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HYDROCARBON POLYMERIC BINDER FOR ADVANCED SOLID PROPELLANT

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TECHNICAL CONTENT STATEMENT

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I. OBJECTIVE

Union Carbide Corporation, Chemicals and Plastics Operations Division has agreed to assist the Jet Propulsion Laboratory, California Institute of Technology, on a level of effort basis, in the development of a new or improved polymeric binder for advanced solid propellant grains. The general objectives are described in Quarterly Report No. 1.

II. ABSTRACT

Gel Permeation Chromatography (G.P.C.) was used to determine the molecular weight distributions in hydroxy-telechelic polyisoprene samples A, B, C and D. The molecular weight distributions were monomodal and narrow with the polydispersity index, \bar{A}_w/\bar{A}_n , increasing with molecular weight from 1.5 at a \bar{M}_n of 1200 up to about 2.0 at a molecular weight of 2900. A very good correlation was obtained between the values of \bar{A}_n determined by GPC and \bar{M}_n values determined by vapor pressure osmometry.

Various experimental factors were examined to determine the source of difficulty in an isoprene polymerization in the 5-gallon reactor which gave a non-uniform product of low functionality. It was concluded that process improvements relating to initiator and monomer purity were desirable, but that the main difficulty was in the initiator feed system. A new pumping system was installed and an analog simulation of the reactor, feed system and initiator decomposition kinetics was devised which permits the selection of initial initiator concentrations and feed rates to use to give a nearly uniform initiator concentration throughout a polymerization run. An isoprene polymerization was run in which the process improvements were implemented. This run resulted in the preparation of an ester telechelic polyisoprene of 2290 \bar{M}_n having an average functionality of $1.98 \pm .02$.

III. SCOPE

The scope of our program remains as previously outlined.

IV. INTRODUCTION

In our previous reports we outlined the preparation and discussed the characterization of four samples of hydroxy-telechelic polyisoprene - samples A, B, C and D. In this report we show the results obtained when these products were analyzed by Gel Permeation Chromatography to determine their molecular weight distribution. In addition to the utility of this analytical tool to characterize the molecular weight distribution in binder prepolymers, evidence is presented which indicates that, once calibrated for a given polymer, GPC may give a more consistently reliable determination of \bar{M}_n than vapor pressure osmometry.

Additional isoprene polymerizations in the 5-gallon stirred autoclave reactor are also described in the report.

V. TECHNICAL DISCUSSION

A. Molecular Weight Distributions of Hydroxy-Telechelic Polyisoprene by Gel Permeation Chromatography

In a previous quarterly report⁽¹⁾ we described the use of Gel Permeation Chromatography (GPC) to determine the molecular weight distribution of 29-EMS-72, a hydroxy-telechelic hydrogenated polyisoprene previously submitted to JPL for evaluation. In the section to follow, we report the use of the same technique to analyze four previously reported hydroxy-telechelic polyisoprenes^(1,2).

1. A. C. Ashcraft, J. E. Potts, E. M. Sullivan, E. W. Wise, "Saturated Hydrocarbon Polymeric Binder for Advanced Solid Propellant", Quarterly Report, August 1, 1970, to October 31, 1970.
 2. ibid, November 1, 1970 to January 31, 1971.
- 5

Using the same GPC system discussed in our previous reports, chromatograms were run on samples A, B, C and D. After correction for baseline drift and normalizing to the same height at the peak maximum, the results shown in Figures 1, 3, 5 and 7 were obtained. These chromatograms were then transformed to integral molecular weight distribution curves using the calibration curve and mathematical methods previously reported, with the results shown in Figures 2, 4, 6 and 8.

Table I summarizes the numerical results obtained. Note that Sample A, the only product made in a batch type reactor, has a broader molecular weight distribution than the others, all prepared in a continuous reactor. This is best seen in the \bar{A}_w/\bar{A}_n ratio.

In Figure 9, \bar{M}_n is shown plotted against \bar{A}_n for each of the four samples.

Note that with the exception of sample A, the points lie close to a straight line corresponding to the equation.

$$\bar{M}_n = Q \times \bar{A}_n, \quad \text{where } Q = 25.7$$

This is to be expected, since the number average molecular weight should correlate linearly with the number average chain length. To the extent that \bar{A}_n actually represents* the number average chain length, we may use GPC determined \bar{A}_n values to calculate \bar{M}_n , once the constant Q has been determined.

*The accuracy of \bar{A}_n as a measure of the number average chain length is primarily limited by two considerations:

- a. Constancy of the differential refractometer detector response as the molecular weight of the eluate varies.
- b. Applicability of the calibration curve of extended chain length versus retention volume determined using polystyrene standard samples of known molecular weight and narrow molecular weight distribution.

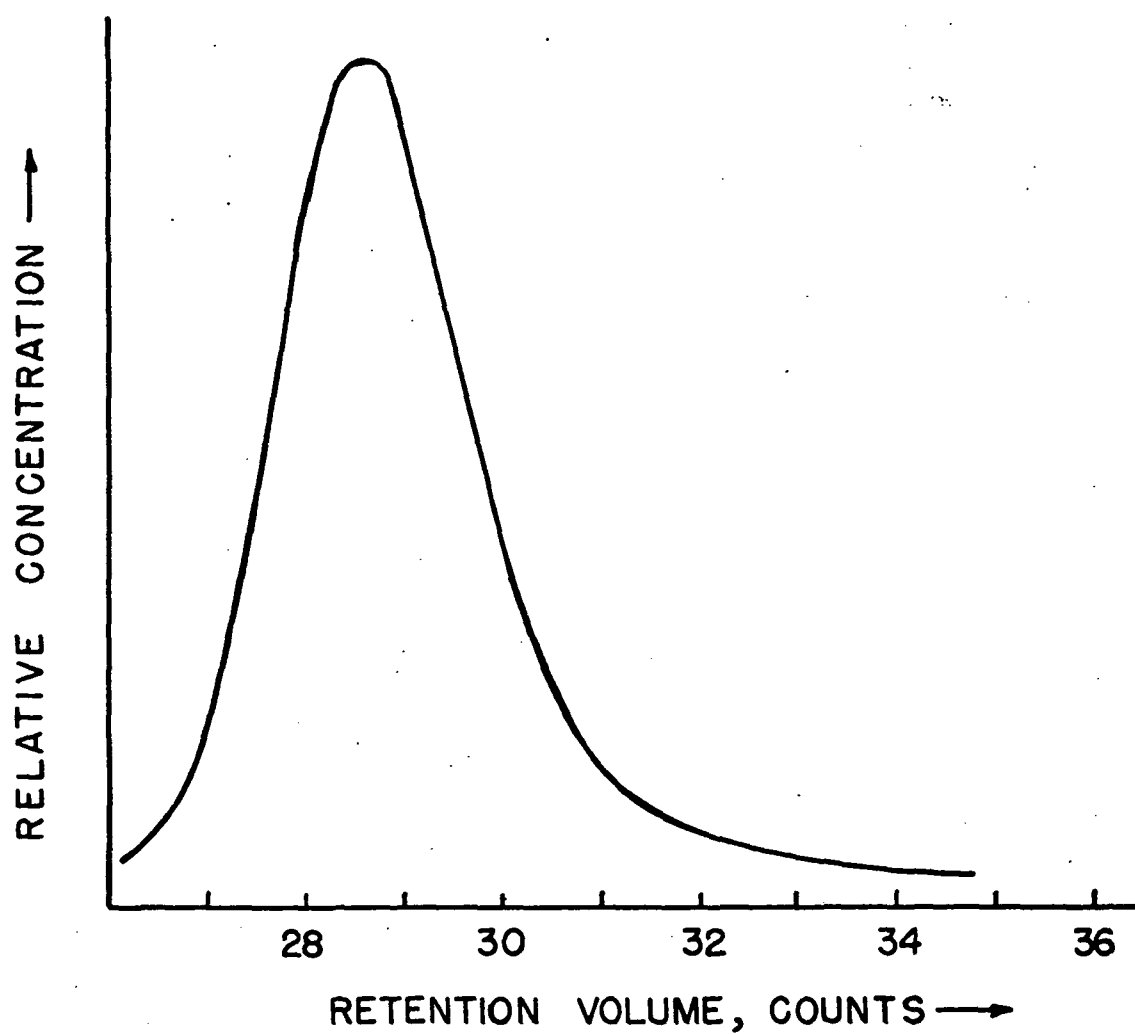


FIG. 1. BASELINE-CORRECTED GEL PERMEATION CHROMATOGRAM OF SAMPLE A

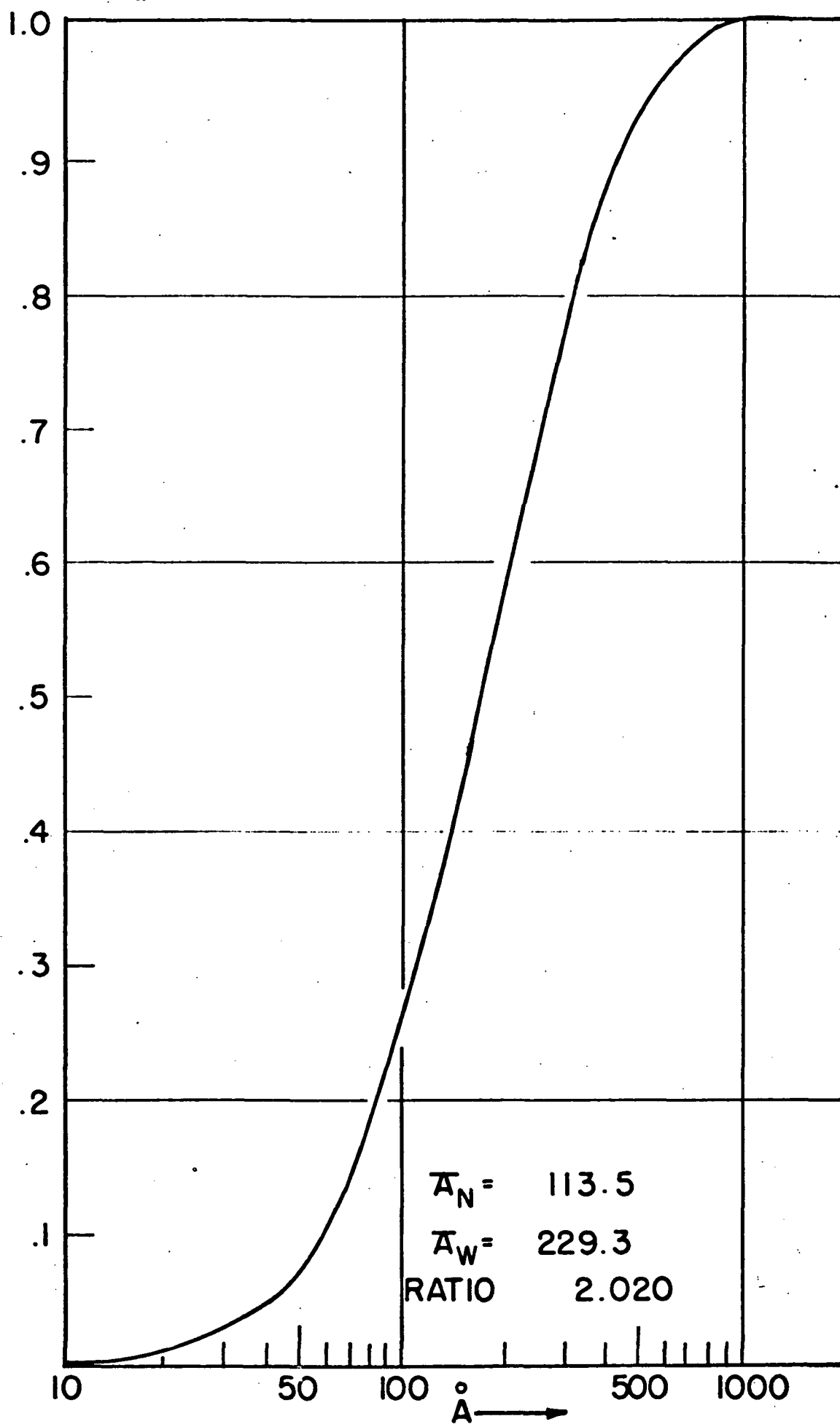
FRACTION OF TOTAL POLYMER \longrightarrow 

FIG. 2-INTEGRAL CHAIN LENGTH DISTRIBUTION, SAMPLE A

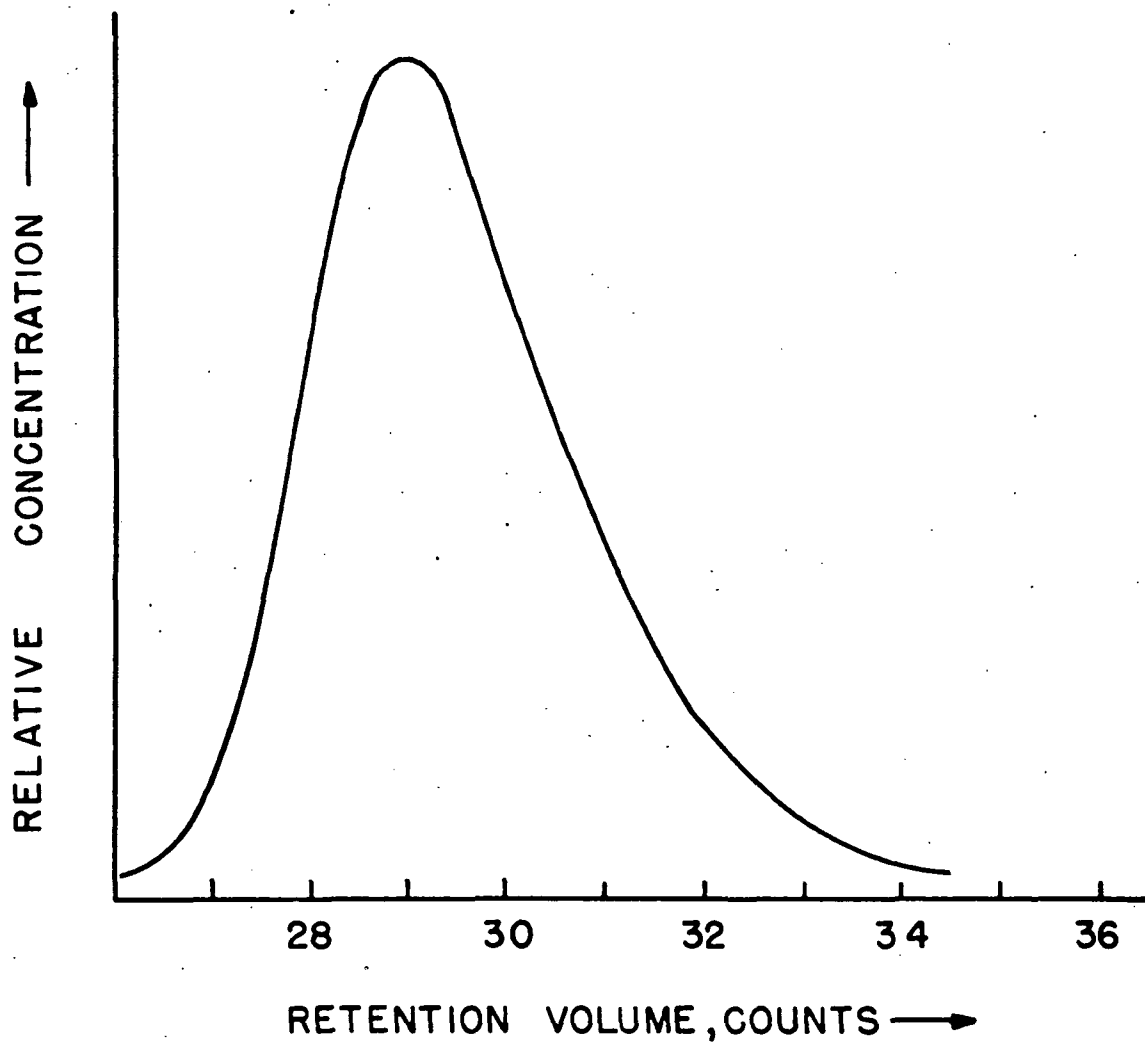


FIG. 3. BASELINE-CORRECTED GEL PERMEATION CHROMATOGRAM OF SAMPLE B

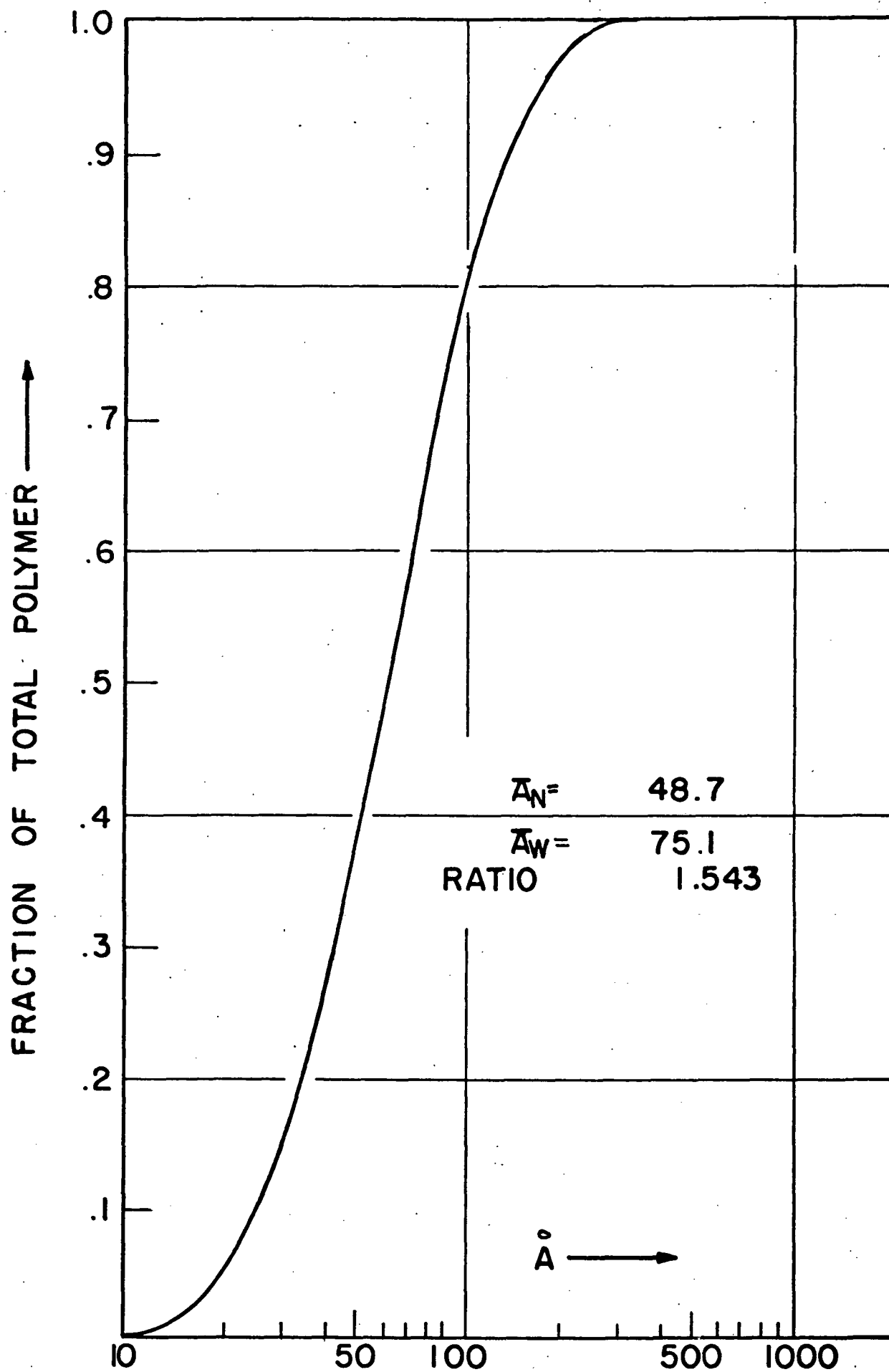


FIG.4-INTEGRAL CHAIN LENGTH DISTRIBUTION

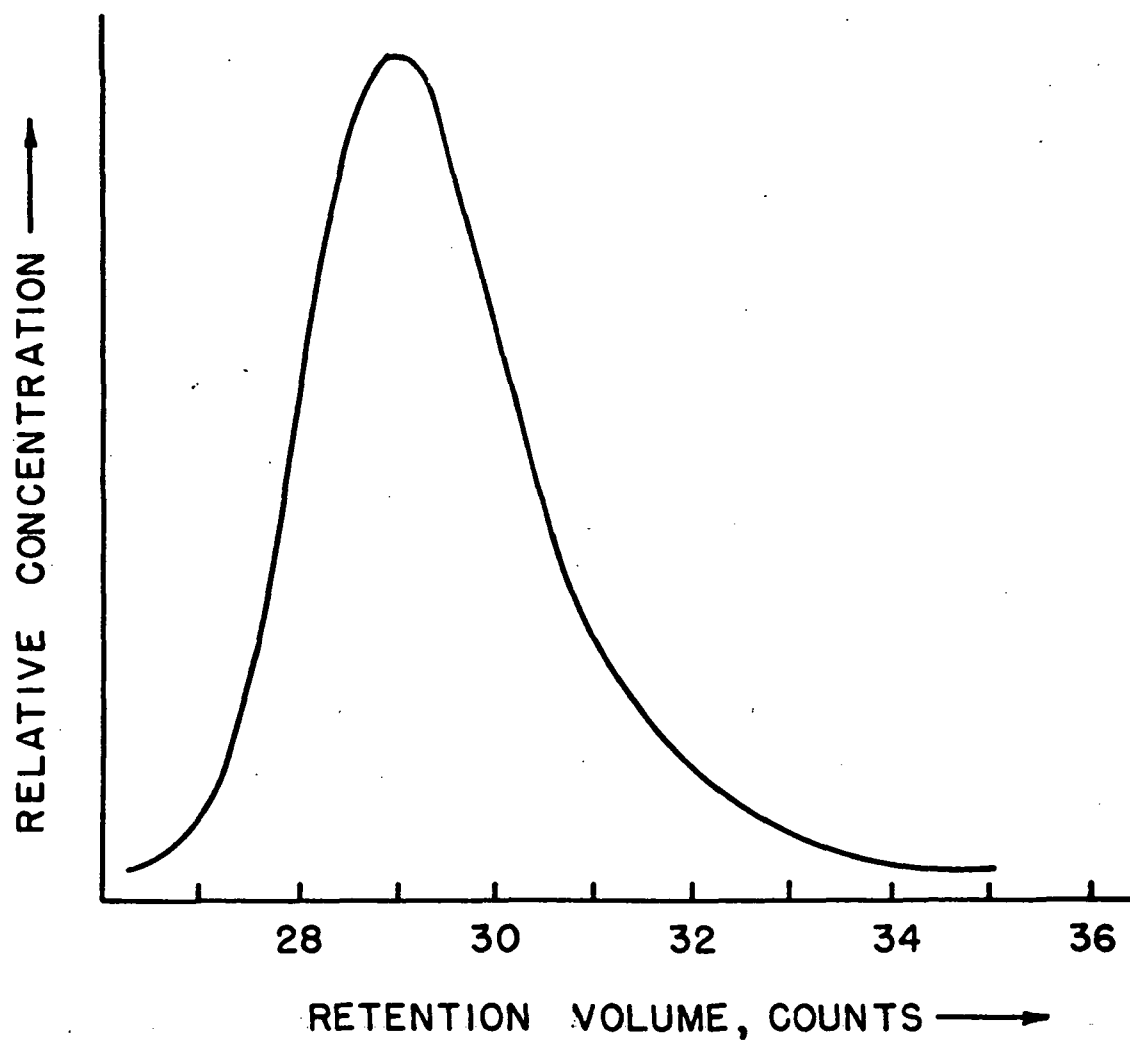


FIG. 5: BASELINE - CORRECTED GEL PERMEATION CHROMATOGRAM OF SAMPLE C

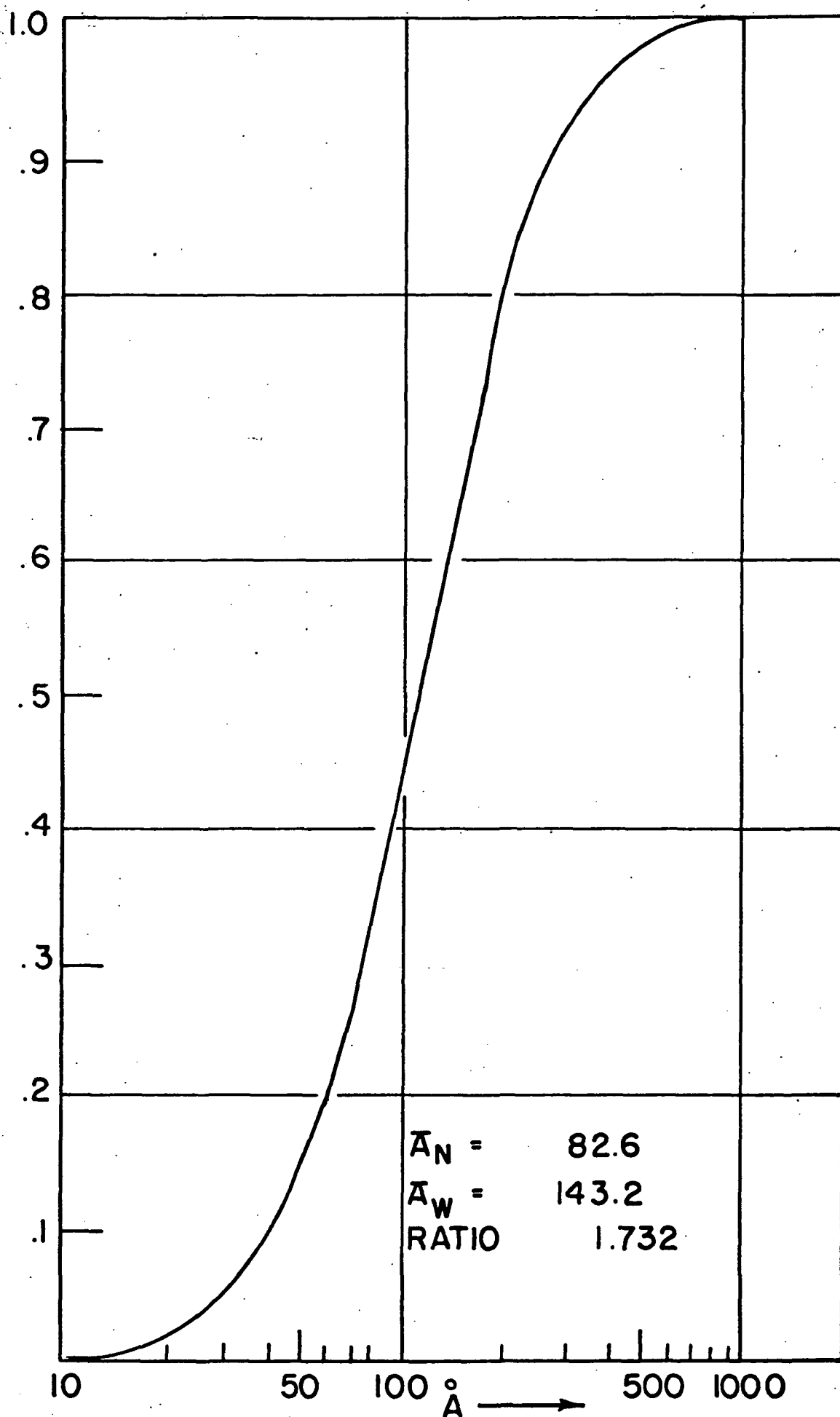
FRACTION OF TOTAL POLYMER \uparrow 

FIG. 6—INTEGRAL CHAIN LENGTH DISTRIBUTION, SAMPLE C

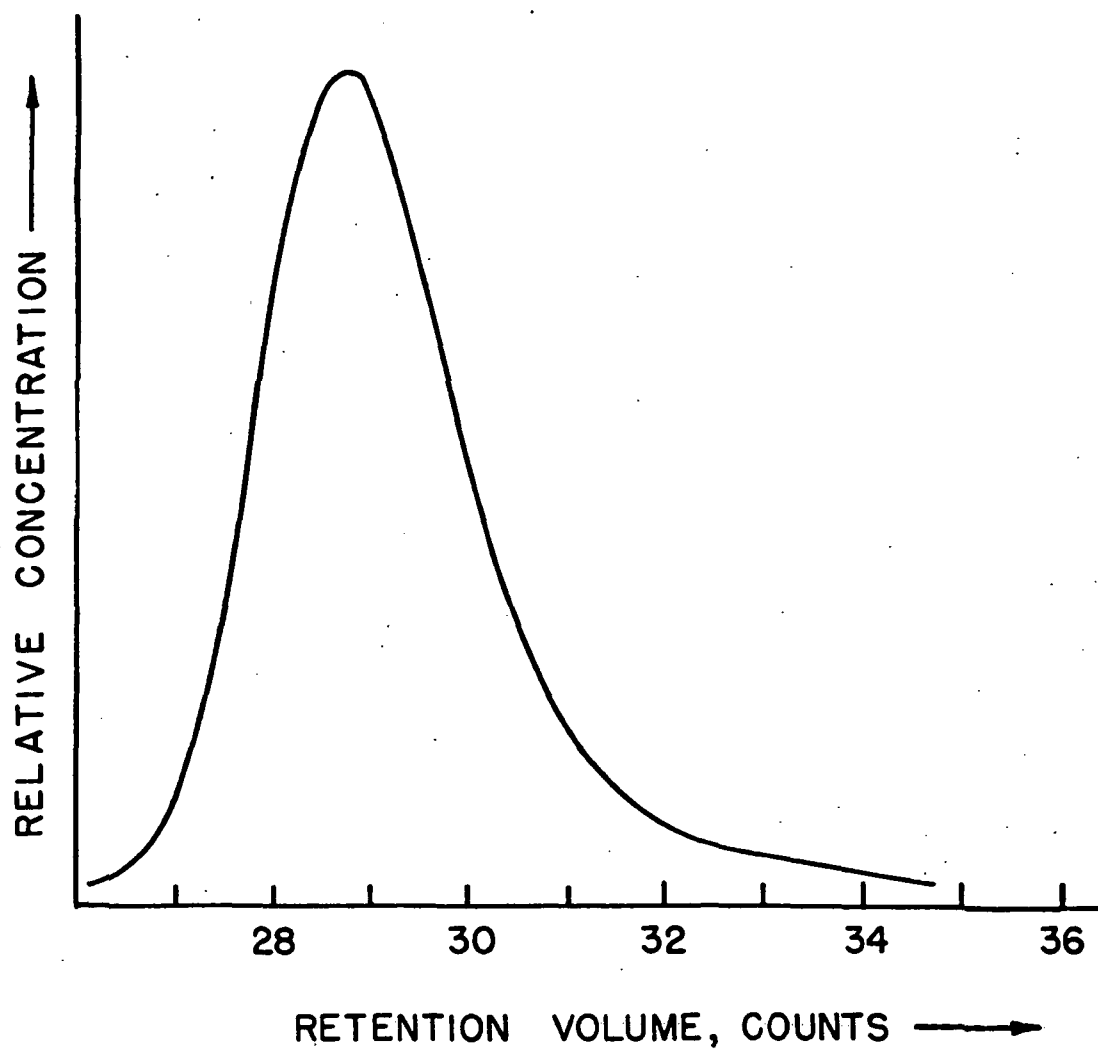


FIG.7. BASELINE - CORRECTED GEL PERMEATION CHROMATOGRAM OF SAMPLE D

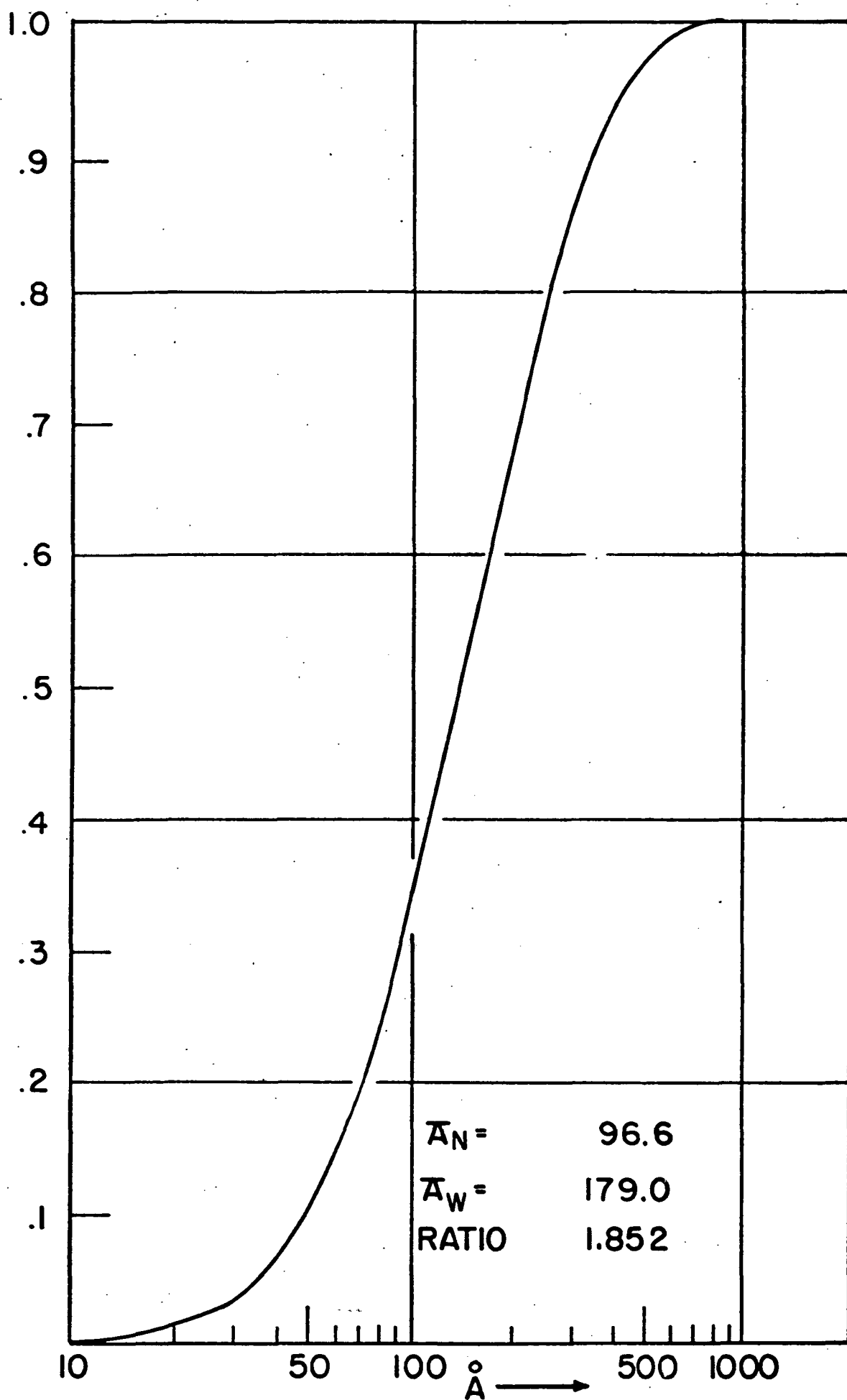
FRACTION OF TOTAL POLYMER \uparrow 

FIG.8-INTEGRAL CHAIN LENGTH DISTRIBUTION,SAMPLE D

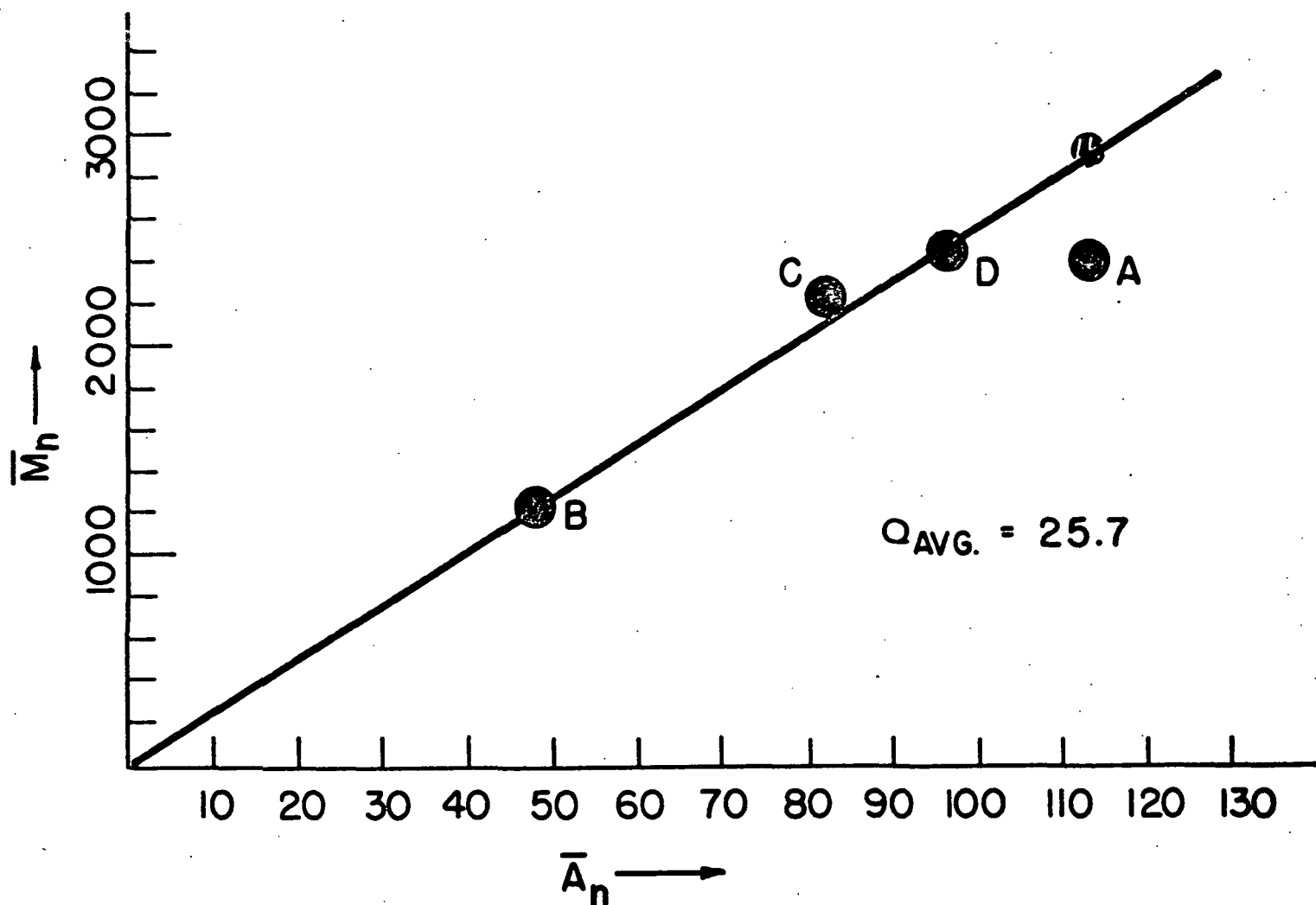


FIG.9 — RELATIONSHIP BETWEEN \bar{M}_n & \bar{A}_n IN HYDROXY-TELECHELIC POLYISOPRENES

TABLE I. NUMERICAL RESULTS, GPC ANALYSIS OF
HYDROXY-TELECHELIC POLYISOPRENE SAMPLES

<u>Sample</u>	<u>\overline{M}_n (a)</u>	<u>\overline{A}_n</u>	<u>\overline{A}_w</u>	<u>$\overline{A}_w/\overline{A}_n$</u>	<u>$Q^{(b)}$</u>
A	2415 \pm 177	113.5	229.3	2.02	21.3
B	1230 \pm 30	48.7	75.1	1.54	25.3
C	2225 \pm 30	82.6	143.2	1.73	26.9
D	2454 \pm 154	96.6	179.0	1.85	25.4

a. Vapor Pressure Osmometry

b. $Q = \overline{M}_n/\overline{A}_n$

These results suggest that the VPO determined value of 2415 ± 177 for the \overline{M}_n of Sample A is in error and that the \overline{M}_n may actually be closer to 2900. If this is the case, Sample A is higher in functionality than we had previously believed (OH equiv. wt. = 1410 by infrared spectroscopic analysis). Because of this possibility we rechecked the molecular weight determination by VPO. When this was done the result shown in Figure 9-A was obtained. With an instrumental calibration factor of 12,800 (determined using pentaerythritol tetrastearate as reference), the intercept of $4.4 \pm .12$ from the V/C vs. C plot gives a value of 2910 ± 80 for the molecular weight of Sample A. This is shown as the half shaded point in Figure 9 and confirms the linear correlation between \overline{M}_n and \overline{A}_n . As further evidence accumulates to support this correlation, Gel Permeation Chromatography may provide a more dependable source of \overline{M}_n data which is not subject to the occasional erratic behavior of the vapor pressure osmometer.

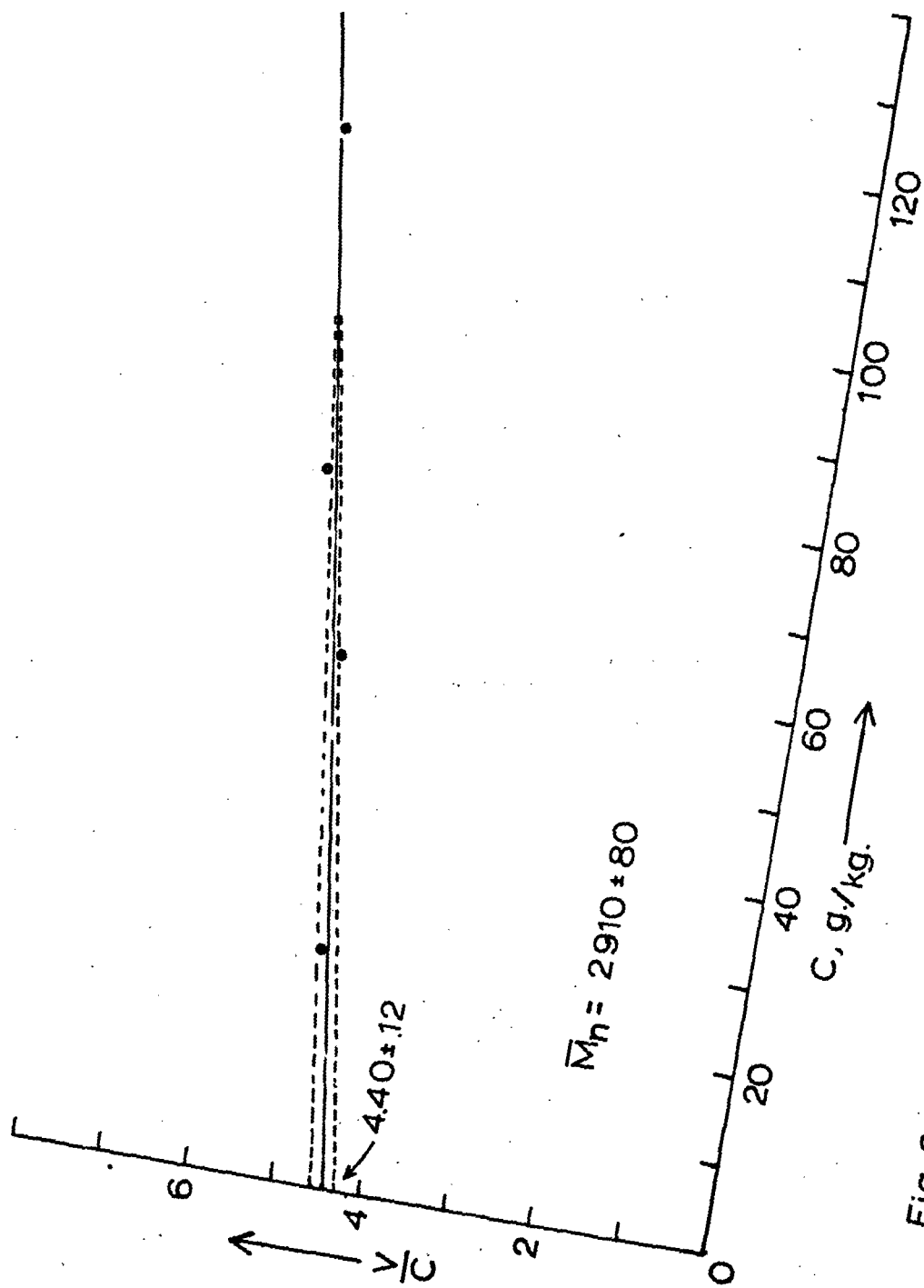


Fig. 9-A V.P.O. Determination of \bar{M}_n , Sample A

3. Preparation Ester-Telechelic Polyisoprene in the 5-Gallon Stirred Autoclave Reactor

In our previous quarterly report we outlined plans to prepare a one-gallon sample of hydroxy-telechelic polyisoprene. This would provide JPL with sufficient material to evaluate the binder prepolymer in propellant formulations on a somewhat larger scale. Our five-gallon batch reactor (previously used to prepare the precursor to "Sample A") can be operated with a ten liter charge of isoprene. At the conversions normally obtained between four and six pounds of ester-telechelic polyisoprene can be prepared in a single run. We considered that two such runs would provide an ample supply of starting material for the preparation of the one-gallon sample of hydroxy-telechelic binder prepolymer described above.

1. Polyisoprene Run No. 9769-CAK-2

The parameters for run 9769-CAK-2 are summarized in Table II. The isoprene was charged to the five-gallon reactor under a nitrogen atmosphere, the port sealed, and the reactor heated with stirring up to 100°C. This required twenty minutes. At this point a pump was started to feed a 10% solution of diethylazobisisobutyrate in benzene into the reactor at a rate of 8.8 ml./min. Over the 4 3/4 hour run, 2500 ml. (containing 250 gms. DEAB) of the solution was fed in. At the end of this time the heat controller was shut off and cooling water used to rapidly lower the temperature of the reactor to 35°C, at which point the contents was discharged into a receiver through the bottom port.

The benzene solvent and unpolymerized isoprene were removed by vacuum evaporation to give 2848 grams colorless hazy liquid polymer having a Brookfield viscosity of 64 poise at 25°C.

Examination of the infrared spectrum of the product disclosed some abnormalities in the 10-13 μ region which contains the C-H "wagging" vibrations associated with double bonds. In a "normal" polyisoprene prepared by free radical polymerization under our conditions the ratio of the vinyl (910 cm^{-1}) to vinylidene (890 cm^{-1}) to trisubstituted double bond (840 cm^{-1}) absorbances are in the ratio of .704 : .930 = 1.00*. However, the spectrum

*Note the extinction coefficient for the trisubstituted C=C absorption is much lower than that for the vinyl and vinylidene. The product actually contains about 90% cis and trans 1-4 polymerized isoprene.

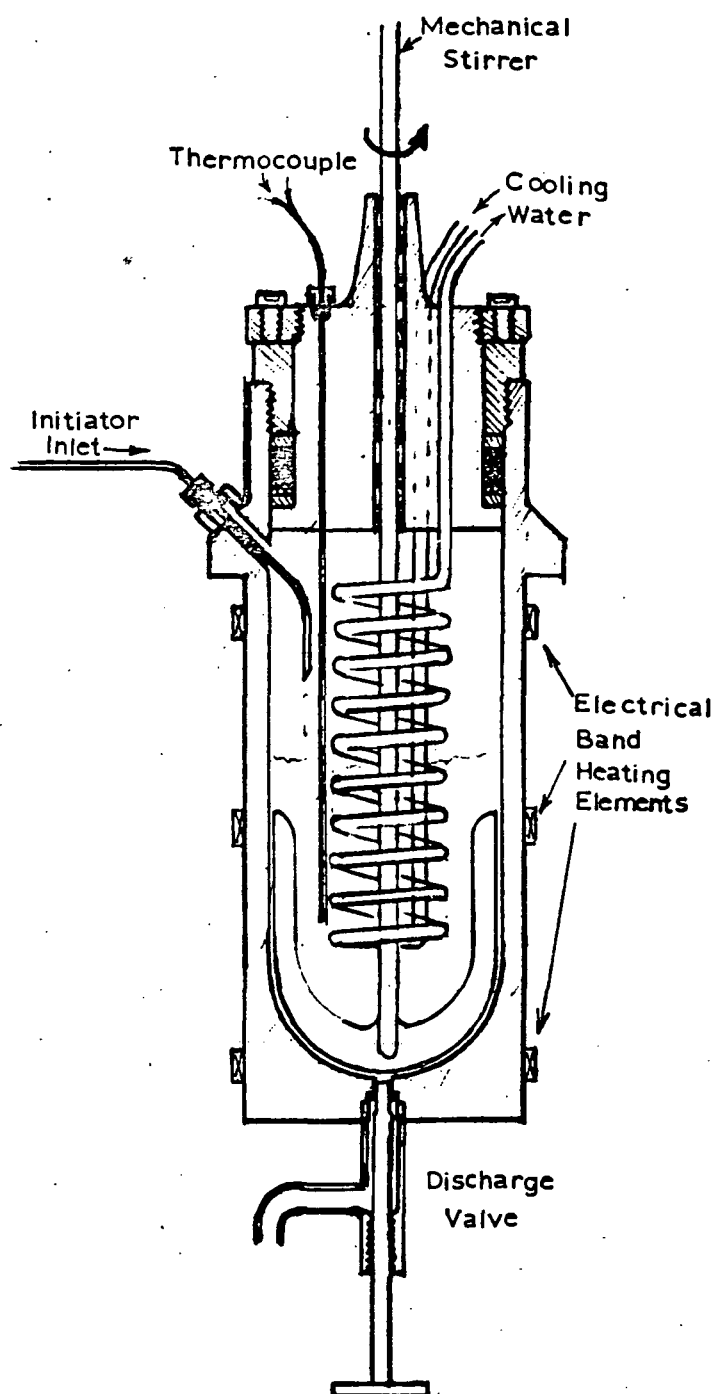


Fig.10.5-Gallon Stirred Autoclave Reactor

TABLE II. POLYISOPRENE RUN NO. 9769-2Charged to Reactor Initially

Isoprene	6860 grams
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Fed During Run

DEAB	250 grams
Benzene	1980 grams

Reaction Conditions

Temperature	99-101°C
Pressure	83-110 psi
Time	4 hours 45 minutes

Productivity

Yield	2848 grams
Conversion	41.2%
Conversion Rate	8.67% per hour

of the product from run 9769-CAK-2 exhibited these absorbances in the ratio of $1.03 = 1.69 : 1.00$, showing a significant enhancement of the 1-2 and 3-4 content as measured by the vinylidene and vinyl absorbances*.

The number average molecular weight of the product from run 9769-CAK-2 was determined by vapor pressure osmometry in toluene at 37°C and found to be 2700 ± 100 . Infrared spectroscopy using ethyl pivalate as a reference standard gave a value of 2150 for the ester equivalent weight. This implies an average functionality of 1.26 ester groups per molecule.

To verify this unexpected result, a small quantity of the product was subjected to lithium aluminum hydride reduction. A solution of 36.5 g. 9769-CAK-2 in 100 ml. abs. ether was added dropwise with stirring to a suspension of 2.1 grams lithium aluminum hydride in 150 ml. abs. ether. After refluxing the mixture for one hour, the excess hydride was decomposed by adding successively 2.1 ml. water, 2.1 ml. 15% NaOH solution and 6.3 ml. water. The clear supernatant ether layer was then decanted, filtered and evaporated to give 28.7 grams colorless oil, showing no ester absorbance in the infrared.

Determination of the hydroxyl equivalent weight by infrared spectroscopy (25% ethyl acetate in CCl_4 used as solvent, reopentyl alcohol used as reference compound) gave the value 2180 g. per equivalent of hydroxyl, quite close to the value 2150 obtained on the ester terminated precursor.

Thin layer chromatography of the hydride reduced product using CH_2Cl_2 as the developing solvent gave a chromatogram showing an elongated streak stretching from the origin of the plate clear up to the solvent front. Under these conditions a difunctional polyisoprene of 2700 molecular weight should show little or no material past $R_f = 0.6$ on the TLC plate.

*This effect is similar to the result noted in a previous experiment, run 8908-CAK-133, in which no DEAB initiator was used at all. The product from this run, the so-called "Thermal-Polyisoprene", was obtained in very low yield ($\sim 7\%$) and was found to be a low molecular weight (~ 700) non-functional polymer. The infrared spectrum showed vinyl to vinylidene to trisubstituted $\text{C}=\text{C}$ absorbances in the ratio of $1.31 : 2.35 : 1.00$.

Two dimensional thin layer chromatography using 2 1/2% ethanol/heptane in the first development, and using acetone in the second development at right angles to the first* gave the interesting result that the polymer contained no monofunctional fraction. The main components were difunctional and non-functional. In addition, the difunctional component showed chromatographic behavior indicative of a very broad molecular weight distribution.

2. Examination of Possible Factors in the Low Functionality Attained in Run 9769-CAK-2

Since none of our previous isoprene polymerizations had yielded products having functionalities appreciably below two, the low ester functionality ($1.26 \pm .04$) measured for the product of run 9769-CAK-2 was interpreted to indicate that something out of the ordinary occurred during the polymerization, either in the way the polymerization was run or in the purity of one of the starting materials. Accordingly we examined each possibility in detail.

a. Monomer Purity

The isoprene used in polymerization run 9769-CAK-2 was Matheson Coleman and Bell, Practical Grade, which had been distilled at atmospheric pressure under nitrogen through a 40" long, 1 1/4" diameter, 32 plate Oldershaw distillation column operated at 100% takeoff. A typical distillation curve is shown in Figure 11.

*A detailed description of the method will be given in a future report.

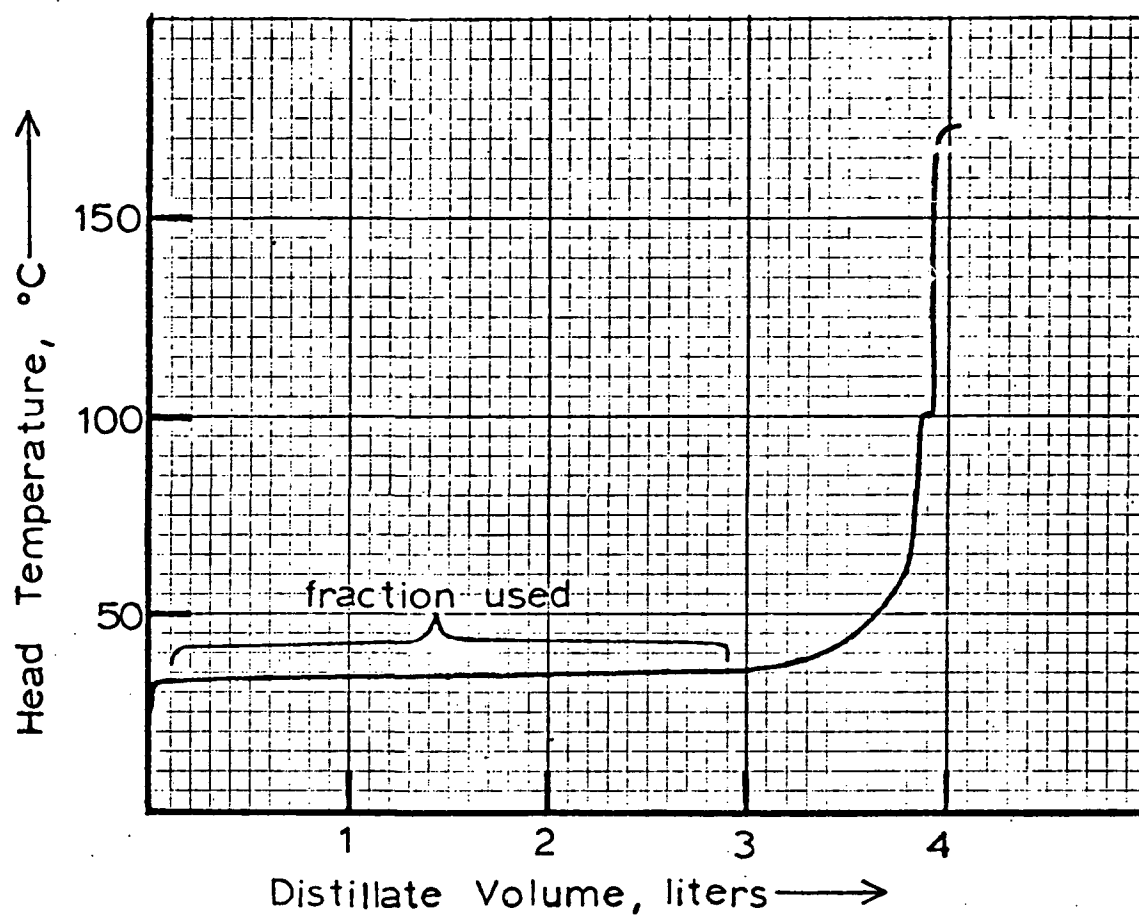


Fig.11. Isoprene Distillation Curve

Gas chromatographic analysis of the fraction distilling over the range 33-35°C gave the result shown in Figure 13*, compared with a similar chromatogram of the starting material in Figure 12. The major impurity in the practical grade isoprene was found to be a higher boiling substance, probably dimeric in nature. Its retention time of 14.2 minutes corresponds to one of the major components in commercial "dipentene" and is probably dl-limonene or a closely related structure. The distillation reduced this component from 5.98% to 0.05%. Two other components of unknown nature were found at 4.7 min. (0.05%) and 6.8 min. (0.25%). The largest impurity in the distilled isoprene was also in the starting material. It had a retention time of 1.1 min. and comprised 0.49% of the starting material and 0.55% of the distilled product. Isoprene comprised 93.23% of the practical grade isoprene and 99.08% of the distilled material used in the polymerization.

When the distillation was run using a reflux ratio of 9:1 (10% takeoff, 90% return to column) it was found that the components of longer retention time than isoprene (C, D, E, F, G, H and I of Figures 12 and 13) could all be eliminated entirely, however, the short retention time component (A) was too close to isoprene in boiling point to be completely separated by distillation. The isoprene obtained in this way was 99.7% purity containing 0.3% of the unknown component "A".

*A Perkin-Elmer Model 990 with hydrogen flame ionization detector coupled to an Infotronics logarithmic attenuator and electronic integrator was used for the analyses. A 2000 cm x 1/8" column of 10% Carbowax 20M on 40/60 Chromosorb T operating at a flow rate of 25 cc/min. gave the required chromatographic separation. The following program was used. Inject 0.2 μ l of sample, operate isothermally for 4 min. at 60°C, program to 175°C at 8°/min., remain at 175°C for duration of chromatogram.

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Fig.12. G.L.C. of M.C.&B. Pract. Isoprene.

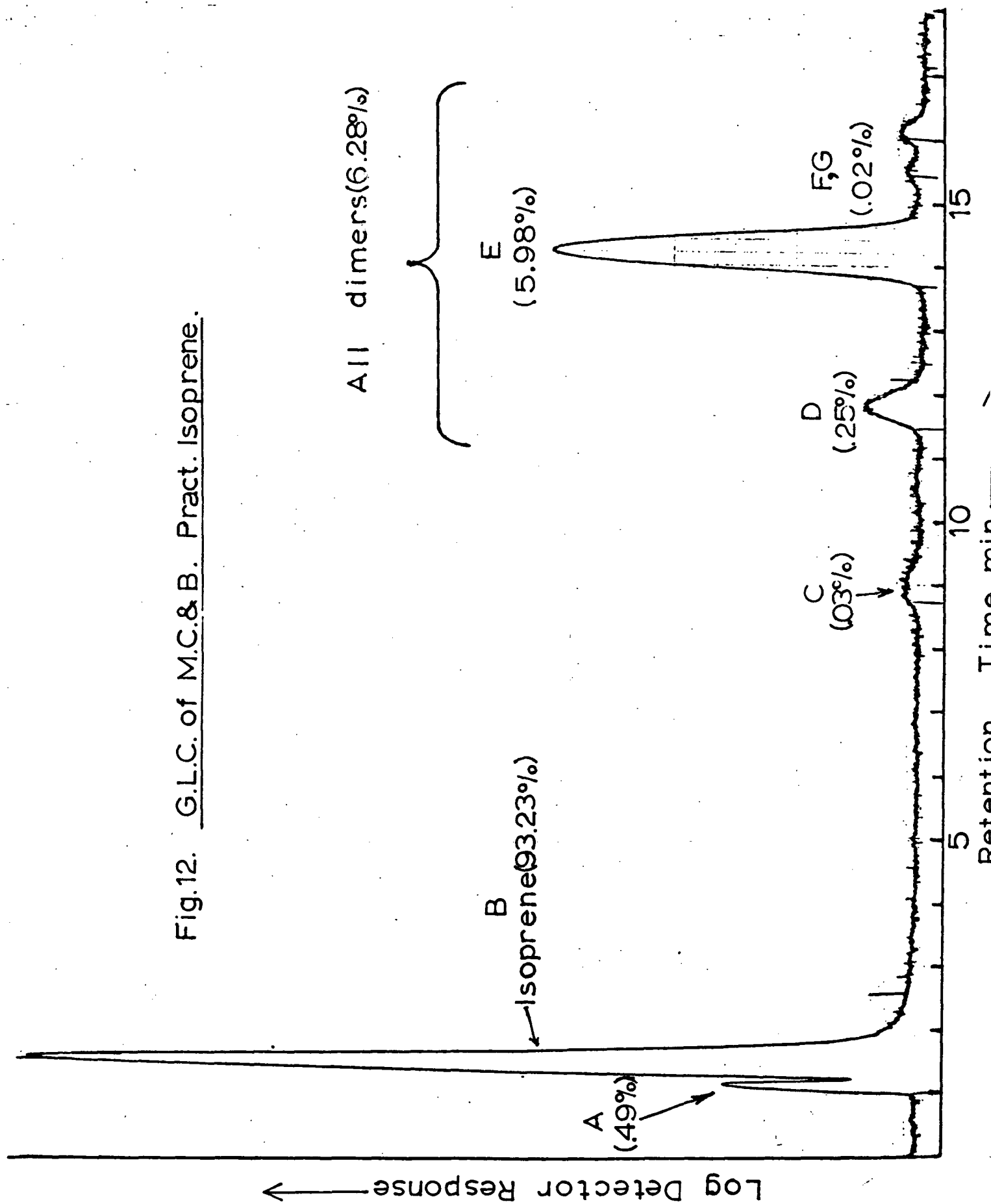
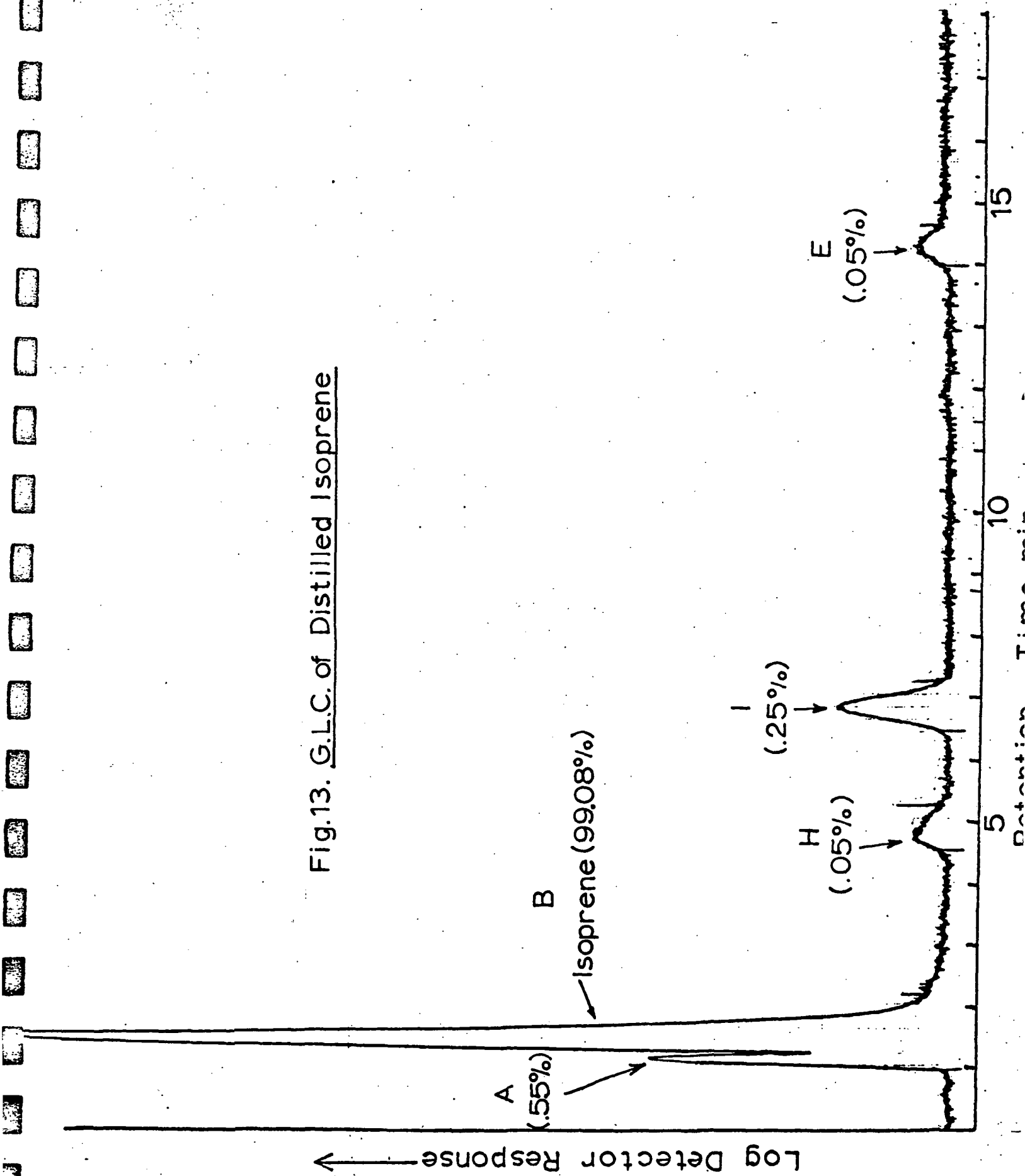


Fig.13. G.L.C. of Distilled Isoprene



When the mass spectrograph was used in conjunction with the gas chromatograph, component A was identified as pentene-2 by its molecular ion at $m/e = 70$ and by its characteristic fragmentation pattern.

In summary, the isoprene used in run 9769-CAK-2 was 99.08% pure and contained 0.05% dimer, 0.55% pentene-2 and 0.30% of two unknown components. A more careful distillation in which a higher reflux ratio was used gave 99.7% pure isoprene containing 0.3% pentene-2 as the sole impurity which should have no effect upon the polymerization.

b. Initiator Purity

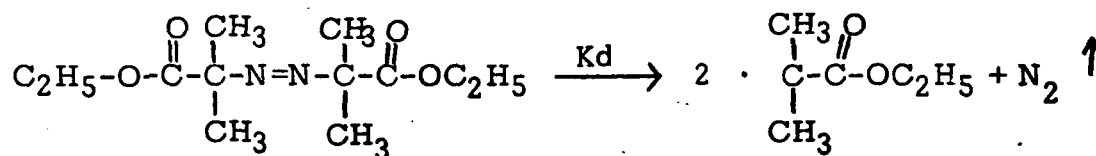
The DEAB used in polymerization 9769-CAK-2 had been prepared March 10, 1969, by treatment of azobisisobutyronitrile with ethanolic HCl and hydrolysis of the resulting iminoether hydrochloride to yield the ester. For details of the preparation see p. 41-42 in our triennial report. Between the preparation in March of 1969 and its use in run 9769-CAK-2 in February of 1971, the DEAB had been stored in a polyethylene carboy, tightly stoppered and placed in a cold room at 0°C.

A sample of the remaining DEAB was taken and analyzed to determine whether deterioration had occurred during the 1 year 11 month storage at 0°C. Melting point analysis showed that the sample was impure - melting commenced at -21°C and was complete at -11°C. A freshly prepared sample of DEAB melts at -10 to -5°C. Comparison of the infrared spectra showed only minor differences, however, chiefly in weak shoulders on major peaks in the spectrum of the DEAB used in run 9247-CAK-2. These weak absorbances were at 1620-1660 cm^{-1} and 940-980 cm^{-1} .

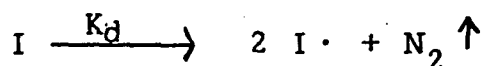
c. Initiator Feed to the Reactor

When the initiator solution feed schedule from run 9769-CAK-2 was examined in detail it was noted that the pumping rate of the Lapp-Diaphragm pump was not constant and required manual correction. Figure 14 shows the rate profile for this run. The dashed line is the desired rate.

The consequences of a variable feed rate of initiator are as follows. DEAB decomposes by the reaction below which follows first order kinetics:



or



where: $\frac{d[I]}{dt} = -K_d [I]$, K_d is the first order rate constant in units of min.^{-1} .

At the same time that the initiator is being destroyed by decomposition to initiator radicals, it is being replenished by the initiator feed into the reactor. This effect upon the initiator concentration is given by:

$$\frac{d[I]}{dt} = K_f$$

where: K_f is the feed rate in $\frac{\text{moles}}{\text{liter-min.}}$

The resultant of these two processes establishes a steady state initiator concentration which is the solution to the differential equation:

$$\frac{d[I]}{dt} = K_f - K_d [I]$$

For the situation in which termination is by recombination of radicals alone, Flory* has derived the relationship between the number average degree of polymerization, \bar{X}_n , and the relative concentrations of initiator and monomer =

$$\bar{X}_n = \frac{K_p}{(fK_dK_t)^{1/2}} \frac{M}{[I]^{1/2}} = C \frac{M}{[I]^{1/2}}$$

where: K_p is the rate of propagation, K_d is the rate of dissociation of initiator and K_t is the rate of recombination of radicals.

We thus see that in order to produce a uniform product with as narrow a molecular weight distribution as possible, the ratio between the monomer concentration and the square root of the initiator concentration must be maintained constant.

*Paul J. Flory, Principles of Polymer Chemistry, p. 133.

What is the effect of an irregular initiator feed rate profile, such as shown in Figure 14, upon the initiator concentration? To answer this question, an analog computer simulation program* was used to provide a model of the polymerization reactor, initiator feed system, and initiator decomposition kinetics. This model will be discussed in detail in a future report. The model allows for an initial programmed heating of the reactor with calculation of the rate of decomposition of the initiator at different temperatures using the Arrhenius equation. In addition, a variable feed rate can be programmed. To simplify the present task, no further chemistry past the point of initiator decomposition was simulated in this model.

The results of an analog simulation of a hypothetical polymerization run are shown in Figure 15. The solid curve gives the feed rate assumed for the run in units of 100 ml. per hour. This feed schedule was chosen so as to exceed the variations normally encountered in our actual polymerizations. In this simulated run, initiator feed commenced at $t = 15$ min., rapidly rose to about 750 ml./hr., decreased to 200 ml./hr., increased to a peak of 1100 ml./hr. and finally stabilized near 700 ml./hr. until the pumping was decreased to zero at the end of the run. The DEAB concentration followed the feed rate, however, it tended to lag behind and showed smoother variations than the feed rate. The quantity D , defined as the reciprocal of the square root of the DEAB concentration, shows an even smaller variation with initiator feed rate. This is shown in Figure 16. Since the quantity D is directly proportional to the degree of polymerization, it is the value of D which is relevant to the molecular weight of the polyisoprene produced at a given point during the run. Thus from $t = 80$ min. to $t = 250$ min. the average molecular weight should vary in proportion to the extremes in the value of D , namely 11 to 13 ($\pm 8\%$ from the mean), rather than in proportion to the extremes in feed rate which varied from 650 to 1100 ml./hr. ($\pm 26\%$ from the mean).

Figure 16 does, however, illustrate the large effect of the low DEAB concentration which was present at the startup of the hypothetical run as well as the effect of stopping feeding the initiator at the end of the run. In our actual polymerization run #9769-CAK-2, the former situation applies since no DEAB was present in the reactor at the beginning of the run. However, the latter situation does not apply since the reactor was cooled and the run terminated at the same time that the feed pump was shut off.

As a result of these studies of the monomer purity, initiator purity and initiator feed rate schedule encountered in run 9769-CAK-2 it was concluded that room for improvement existed in each of the areas examined, but that the

*IBM Continuous System Modeling Program, 1130-CX-13X.

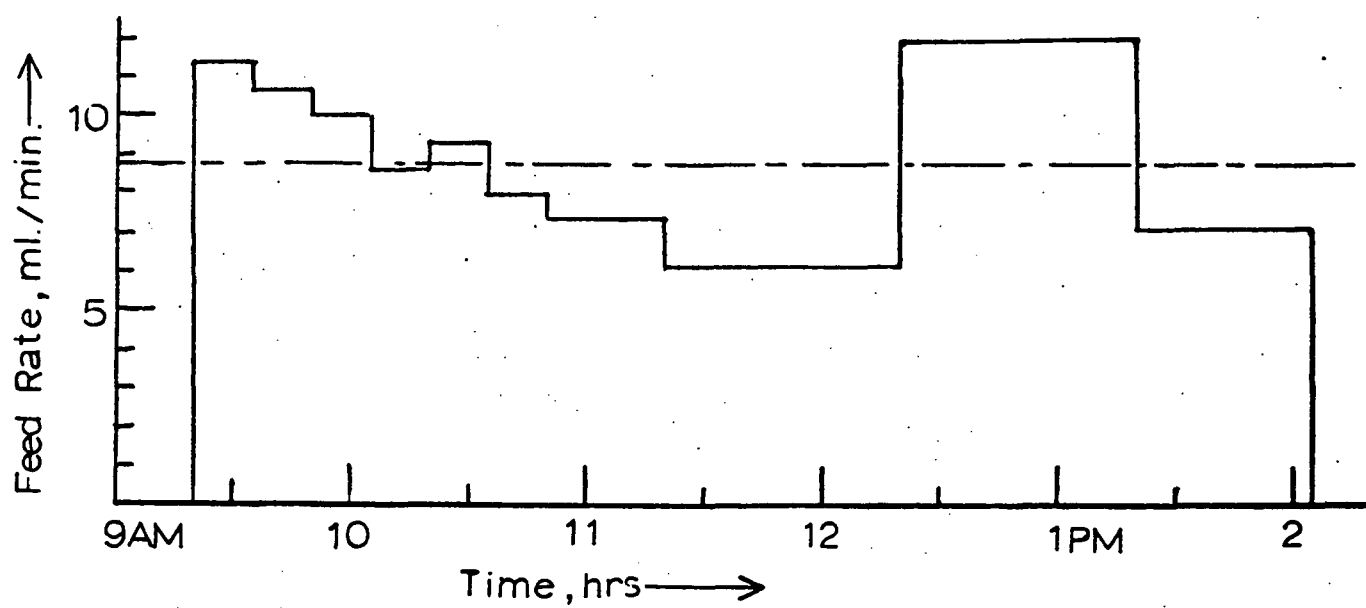


Fig.14. Initiator Feed Rate Profile, Run 9769-CAK-2

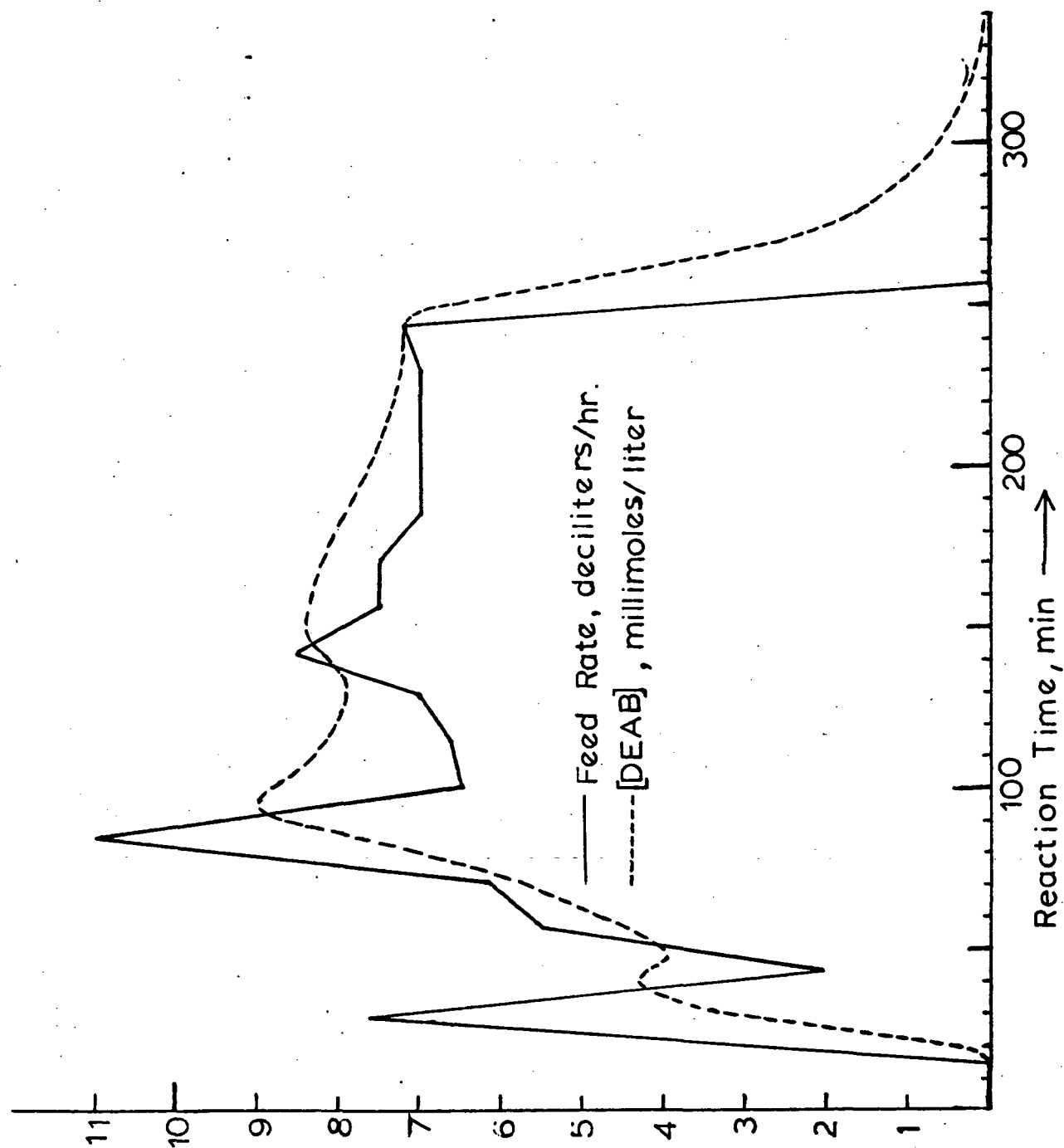


Fig.15. Initiator Concentration vs Feed Rate

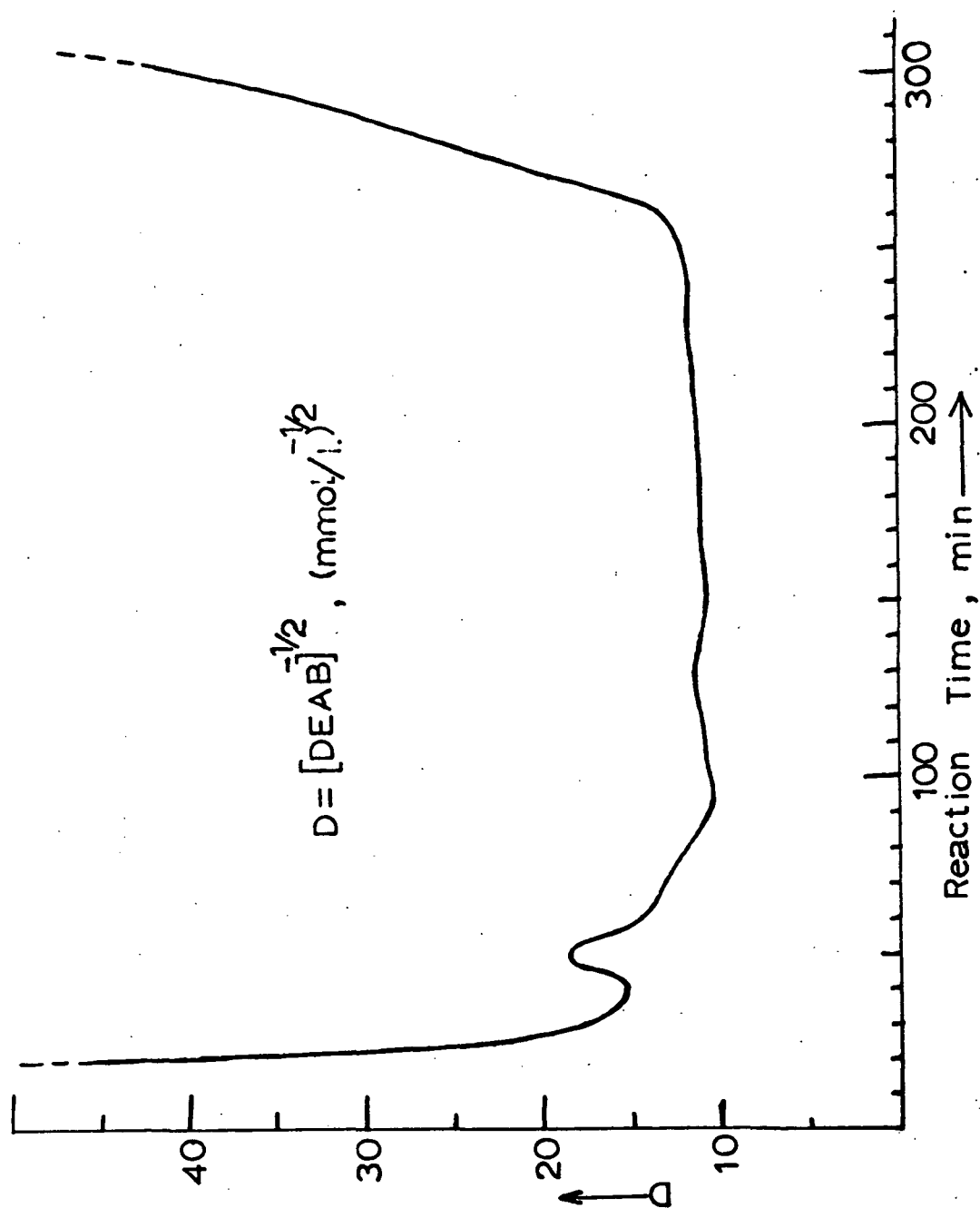


Fig. 16.

most probable cause of the low functionality was related to the non-uniformities of pumping the initiator into the reactor.

It was decided that the following improvements would be put into effect in subsequent isoprene polymerizations:

- a. Modify the initiator feed system to allow a more uniform feed rate.
- b. Optimize the feed rate and initial DEAB concentration to avoid the low DEAB level noted in the beginning of the run in Figure 15.
- c. Use freshly prepared DEAB.
- d. Use a higher reflux ratio in the isoprene distillation to minimize dimer content.

3. Implementation of Process Improvements

a. Change Initiator Feed Pump

The balky pump responsible for the erratic initiator feed rate profile shown in Figure 14 was replaced with a chemical proportioning pump of the constant rate positive piston displacement type*. In this pump a cylinder containing the entire charge of initiator is traversed by a piston driven by an 8-pitch screw powered by a constant rate mechanical drive. The single stroke discharges the 800 ml. contents of the cylinder at a rate which can be set over the range from 0.1 to 12.2 ml. per minute. This allows run times from a little over an hour at the fastest rates to several days at the slower rates.

Since the maximum feed volume is limited in the new pump, we decided to change the DEAB concentration in the feed solution from 10% to 50%.

b. Feed Rate Optimization Using Analog Simulation

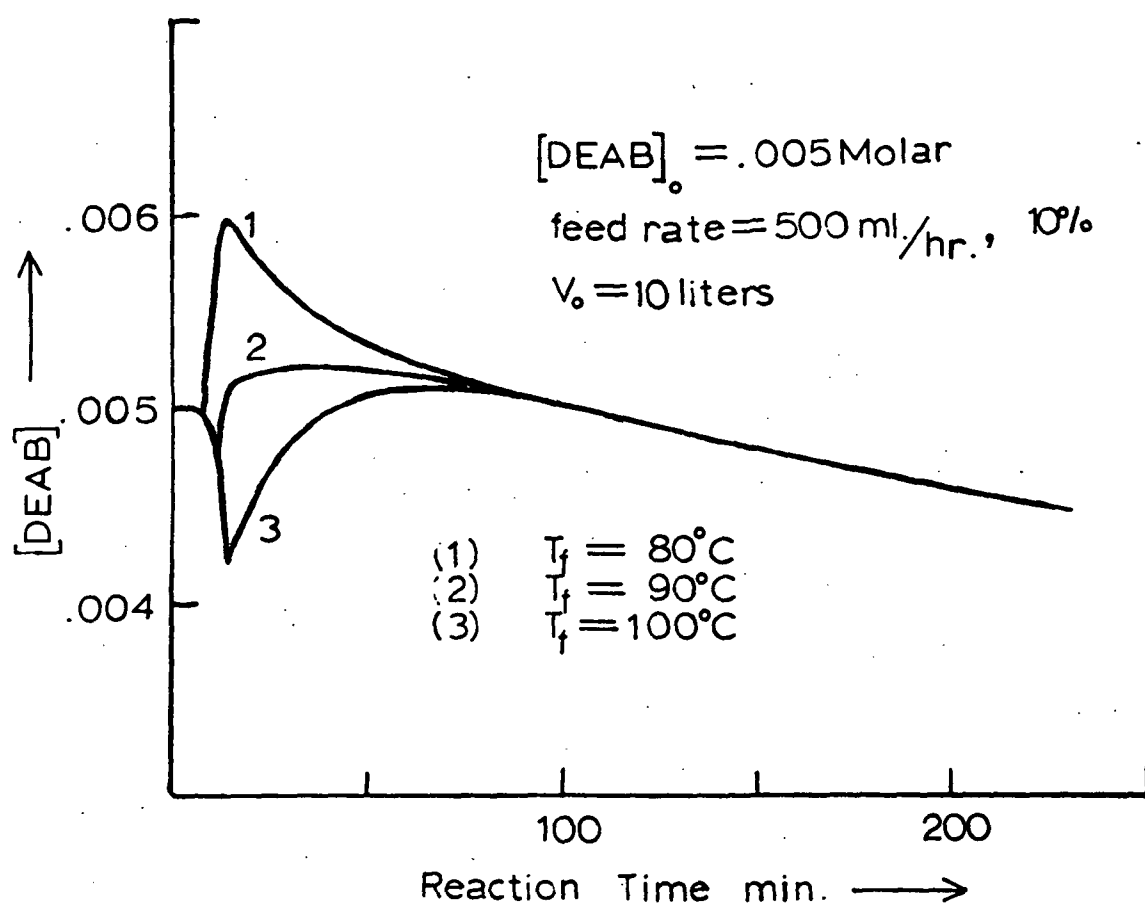
The IBM continuous systems modelling program (CSMP) referred to in section 2-C was used to simulate an analog computer model of the initiator feed system and DEAB decomposition kinetics. This simulation enabled us to determine optimum initial DEAB concentrations as well as feed rate schedules to give a uniform DEAB concentration for the duration of a batch polymerization in the 5-gallon autoclave.

*B-I-F Industries Model 1180-20.

To facilitate the actual use of the results in polymerization runs, a constant rate of feed was selected, commencing when the reactor temperature (determined by a realistic initial heating profile) reached a preselected point. It was found that starting the DEAB feed at a temperature below 80°C resulted in an initial peak in DEAB concentration. This resulted from the low decomposition rate of DEAB at temperatures below 80°C. Conversely, waiting until the reaction temperature had reached the operating temperature of 100°C resulted in an initiator starved condition early in the run. This was caused by the decomposition of the initially charged DEAB before feed was started. A good compromise was achieved when the feed was started at 90°C. Figure 17 illustrates this effect for pumping a 10% solution of DEAB into a 10 liter initial volume at a rate of 500 ml./hr. In these simulated runs the initial DEAB concentration $[\text{DEAB}]_0$ was set at 0.005 M. Note that after 80 minutes pumping all three runs converged to the same initiator level.

To determine the optimum feed rate and initial concentration to achieve a given initiator concentration profile, a series of simulated runs were made on the computer using feed rates of 100, 200, 300, 400, 800 and 1200 ml./hr. of 50% DEAB solution. In all runs pumping was started when the reactor temperature reached 90°C. The initial DEAB concentration for each run was determined by trial and error for the 200 ml./hr. run and merely scaled up or down to provide an appropriate starting point for the other runs. The result of these simulated runs is given in Figure 18 and the data summarized in Table III. In Figure 19 is shown the virtually linear relationship between $[\text{DEAB}]_m$, the initiator concentration at the mid point of a run (after 400 ml. had been fed in), and the initiator feed rate.

These results allow selection of feed schedules appropriate for the production of uniform polymer of any desired molecular weight, once the constant of proportionality between $[\text{DEAB}]_m^{-1/2}$ and \bar{M}_n is determined.

Fig.17. Effect of T_f Upon Initiator Level.

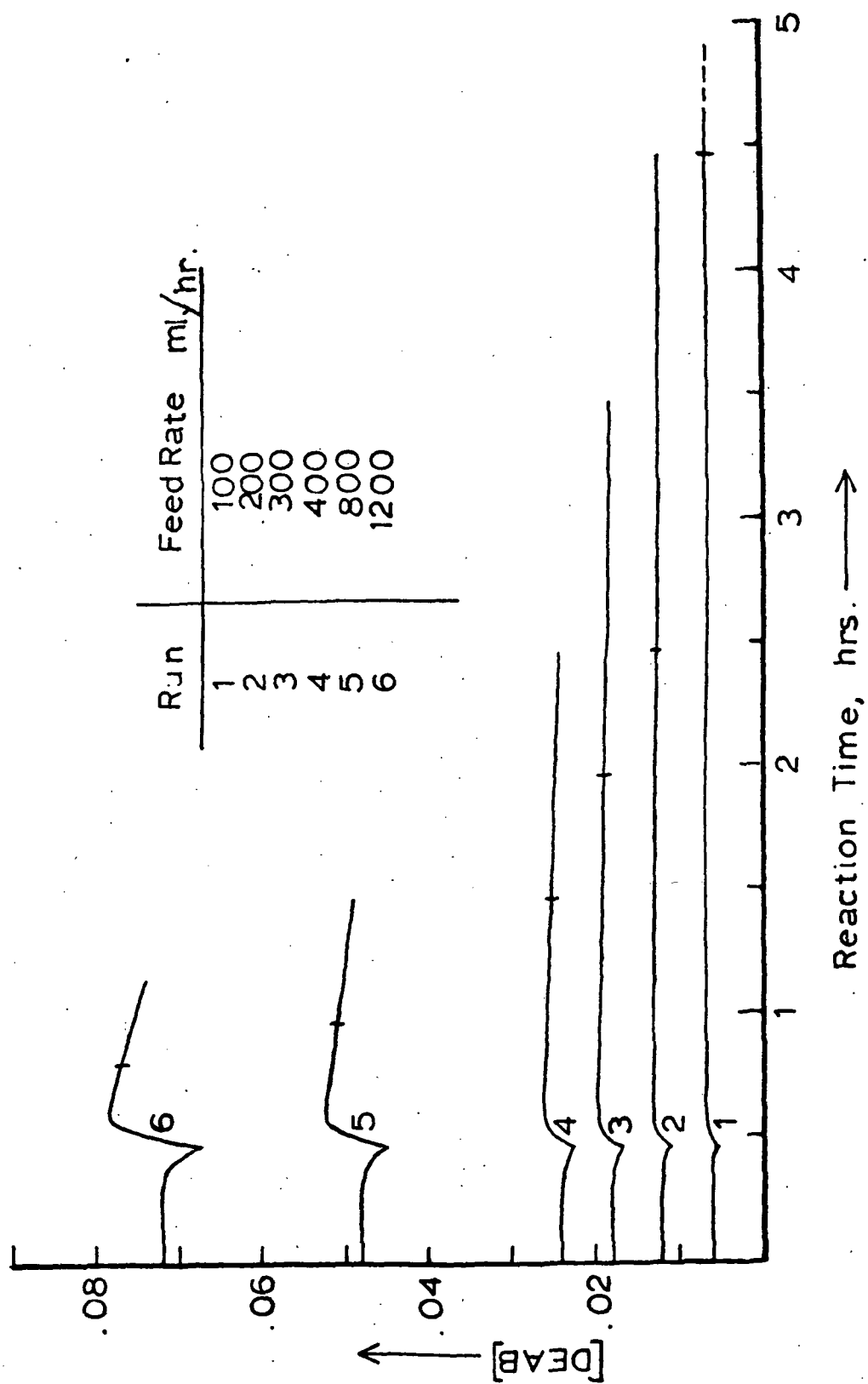


Fig.18. Relationship Between Feed Rate and DEAB Level.

TABLE III. RELATIONSHIP BETWEEN FEED RATE AND INITIATOR LEVEL

<u>Simulated Run No.</u>	<u>Feed Rate, Ml./Hr.</u>	$[\text{DEAB}]_0$	$[\text{DEAB}]_m$	$[\text{DEAB}]_m^{-1/2}$
1	100	.006	.0061	12.80
2	200	.012	.0124	8.98
3	300	.018	.0186	7.33
4	400	.024	.0250	6.32
5	800	.048	.0508	4.44
6	1200	.072	.0768	3.61

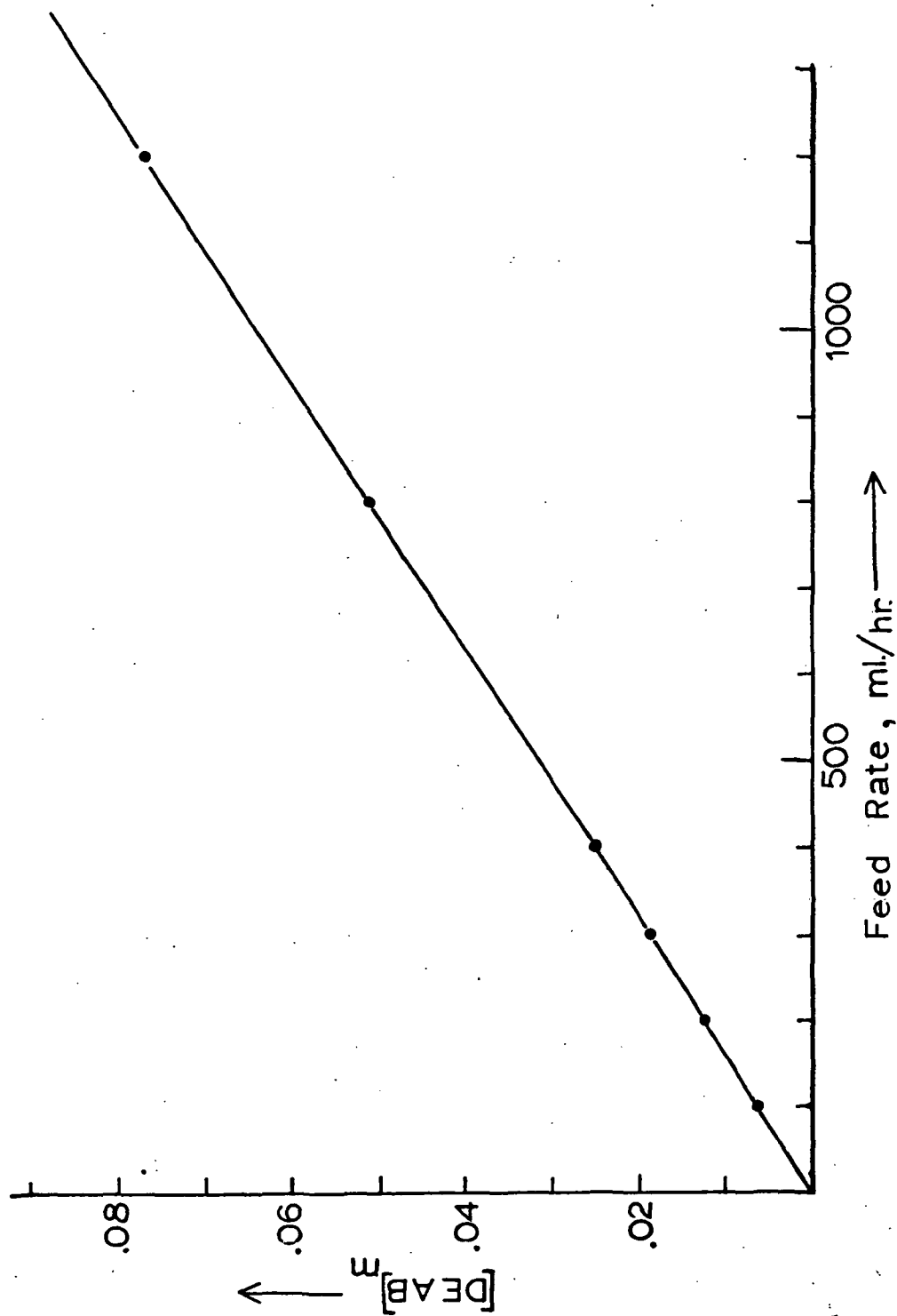
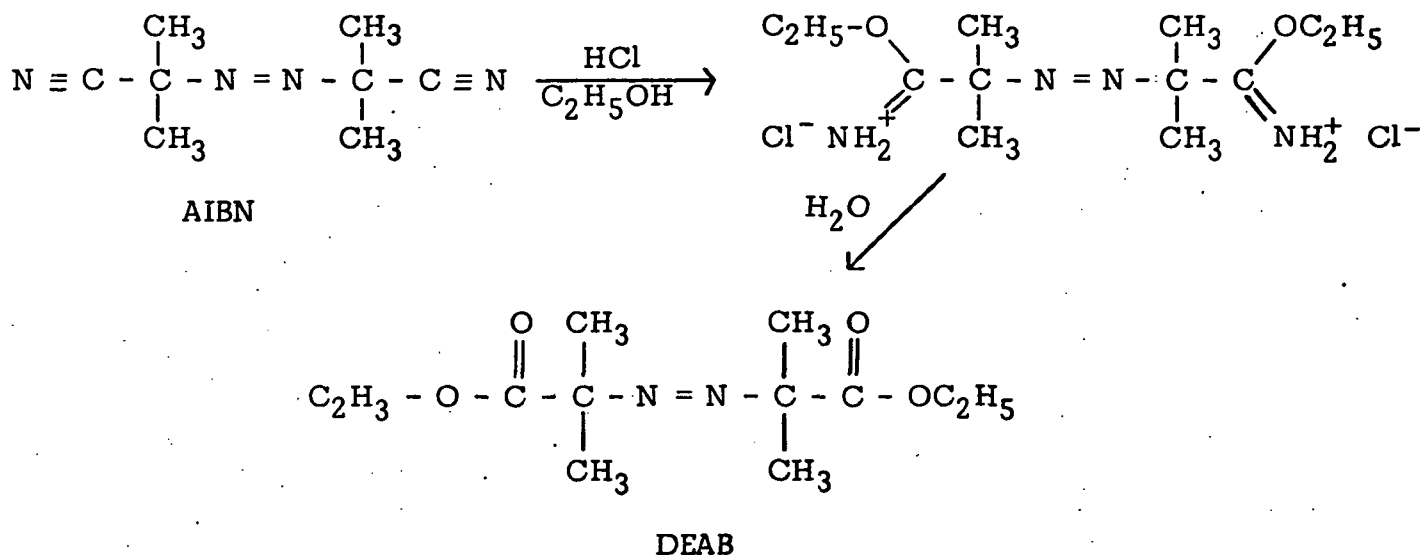


Fig.19. Initiator Concentration at Midrun, Dependence
Upon Feed Rate of 50% DEAB Solution.

c. Initiator and Monomer Preparation

A fresh supply of DEAB was prepared by treating a suspension of azobisisobutyronitrile in anhydrous ethanol with anhydrous hydrogen chloride, followed by hydrolysis of the resulting iminoether hydrochloride:



Freshly prepared DEAB has a melting point of -10 to -5°C .

M.C.&B practical grade isoprene (93% pure by gas chromatography) was distilled through the Oldershaw column described in section C with the addition of a partial reflux head equipped with a timer. Gas chromatographic analysis of the distillate shows it to be 99.7% isoprene and 0.3% pentene-2.

4. Polyisoprene Run No. 9706-ACA-105

Using the process improvements described in the preceding paragraphs, an isoprene polymerization was run in the 5-gallon reactor. Run No. 9706-ACA-105 was made with a 6820 g. (100 l.) charge of isoprene containing 46.5 g. DEAB. This gave a solution which was 0.018 molar in initiator. After a thorough nitrogen purge, the reactor was sealed and heated under stirring up to the polymerization temperature. When the temperature reached 90°C a 50% solution of DEAB in benzene was pumped in at a constant rate of 300 ml./hr. (This initial concentration and feed rate should give an initiator concentration profile like line 3 in Figure 18, with a DEAB concentration midway through the run of 0.0186 molar.) The polymerization temperature was controlled at $100^\circ\text{C} \pm 3^\circ$ over the 2 hours 23 minutes duration of the run, during which time the pressure rose to 118 psi.

When a total of 714 ml. of DEAB solution had been fed in, pumping was stopped, the internal cooling coils turned on, and the run terminated. The data are summarized in Table IV.

The unreacted isoprene was removed by vacuum evaporation on a rotary evaporator, and the residue devolatilized by passing through a falling film molecular still at 170°C/0.2 mm Hg pressure. A yield of 2495 grams (37% conversion) clear colorless liquid polymer was obtained, the functionality of which was $1.98 \pm .02$ by Vapor Pressure Osmometry ($\bar{M}_n = 2290 \pm 20$) and infrared spectroscopic analysis for ester end groups (Eq. Wt. = 1154).

A polyisoprene of 2290 \bar{M}_n having end groups derived from DEAB has a number average degree of polymerization, \bar{X}_n , of 30.3. This fact permits us to make use of the equation in section 2C:

$$\bar{X}_n = C \frac{[M]}{[I]^{1/2}}$$

$$\text{For } [I]_m = 0.0186, \bar{X}_n = 30.3 \therefore C [M] = 30.3 \sqrt{.0186} = 4.13$$

Having evaluated this product, we can select a concentration of DEAB required to give any desired molecular weight product.

$$\text{Since } \bar{X}_n = \frac{\bar{M}_n - 230}{68}$$

$$\text{we have - } [I] = \left[\frac{4.13}{(\bar{M}_n - 230)/68} \right]^2$$

Thus to prepare a 3000 molecular weight ester telechelic polyisoprene, the initiator concentration required is:

$$[I] = \left[\frac{4.13}{(3000-230)/68} \right]^2 = 0.0103$$

And, according to Figure 18, a feed rate of about 170 ml./hr. would be required using a 50% DEAB solution.

TABLE IV. 5-GALLON BATCH ISOPRENE POLYMERIZATIONRUN NO. 9706-105Charged Initially

Isoprene, gms.	6820
DEAB, gms.	46.5
[DEAB] ₀ , molar	0.0180

Fed During Run

Ml. 50% DEAB/Benzene	714
Feed Rate, ml./hr.	300
[DEAB] _m , molar ^a	0.0186

Reaction Conditions

Temperature ^b	100 ± 3°C
Pressure, psi	70-118
Total Time	2 hrs. 23 minutes

Productivity

Yield	2,495
Conversion	37%
Conversion Rate	15%/hr.

Product Description

Appearance	Clear, colorless liquid
\bar{M}_n (V.P.O. in toluene, 37°C)	2290 ± 20
Ester Equivalent Weight (infrared)	1154
Ester Functionality	1.98 ± .02

a. From Figure 18.

b. After reaching control temperature.

VI. PLANS FOR FUTURE WORK

In the quarter to come we plan to use hydride reduction to convert the ester telechelic product C706-ACA-105 into a hydroxyl telechelic pre-polymer.

Additional polymerizations will be run using the improved operating procedures developed last quarter.

The analog computer simulation of the initiator feed system and decomposition kinetics will be presented in our next report, as well as a discussion of two dimensional thin layer chromatography as applied to the analysis of functionality distribution.