7

MADE IN U.S.A.

012

TEXAS INSTRUMENTS INCORPORATED, HOUSTON, TEXAS, U.S.A.

CHART WK7

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17

#16 #17

MIX OF

OSC

FIGURE 7

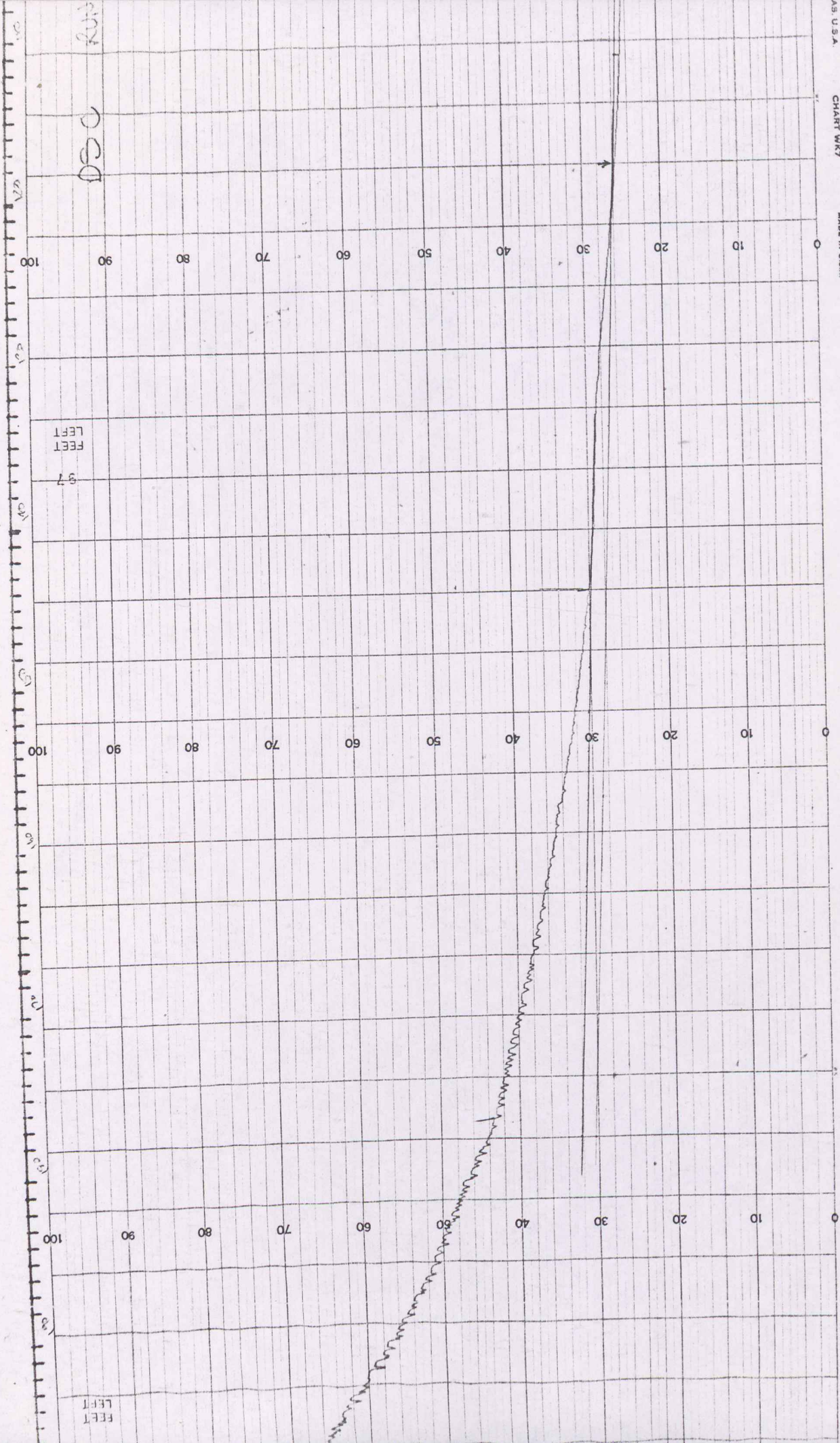


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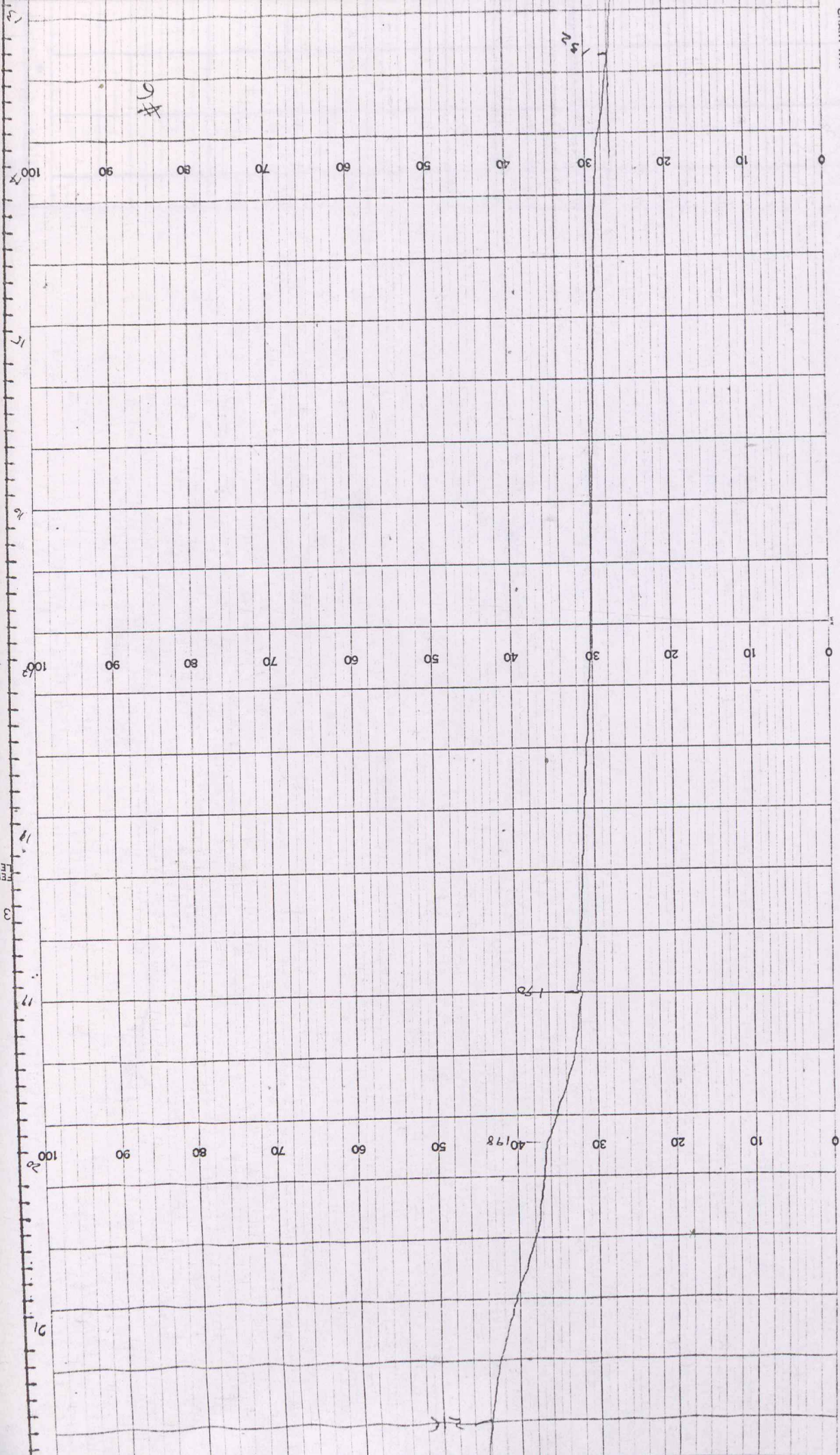
18

TEXAS INSTRUMENTS INCORPORATED, HOUSTON, TEXAS, U.S.A.

CHART WK7

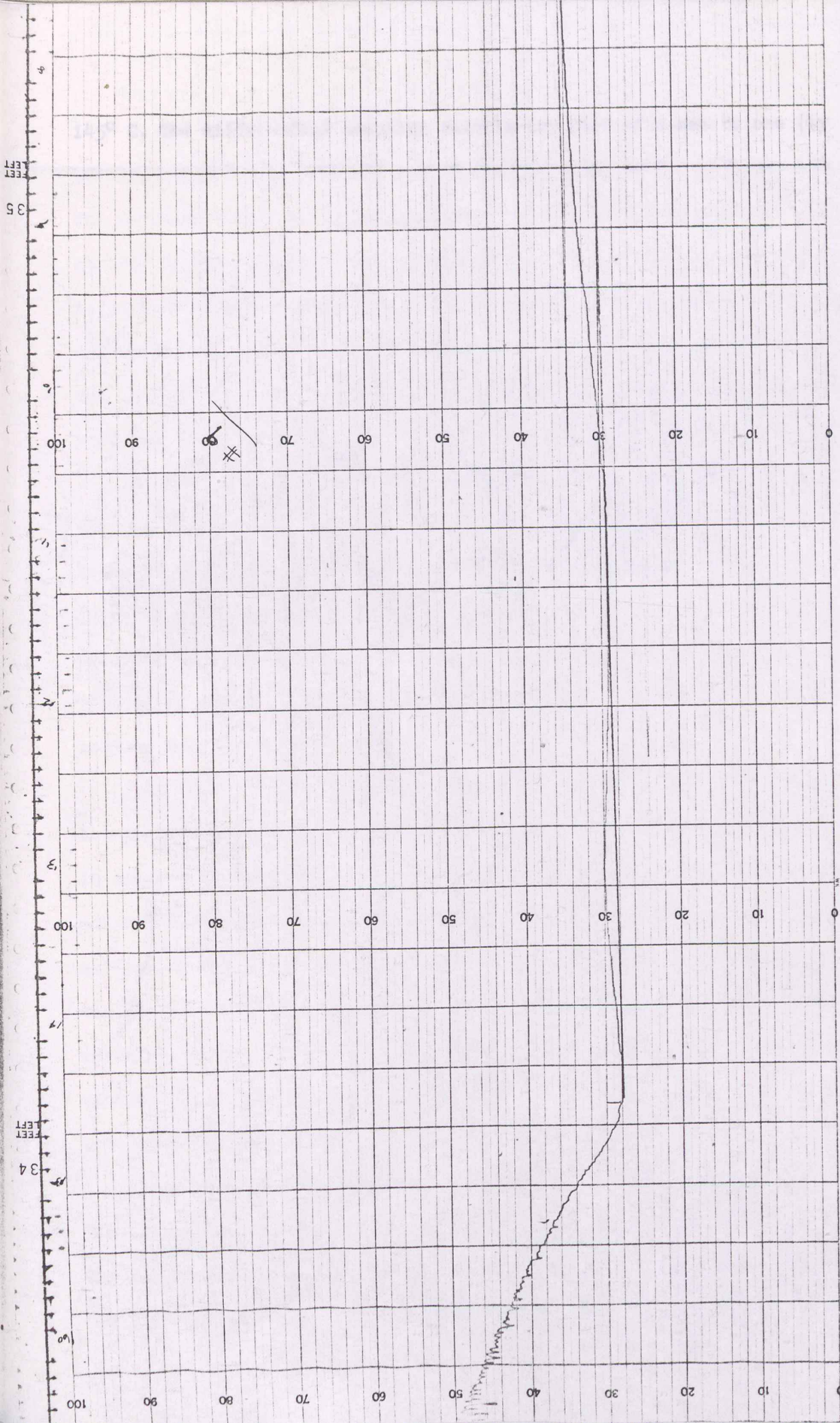
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FIGURE 8 OSC OF BATCH #6



19

FIGURE 9 DSC OF BATCH #9



145° C. The differential scanning calorimetry plot of a one to one (by weight) mixture of Batches #6 and #9 was the next one done. (Figure 10). The exotherm begins at 84° and melting at 136°, with decomposition starting at 140° C. It is noteworthy that the exotherm is higher and the only melting inflection occurs between the values predicted. The polyB-pinene homopolymer decomposes at a slightly lower temperature than the previous batches, but the spiking is very evident. With this information, the rest of the batches were run.

Batch #15, one to four molar ratio of B-pinene to styrene at -78° C, was the first. It shows a very smooth plot, melting occurring at 129° C. There is no spiking, but there are two slight changes at 158° and 172° C. (See Figure 11). Next, #13, the same as #15, except a one to one molar ratio, was done next. (Figure 12). It shows slope changes at 165° and melting was visually confirmed at 178° C. Decomposition begins above 180° C and the polymer smokes and turns brown.

From these two plots and the information gained from the plots of the homopolymer mixtures, it might be speculated that a mixture of homopolymers is present in Batch #13 and a copolymer comprises #15. Further work with other batches showed that Differential Scanning Calorimetry was not a sufficient method for determining copolymer and homopolymer mixtures. This was because the instrument had an old sample holder, which reduced the reproducibility. The differential scanning calorimetry plots of solvent washed batches showed large differences, even when the product was totally insoluble in that solvent.

Despite the difficulties encountered, much useful information was obtained. The temperatures at which the polymers undergo thermal change is very important when considering whether to use that polymer for a specific application. The polyB-pinene homopolymer decomposes between 140° and 170°, and this is

6# 29# X1W1 JSC 250
FIGURE 10

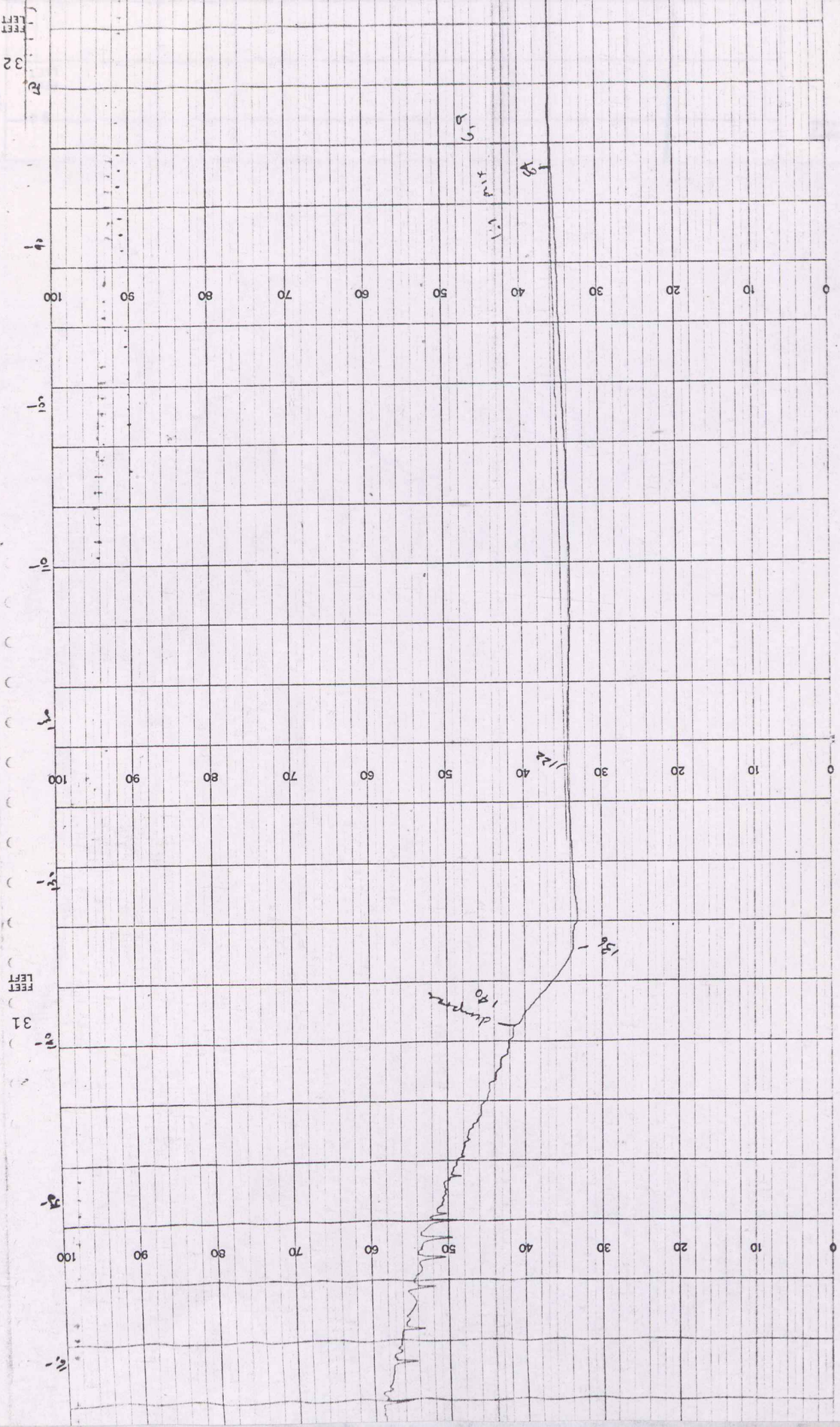


FIGURE 11 DSC OF BATCH #15

DSC RUN #5 "Capd-mag" #15

FEEJ LEFT

94

100

90

80

70

60

50

40

30

20

10

0

100

90

80

70

60

50

40

30

20

10

0

FEEJ LEFT

93

100

90

80

70

60

50

40

30

20

10

0

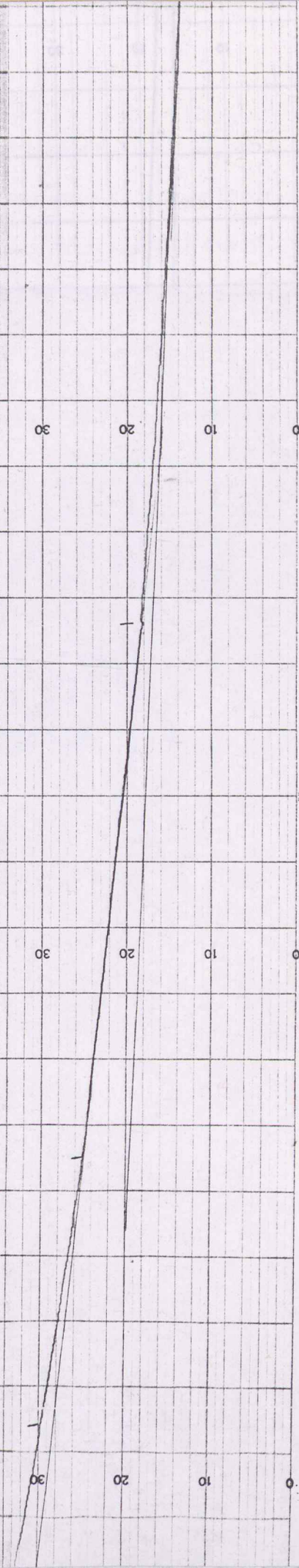
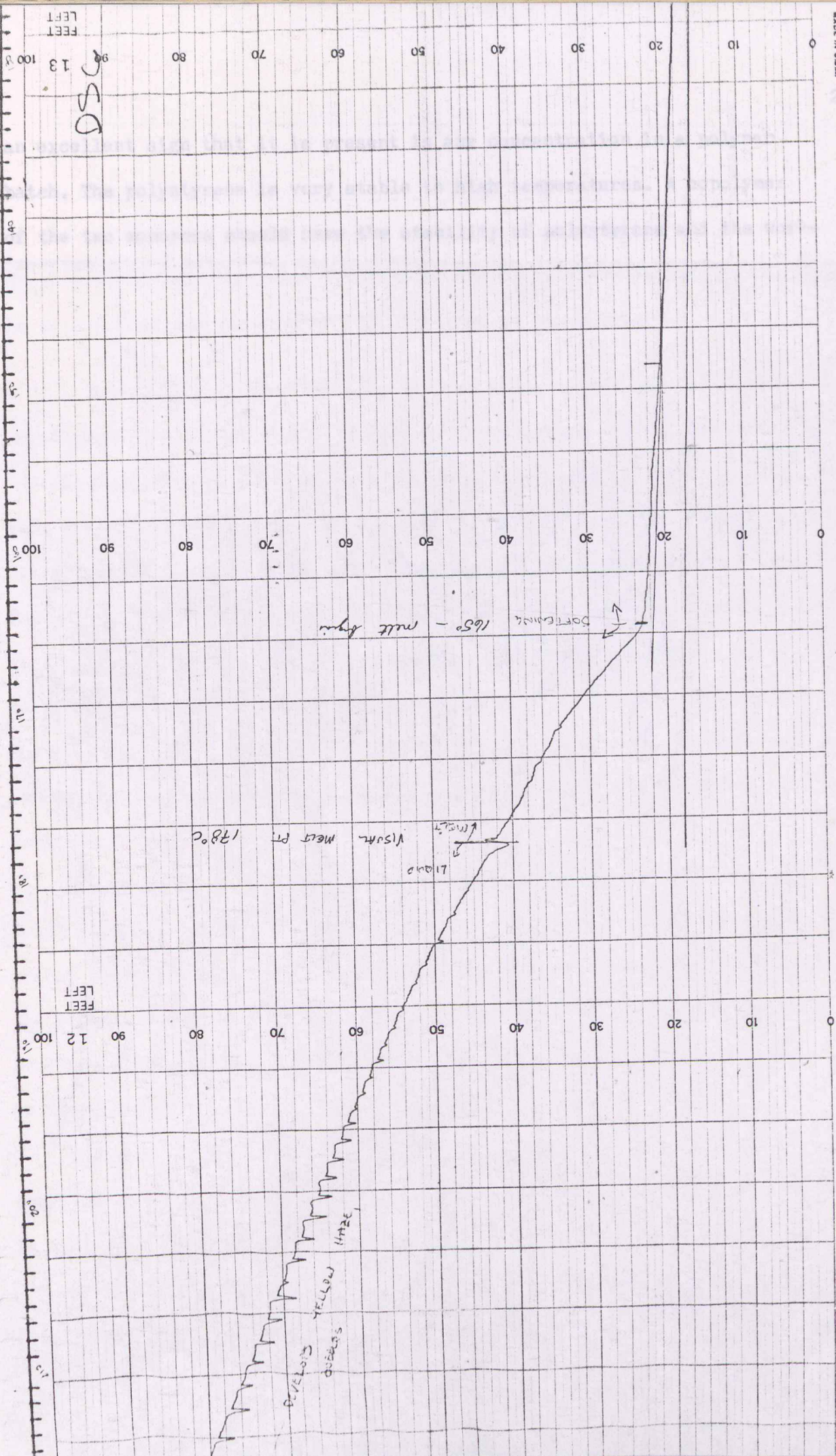


FIGURE 12 DSC OF BATCH #13



FEEET LEFT

13

DSC

FEEET LEFT

12

FEEET LEFT

an excellent sign that it is present in any concentration in a polymer batch. The polystyrene is very stable to high temperatures. A copolymer of the two monomers should have the stability of polystyrene and the workability of the polyB-pinene. In spite of the information gained, it could not be ascertained whether a batch was copolymer or homopolymers.

The next technique for separation of homopolymers was Gel Permeation Chromatography. A Waters Gel Permeation Chromatograph was calibrated using ten standard samples (See Appendix B). Once calibrated at the flow rate giving best resolution, an attempt to separate homopolymers was made. First, each homopolymer was run to determine molecular weight and dispersity. (Tables 2-7). The gel permeation chromatogram of Batch #16 (polyB-pinene) is shown in Figure 13. The peak is small and disperse, with a peak retention volume of over 19 units. The gel permeation chromatogram of Batch #17 (polystyrene) is shown in Figure 14. It is unusual that there are two peaks; the side shoulder is very high molecular weight. There is a very slight tail on the low molecular weight side.

If one predicts the graph for a mixture of Batches #16 and #17, one would expect a shoulder on the main peak and a long low molecular weight tail, rather than two peaks. This is because the polyB-pinene has such small peaks. The results of a one to one (by weight) mixture of Batches #16 and #17 is a broad peak with a shoulder. A long tail on the low weight side can barely be discerned.

The procedure was then repeated for Batches #6 and #9, polystyrene and polyB-pinene, respectively. Figure 16 shows Batch #9, polyB-pinene. The peak is very small and disperse, with a peak retention volume of 19 units. The gel permeation chromatogram of Batch #6 is shown in Figure 17. It has a long low molecular weight tail on a large peak, with a retention volume of 18.6 units.

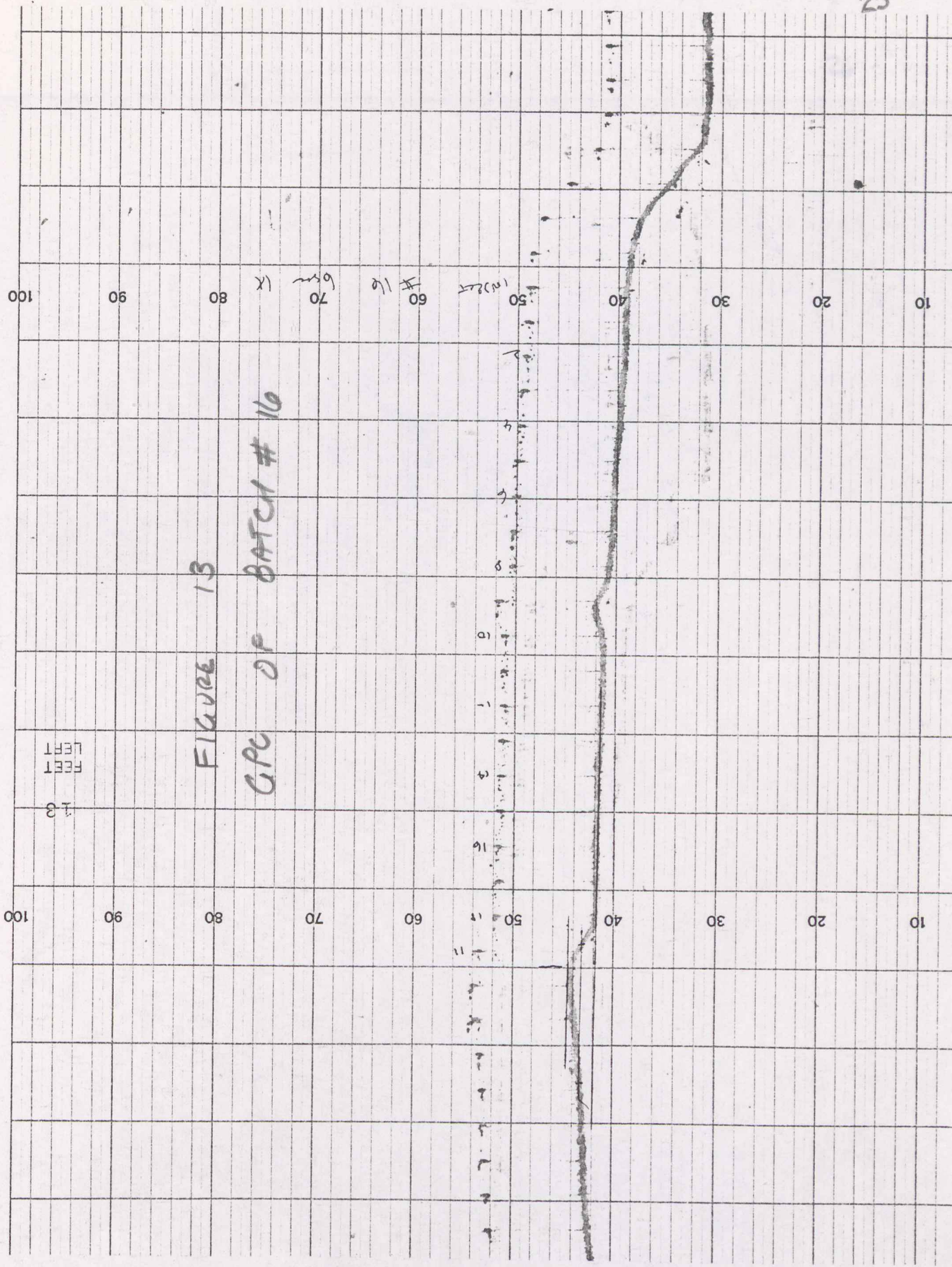
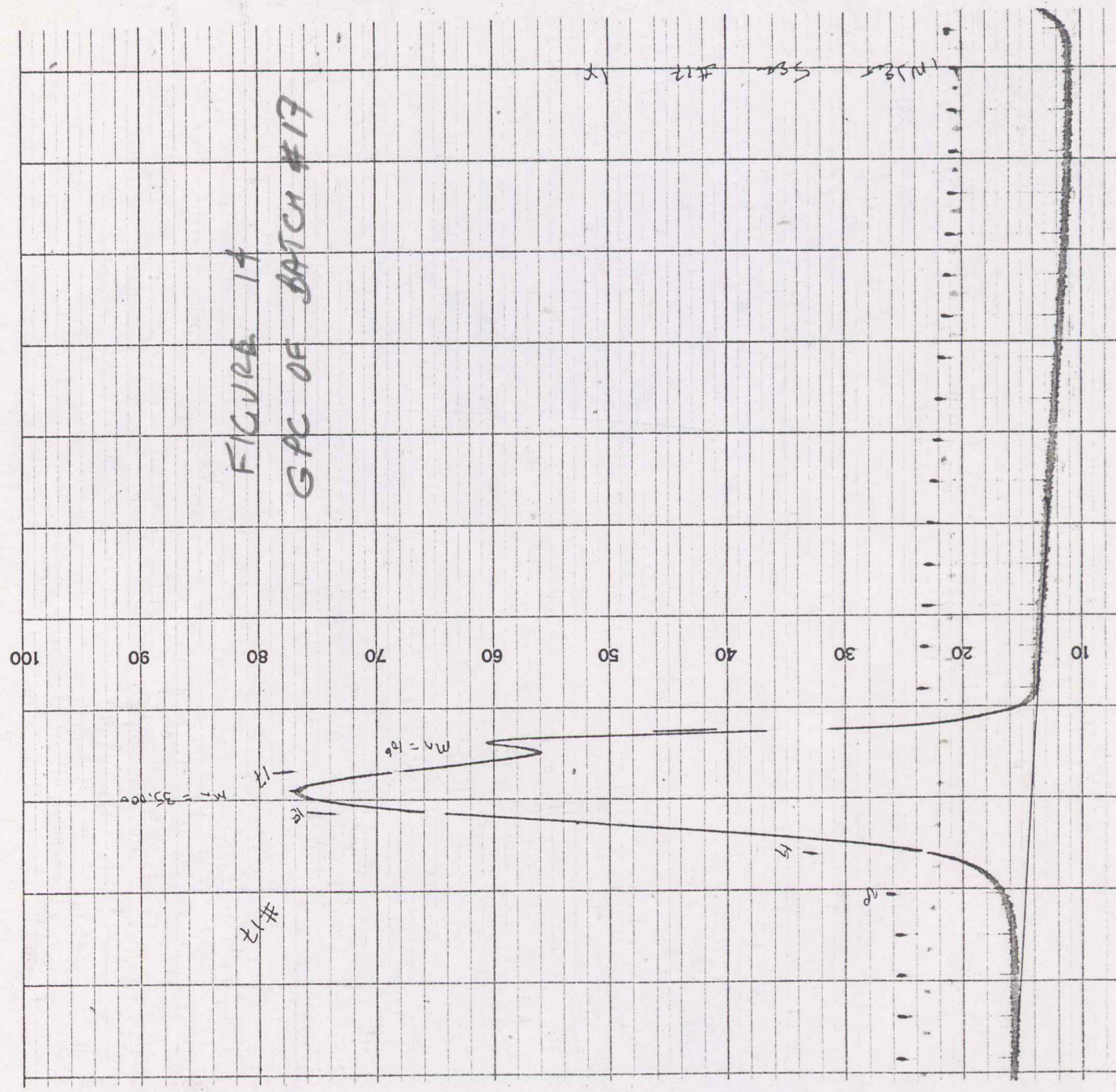


FIGURE 14
GPC OF BATCH #17



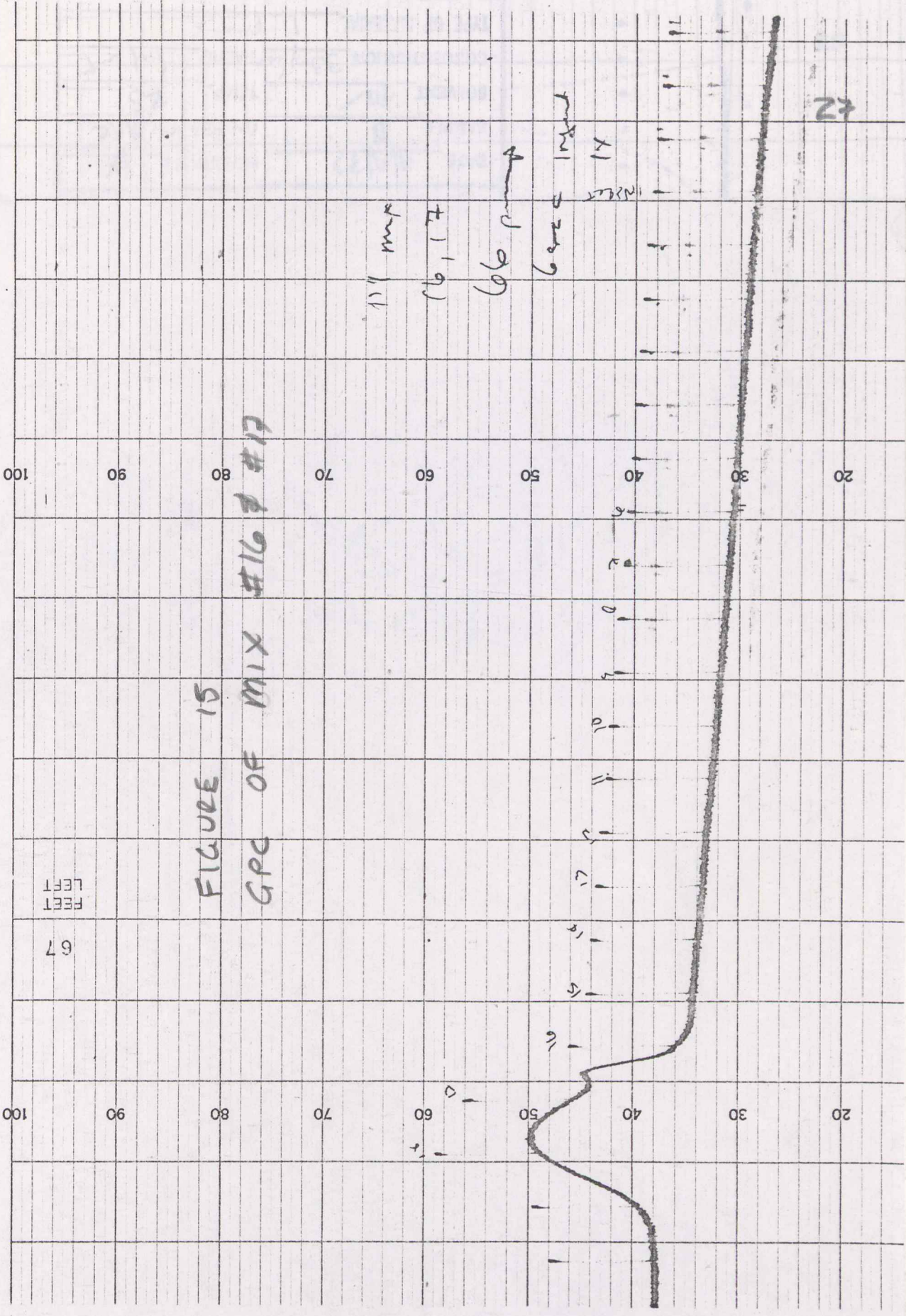
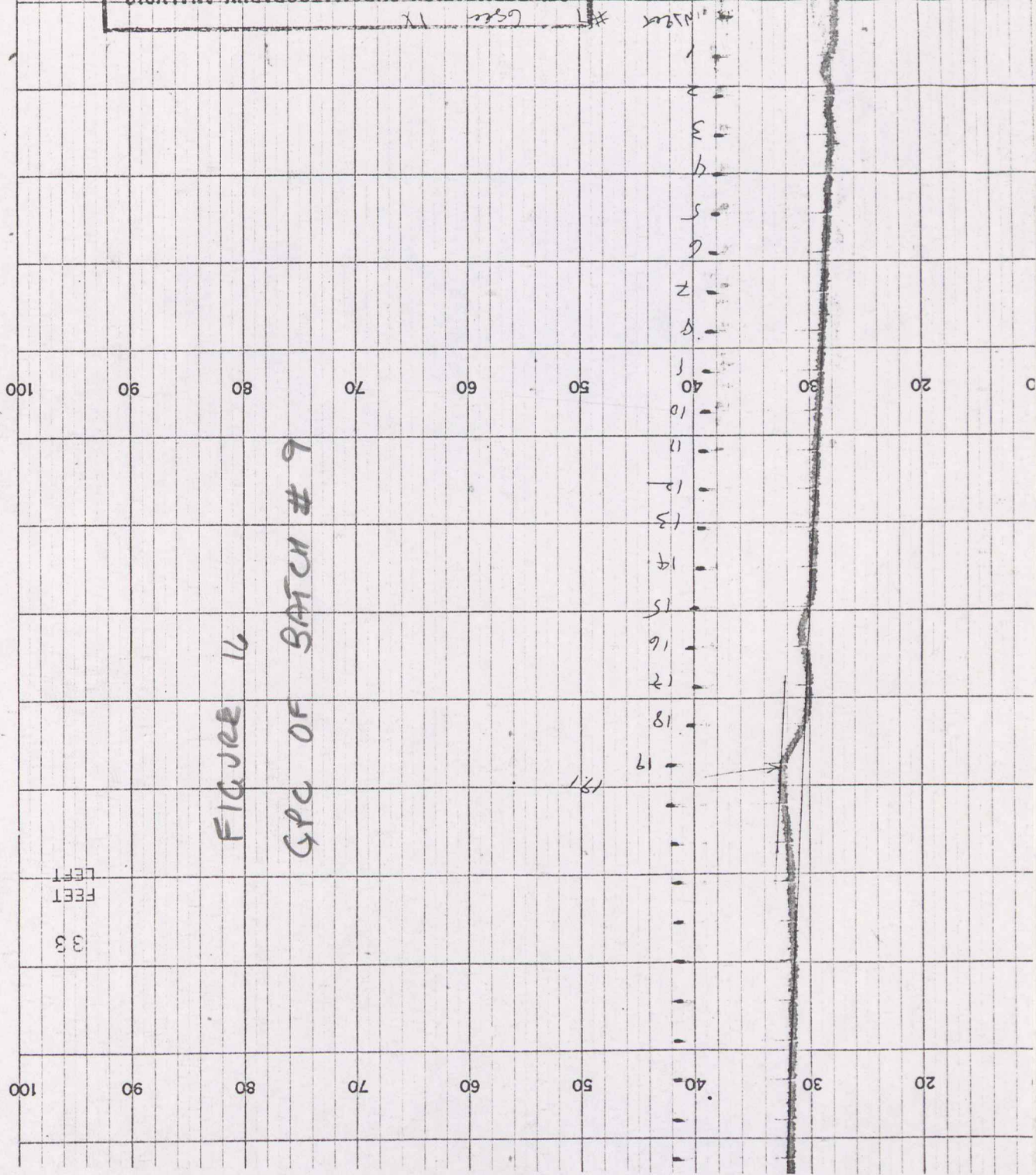


FIGURE 15
 GPC OF MIX #16 & #17

67

GEL PERMEATION CHROMATOGRAPHY ANALYSIS	
DATE	4/9/33
SAMPLE	B
SOLVENT	tol
CONCENTRATION	3.5mg/ml
TYPE OF MATERIAL	Polystyrene
SENSITIVITY	X
CALIBRATION	MWC
TEMP.	25



FEET
33

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

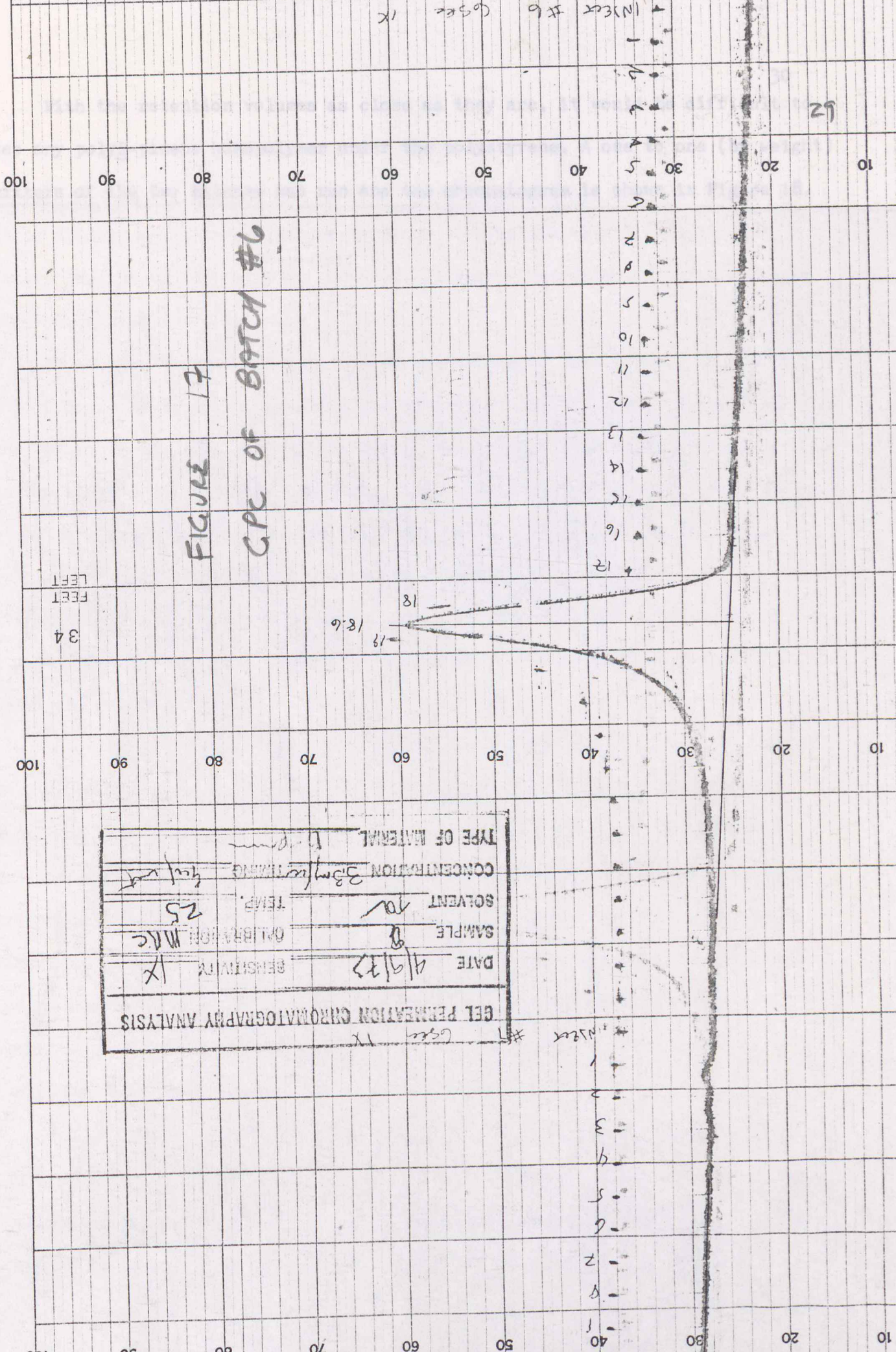


FIGURE 17
GPC OF BATCH #6

FEET LEFT
34

18.6
18

GEL PERMEATION CHROMATOGRAPHY ANALYSIS	
DATE	4/9/33
SAMPLE	8
TEMP.	25
CONCENTRATION	3.5 mg/ml
TYPE OF MATERIAL	Polystyrene
SENSITIVITY	1X
CALIBRATION	MWC

INJECT #6
1
2
3
4
5
6
7
8
9
10

INJECT #6
1X

With the retention volumes as close as they are, it would be difficult to see any polyB-pinene homopolymer under the polystyrene. A one to one (by weight) mixture of the two batches was run and the chromatogram is shown in Figure 18. It is a large peak, very similiar to Batch #6. The low weight tail is much longer than it was on Batch #6, however. It seems that detection of a mixture might be plausible.

To further check the possibilty of separation by this method, the homopolymers made in m-xylene were run (Figure 19 is Batch #25, polyB-pinene and Figure 20 is Batch #26, polystyrene). The polyB-pinene shows a single medium sized peak with a low molecular tail. The polystyrene shows three peaks. With three peaks due to very low molecular weight, separation is possible, but not useful. This is because under copolymerization reaction conditions, the molecular weights of homopolymers being formed would probably differ by a large amount. Thus, the polystyrene homopolymer (Batch #26) is not representative and cannot be used.

The next step is to apply the information to the other batches. The shape of a copolymer chromatogram would be almost gaussian. It would not show any excess material of higher or lower molecular weight. A mixture of two homopolymers would have a low molecular weight tail of polyB-pinene (in most cases polyB-pinene is lower molecular weight than polystyrene, and it should elute last). It is due to difficulties with the detector that the polyB-pinene peaks are so small, hence a tail, and not a second peak. This fact practically eliminates the ability to judge whether a peak represents a copolymer or a mixture of homopolymers.

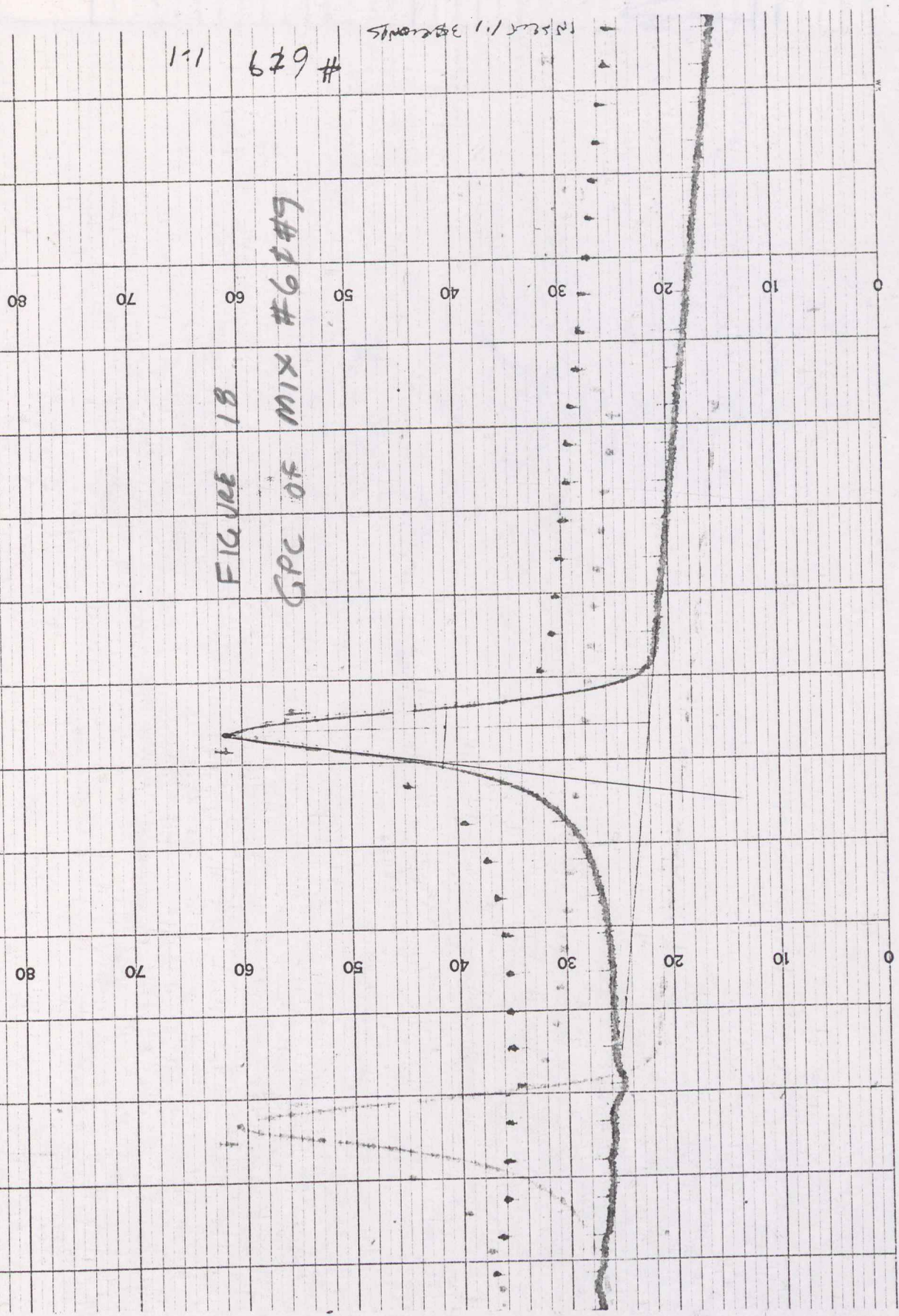
The first Batch was #13. (Figure 21) is a one to one molar ratio. It shows nearly symetric peak with a retention volume of about 18 units. It also shows a slight low molecular weight tail. The chromatogram of Batch #15 (Figure 22), a one to four molar ratio of B-pinene to styrene, is symetrical. It has no low molecular weight tail. One could conclude that #13 is a mixture of homopolymers

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#679 1:1

INSTRUMENTS

FIGURE 18
GPC OF MIX #679

100 90 80 70 60 50 40 30 20 10

32

x 5 b m 3.37/cc

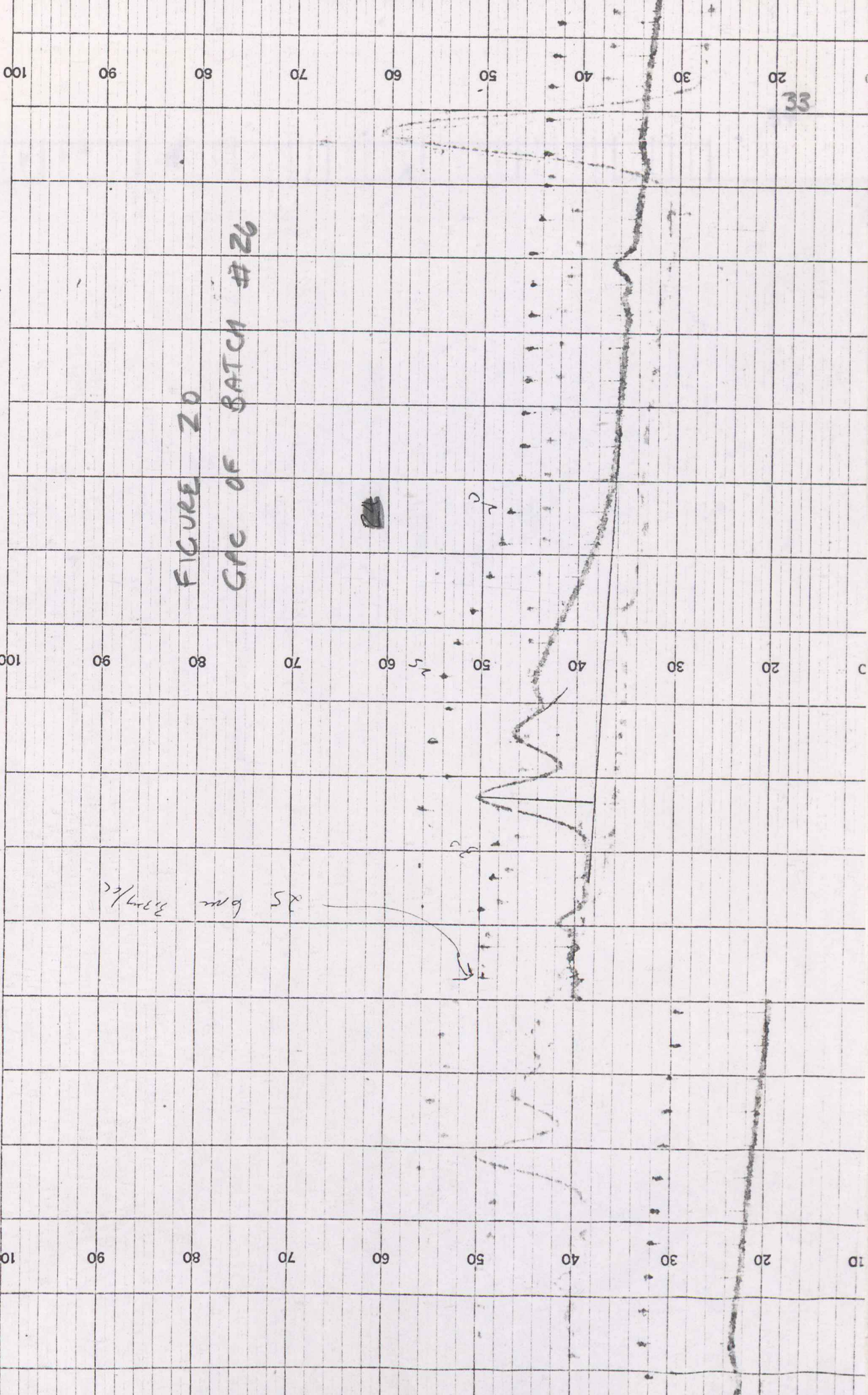
100 90 80 70 60 50 40 30 20 10

FIGURE 19
GPC OF BATCH # 25

25

RETRACT - 121 - G.P. 54, 52 (A250) 58

84
FEET
LEFT



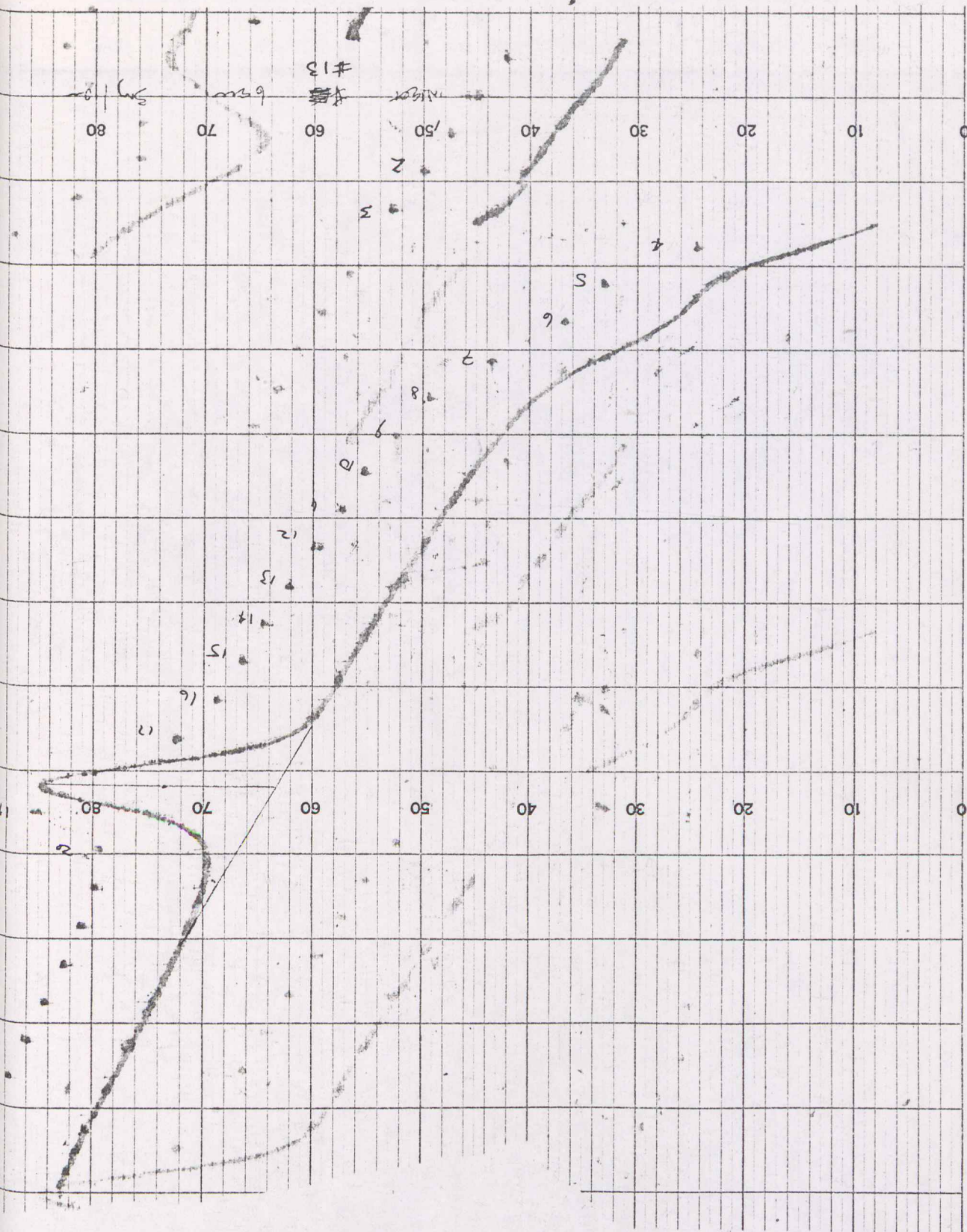
33

FIGURE 20
GPC OF BATCH #26

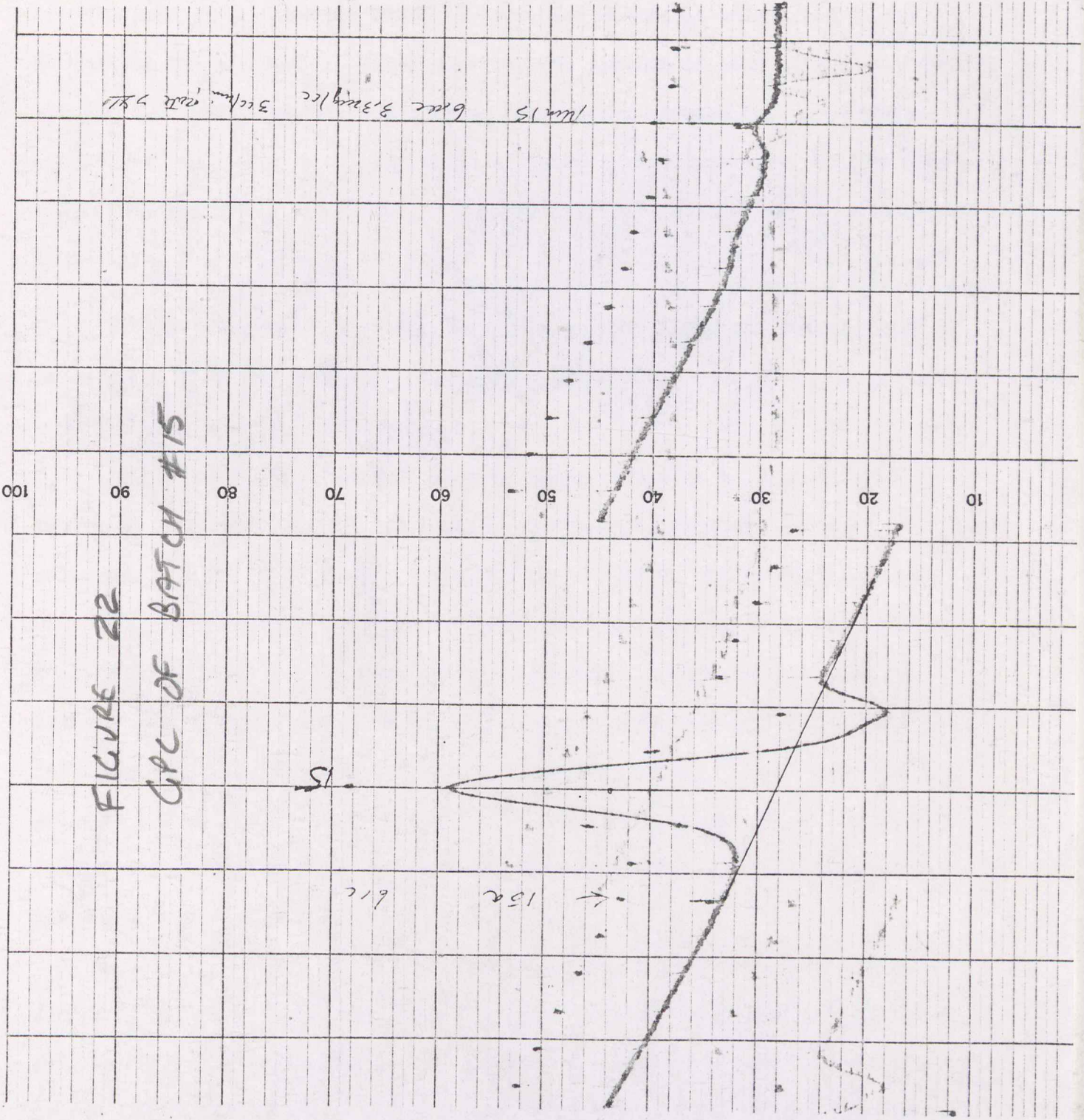
25 b.m. 3.27/60

FEET
LEFT
85

FIGURE 21 GPC OF BATCH #13



FEET
LEFT
89



molecular weight tail. One could conclude that #13 is a mixture of homopolymers and #15 is a copolymer. This is consistent with all previous work.

The rest of the batches were also run, for molecular weight and dispersity as well as the separation. Unfortunately, the problem of peak height difference and the fact that the room temperature homopolymer batches have nearly the same molecular weight made separation of homopolymers (assuming all one to one ratios are mixtures) impossible. The other information obtained is no less important.

Both Differential Scanning Calorimetry and Gel Permeation Chromatography are able to indicate if there is polyB-pinene present. This is the only positive conclusion which can be reached.

May trends can be observed, however. With reference to the appropriate table, it is seen that: At 30° C in methylene dichloride and a one to one molar ratio, the yield and the mole percent styrene in the product increase with increasing catalyst; molecular weight decreases with increasing catalyst concentration; there is decreasing insolubility in acetone with increasing catalyst concentration (as per the increasing styrene content). At a four to one molar ratio of B-pinene to styrene, the insolubility in both solvents is greater; the acetone insoluble portion should have a higher molecular weight (the lower molecular weight polystyrene is washed away) and this is shown by the Vapor Phase Osmometry Molecular Weights.

Further trends can be seen for batches made at -78° C in methylene dichloride: one to one ratios at one percent catalyst do not react; the poly-B-pinene is of much lower yield and molecular weight. Both one to one and one to four molar ratios show increasing yield with increasing catalyst concentration; all one to four batches are completely insoluble; all one to one batches are soluble in hexane. This suggests that the solubility parameter of Batch #13 is lower than Batch #15, thus, #15 is insoluble in hexane, while #13 is totally soluble. The mole percent styrene content in both the crude

#13 is totally soluble. The mole percent styrene content, ^{is constant} in both the crude and insoluble portions of the one to four batches. The molecular weights are generally higher than the batches reacted at room temperature, and the dispersities are lower. Generally, molecular weights of the crude and acetone insoluble portions should be the same.

At -78° C in m-xylene it can be observed that: molecular weights are very low; polystyrene is the lower of the two homopolymers; yields are low in comparison to methylene dichloride work, except for B-pinene, which shows excellent yield in comparison. It appears that the roles of the monomers have been reversed in m-xylene. The low molecular weights and also the possibility that there is m-xylene in the product (chain transfer to solvent) allow for total solubility in both solvents. The molecular weight decreases with increasing catalyst concentration, solubility increases with increasing catalyst concentration.

There is a study of mole percent conversion versus time in progress. It is hoped that the analysis of these kinetic studies (percent styrene of the product which has reacted) will yield information which can be interpreted for or against the formation of copolymer products.

CONCLUSIONS

It is not yet possible to determine copolymer or homopolymer mixture using one instrument. Using the combined information from several instruments, it is only possible to speculate that one is copolymer and one is a mixture- the other eleven batches need further work. Each of the batches has been characterized by M_n (VPO), M_{PEAK} (GPC), d_{4800} , DSC plots, and NMR data has been done on some. Further work on kinetic studies, NMR on crude and solvent washed products will probably lead to definite conclusion about the constituents of each product. Then it might be possible to predict what products will form under different reaction conditions, and ultimately, a further insight into cationic polymerization mechanisms may be gained.

SUGGESTIONS FOR
SUGGESTIONS FOR FUTURE WORK

The NMR analysis of the remaining samples should be done. The role that the solvent plays in the polymerization reaction is an area which could be investigated. Other catalysts might be tried. Other methods for characterization might be tried; thermal gravimetric analysis is available and it might give valuable information regarding the decomposition of the polyB-pinene in the product. Other styrene to B-pinene feed ratios might be tried to determine if there is any limit on copolymerization imposed merely by the feed ratio.

TABLE 2

COPOLYMERIZATION OF B-PINENE AND STYRENE IN METHYLENE DICHLORIDE AT 30° C

RUN	AlCl ₃	FEED RATIO	YIELD (WT%)	MOLE % STYRENE (GPC PEAK)	WT% INSOLUBLE (ACETONE)	MOLE % STYRENE (ACETONE INSOLUBLE) NMR GPC	WT % INSOLUBLE (HEXANE)	MOLE % STYRENE (HEXANE INSOLUBLE) NMR GPC
6	1.0	styrene	100					
9	1.0	B-pinene	62					
3	0.5	1:1	66	20	100	20	20	0
4	1.0	1:1	82	40	84	34	40	1
7A	5.0	1:1	92	40	64	43	40	2
10	1.0	1:4	85	60	68	67	60	83
								74

Mole 5 styrene (GPC peak) is estimated from peak height graph (Figure 3)

TABLE 3

COPOLYMERIZATION OF B-PINENE AND STYRENE IN METHYLENE DICHLORIDE AT -78° C

RUN	AlCl ₃	FEED RATIO	YIELD (WT%)	MOLE % STYRENE (GPC PEAK)	WT% INSOLUBLE (ACETONE)	MOLE % STYRENE (ACETONE INSOLUBLE) NMR	WT% INSOLUBLE (HEXANE)	MOLE % STYRENE (HEXANE INSOLUBLE) NMR	GPC
17	5.0	styrene	100						
16	5.0	B-pinene	23						
19	5.0	B-pinene	33						
12	1.0	1:1	0						
14	1.0	1:1	0						
18	1.0	1:4	93	70	99	72	100		70
13	5.0	1:1	94	40	100	36	2		
15	5.0	1:4	100	70	98	63	98		70

Mole % styrene (GPC peak) is estimated from peak height graph (Figure 3)

TABLE 4

COPOLYMERIZATION OF B-PINENE AND STYRENE IN m-XYLENE AT -78°C

RUN	AlCl ₃	FEED RATIO	YIELD (WT%)	WT % INSOLUBLE IN ACETONE	WT % INSOLUBLE IN HEXANE
26	5.0	styrene	79		
25	5.0	B-pinene	84		
24	5.0	1:1	71	0	0
23	5.0	1:4	59	0	0
28	1.0	1:1	LOW	3	7
27	1.0	1:4	LOW	31	66

TABLE 5

MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION
 FOR THE COPOLYMERIZATION OF B-PINENE AND STYRENE
 IN METHYLENE DICHLORIDE AT 30°C

RUN	AlCl ₃	FEED RATIO	CRUDE POLYMER		ACETONE INSOLUBLE	
			M _n (VPO)	M _{PEAK} (GPC)	M _n (VPO)	M _{PEAK} (GPC)
6	1.0	styrene	3500	9200	3000	8000
9	1.0	B-pinene	3200	4500	3700	8200
3	0.5	1:1	3100	9200	3000	8000
4	1.0	1:1	3700	7000	3700	8200
7A	5.0	1:1	1900	7000	3500	6600
10	1.0	1:4	3600	9500	6000	10,000

d4800

1.6

3.4

1.5

1.6

1.8

1.6

1.3

TABLE 6

MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION
FOR THE COPOLYMERIZATION OF STYRENE AND B-PINENE
IN METHYLENE DICHLORIDE AT -78° C

RUN	AlCl ₃	FEED RATIO	CRUDE POLYMER		ACETONE INSOLUBLE		HEXANE INSOLUBLE		
			Mn (VPO)	M _{PEAK} (GPC)	Mn (VPO)	M _{PEAK} (GPC)	Mn (VPO)	M _{PEAK} (GPC)	
17	5.0	styrene	18000	35000	2.4				
16	5.0	B-pinene	1800	4500	4.2				
19	5.0	B-pinene	2800	7800	1.7				
13	1.0	1:1	6500	11500	1.6	6400	110500	1.6	
18	1.0	1:4	15500	17000	1.4	12000	17000	1.6	
15	5.0	1:4	8600	17000	1.4	8100	17000	1.5	
								21000	1.6
								17000	1.6

TABLE 7

MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION
FOR THE COPOLYMERIZATION OF STYRENE AND B-PINENE

IN *m*-XYLENE AT -78° C

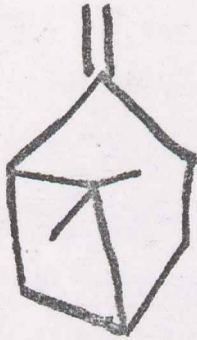
RUN	AlCl ₃	FEED RATIO	CRUDE POLYMER		d ₄₈₀₀
			Mn (VPO)	M _{PEAK} (GPC)	
26	5.0	styrene	370	320	1.1
				530	1.7
				700	BROAD
25	5.0	B-pinene	3900	9000	1.2
24	5.0	1:1	700	3500	4.5
23	5.0	1:4	500	190	5.1
				310	
				1050	
28	1.0	1:1	450	24000	1.8
27	1.0	1:4	2600	11000	1.8

TABLE 8

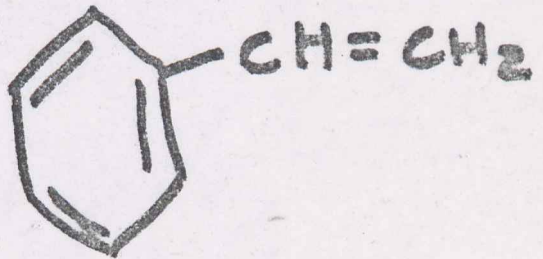
DIFFERENTIAL SCANNING CALORIMETRY PRIMARY INFLECTION POINTS (°C)

RUN	FEED	EXOTHERM	MELT	DECOMPOSITION
16	<u>B</u> -pinene	61-108	138	145
17	styrene	none	137-193	
16&17	mix	70	129-146	155
9	<u>B</u> -pinene	70-111	145	153
6	styrene	84-132	132, 190	
9&6	mix	84-122	136	140
15	1:4		109-175	
15A			125-180	
15H			107-171	140
18	1:4	115	132-167	
18A			112-118	
18H			62-182	124
13	1:1	83-116	165	182
3	1:1	81-130	142	142
4	1:1	87-112	156-166&172-176	
7A	1:1	83-113	162	
8	1:1	66-99	136	138
10	1:4	70-89	103-142	
11	1:4	72-106	148	155

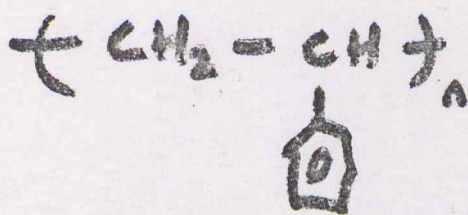
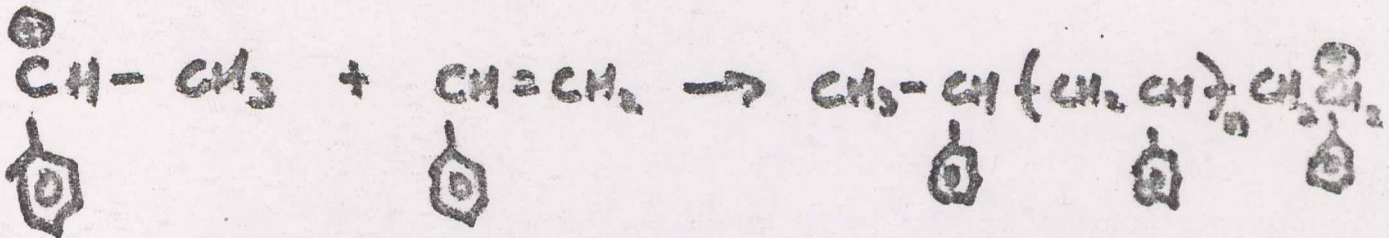
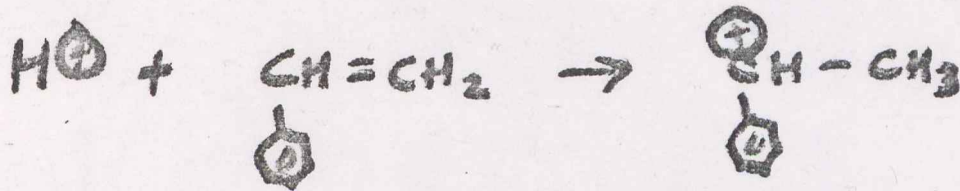
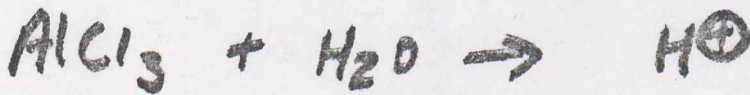
APPENDIX A



β -PINENE



STYRENE



STYRENE REPEAT UNIT



β -PINENE REPEAT UNITS

APPENDIX B

CALIBRATION CONDITIONS FOR THE WATERS GPC/ALC 301

SOLVENT: Toluene

TEMPERATURE: Room ambient

COLUMNS: One coarse, one medium, three fine

FLOW RATE: 3.71 ml/minute Pump at 99.0

STANDARDS USED:	M _{PEAK}	ELUTION VOLUMES (One unit = 5 ml)
	50000	17.30
	34500	17.48
	19750	18.06
	10000	18.32
	4800	19.12
	3900	20.80
	2020	21.62
	1220	22.90
	790	24.76
BENZIL = 210		30.70

All inject times were for 6 seconds at a concentration of 3.33mg/ml

FOOTNOTES

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