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RE-ORDER NO. 72-255

HYDROCARBON POLYMERIC BINDER FOR ADVANCED SOLID PROPELLANT

PERIOD COVERED: August 1, 1971
to
July 31, 1972

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, as sponsored by the National Aeronautics and Space Administration under Contract NAS 7-100.

Report Edited By: James E. Potts

Contributors: A. C. Ashcraft, Jr.
J. E. Potts UCC
E. W. Wise

Publication Date: August 31, 1972

Jet Propulsion Laboratory Contract No. 951210

Technically Managed By: H. E. Marsh, Jr. - JPL

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UNION CARBIDE CORPORATION
CHEMICALS AND PLASTICS
Polymer Research and Development
Bound Brook, New Jersey

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PREFACE

As technical manager of this contract, I would like to offer some observations on the significance of its results.

The crowning achievement of this work is a process, which in high volume should be relatively inexpensive, for making hydrocarbon prepolymers that consist of difunctional molecules, free from measurable amounts of zero-, mono-, tri-, and other functionalities. Pure (or nearly pure) difunctionality is not obtainable at low cost in hydrocarbons from other synthesis methods.

The value of high levels of difunctionality in prepolymers lies in their capacities for chain extension in solid propellant binders and other liquid rubber compositions. This is particularly important in propellants for spacecraft motors, where high elongations are needed. We have strong indications from limited propellant formulating experiments that the expected advantage of difunctional hydrocarbon prepolymers is being demonstrated. The most spectacular result is the achievement, with one formulation, of a tensile capacity (parameter representing combined tensile strength and elongation effects) equivalent to propellants based on polypropylene oxide prepolymer, which has nearly perfect difunctionality. We have so far been unable to do this with any other hydrocarbon prepolymer.

High difunctionality was one of the major objectives of this program. Some of the others were (1) capability for either carboxyl or hydroxyl terminals, (2) either saturated or unsaturated backbone, and (3) improvement in viscosity and low-temperature properties in the saturated hydrocarbon materials. The synthesis developed by Union Carbide has been shown to be capable of producing either kind of termination with equal quality. Although it hasn't been thoroughly evaluated, some benefit is expected in pot life from the fact that the hydroxyls are sterically hindered. Since the general route of this synthesis is addition of diene monomers, the untreated products are unsaturated. When the monomer is isoprene, and the product is hydrogenated, it is still liquid.

The hydrogenated polyisoprenes are very viscous, something like three times the unsaturated precursor. We have shown that this characteristic does not prevent the processing of propellant, but it does make the job more difficult. In pursuit of the third objective listed above, Drs. Potts and Ashcraft showed that the same synthesis scheme works with higher 1, 3-diene homologues of butadiene. The result expected from the presence of longer pendent side chains on the saturated prepolymers was obtained. The viscosity of poly-1, 3-nonadiene was only 70% higher than that of unsaturated polyisoprene of equivalent molecular weight. A corresponding effect on T_g was observed also.

I believe the results of this program merit the attention of those interested in formulating better castable hydrocarbon elastomer products. In particular, I expect HTPB propellants with improved mechanical properties to result from the use of this technology.

H. E. Marsh, Jr.
JET PROPULSION LABORATORY
February 20, 1973

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

A series of DEAB initiated isoprene polymerizations were run in the 5-gallon stirred autoclave reactor. Polymerization run parameters such as initiator concentration and feed rate were correlated with the molecular weight to provide a basis for molecular weight control in future runs.

A first production attempt directed toward the preparation of a uniform twenty pound sample of 2800 molecular weight hydroxy-telechelic polyisoprene was unsuccessful. The product obtained was higher in molecular weight and lower in functionality than expected. The problem was traced to impurities in the batch of initiator used.

A second production attempt was successfully made using a better initiator batch. In this series of polymerizations, five runs were made giving a total of 24 lbs of hydroxy-telechelic polyisoprene. Analysis of the composite product showed that it was difunctional and had a molecular weight of 2786.

Synthetic methods were developed for the preparation of n-1, 3-alkadienes. By these methods, 1, 3-octadiene and 1, 3-nonadiene were prepared. 1, 3-nonadiene was polymerized using DEAB initiator to give an ester-telechelic polynonadiene. This was subsequently hydrogenated with copper chromite catalyst to give a hydroxyl terminated saturated liquid hydrocarbon prepolymer having greatly improved viscosity characteristics and a Tg 18 degrees lower than that of the hydrogenated polyisoprenes.

The hydroxyl-telechelic saturated polymers prepared by the hydrogenolysis of ester-telechelic polyisoprene were reacted with diisocyanates under conditions favoring linear chain extension gel permeation chromatography was used to monitor this condensation polymerization. Fractions having molecular weights above one million were produced.

III. SCOPE

The scope of our program remains as previously outlined.

IV. INTRODUCTION

In the previous annual report we described the preparation of hydroxy-telechelic liquid hydrocarbon prepolymers, both saturated and unsaturated, based upon the free radical polymerization of isoprene. When the polymerization of isoprene was initiated by diethylazobis-isobutyrate, a telechelic difunctional polyisoprene resulted, terminated with ester groups and containing predominantly trans-1, 4 isoprene units.

We were able to hydrolyze the end groups to give carboxy-telechelic polyisoprene, chemically reduce them to give hydroxy-telechelic polyisoprene, and most importantly, by catalytic hydrogenation using copper chromite as catalyst, we were able to prepare a saturated liquid hydrocarbon polymer, difunctional and telechelic with hydroxyl end groups. This achievement marked a fulfillment of one of the original goals of our research for the Jet Propulsion Laboratory.

These isoprene based polymers were prepared in a variety of reactors at only moderate pressure, both batchwise and continuously. After the development of an analog computer simulation of a batch reactor we found that by using a continuous feed of initiator we could make polymer of quality equal to that made in a continuous reactor using a 5-gallon batch stirred autoclave reactor. Since these runs gave 4 to 5 lbs of ester-telechelic polymer per run we were thus able to prepare the larger quantity of polymer needed to do a more complete evaluation in propellant formulations at J. P. L.

In the report which follows we will describe the use of the 5-gallon stirred autoclave reactor to prepare twenty pounds of a uniform highly difunctional hydroxy telechelic polyisoprene. We will also give the results of a limited program aimed at producing saturated hydrocarbon polymers of improved viscosity and low temperature properties.

V. TECHNICAL DISCUSSION

A. Preparation of a Twenty Pound Sample of Hydroxy-Telechelic Polyisoprene

Part 1: Preliminary Experiments in the 5-gallon Stirred Autoclave Reactor

In a previous report[1] we described the preparation of ester terminated telechelic polyisoprenes and their conversion into carboxyl-telechelic and hydroxyl telechelic liquid hydrocarbon polymers, both saturated and unsaturated. Much of this work was done in a continuous reactor, however we found that larger quantities could be readily prepared in a batch reactor provided initiator was added to the reactor continuously during the polymerization.

Following some process improvements to facilitate the addition of initiator solution in a uniform manner, the preparation of a 5 1/2 lb sample of a difunctional product was achieved in a single run. This run was one of a series of range finding experiments designed to relate polymerization parameters to product molecular weight.

The remainder of the runs in this series have been completed and the whole series is summarized in Table I.

In these polymerizations isoprene (freshly distilled, M. C. & B technical grade) was charged to the reactor under an atmosphere of nitrogen along with enough diethylazobisisobutyrate to give the correct molar concentration of initiator anticipated for the run.

The reactor was then sealed and heated to 100°C while being stirred vigorously. When the reactor temperature reached 90°C, the one-stroke piston pump was activated and the initiator feeding phase of the run begun. During this phase a benzene solution (generally near 500 g/liter concentration) of DEAB was fed in at a constant rate selected in advance with the analog simulation program. When the contents of the pump (generally about 700 ml 50% DEAB solution) had been all fed in, the run was rapidly quenched using the interna cooling coil, and the polymer solution collected in glass jugs from the bottom exit of the reactor.

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1) Second Annual Addendum to Triennial Report, "Hydrocarbon Polymeric Binder for Advanced Solid Propellant. Dec. 31, 1971, J. P. L. Contract 951210

TABLE I

Isoprene Polymerizations in the 5-Gallon Stirred Autoclave Reactor

	← 9706 →				← 9926 →	
Run No. →	68	102	105	124	6	8
Charged Initially						
Isoprene, gms	6033	6860	6820	6860	6820	6860
DEAB, gms	31	46. 6	46. 5	9. 6	46. 6	46. 6
Initial Volume, liters	8. 859	10. 073	10. 015	10. 073	10. 015	10. 073
Initial DEAB conc. M	0. 014	0. 018	0. 018	0. 004	0. 018	0. 018
DEAB Solution Fed During Run						
DEAB Concentration g/ml	. 500	. 500	. 500	. 100	. 500	. 500
Total Volume fed, ml	669. 2	673. 4	713. 8	678. 4	723. 7	739. 5
Conditions During Run						
Temperature Range, °C	100-106	98-100	99-105	102-110	100-103	98-103
Pressure Range, psi	85-112	70-115	50-118	90-100	90-107	55-115
Feed Rate, ml/hr	180. 9	297. 1	299. 5	306. 0	299. 5	295. 8
Length of Run, hrs	3. 70	2. 27	2. 38	2. 22	2. 41	2. 50
Run Parameter, Y	9. 90	8. 23	8. 18	18. 14	8. 18	8. 25
Productivity						
Yield after Stripping	2897	2318	2495	1395	2350	2040
Rate, g/hr	783	1021	1047	629	1098	816
Conversion, %	45	32	35	20	33	28
Conversion Rate %/hr	12	14	14	9	15	11

The polymer was subsequently recovered by vacuum stripping on a rotary evaporator and then devolatilized by passage through a molecular distillation apparatus at 170°C/30μm pressure.

All of the products in this series were clear colorless liquids. Characterization was by vapor pressure osmometry, gel permeation chromatography and infra red spectrophotometry as described in previous reports. Note that within experimental uncertainty all of these products are difunctional.

Small aliquots (1→5g.) of each of these products were treated with a large excess of sodium bis(methoxyethoxy)-aluminum hydride ("Vitride")* to convert them to hydroxyl terminated form. These reduced products were examined using thin layer chromatography and were found to contain no non- or monofunctional components. The major component in all cases except run 124 was detected as a spindle shaped streak from Rf = 0.0 to about 0.45 (using 1% ethanol in benzene as the developer and aqueous ammonium sulfate spray followed by heating to visualize the chromatogram) on the plate. In run 124 the lower polarity caused by the much higher molecular weight resulted in an extremely elongated but still uniform streak from R_f = 0.0 to 0.9 (in 2% Ethanol/benzene). A minor component (1 to 2% by area) was present in all chromatograms as a spot at R_f = 0.0.

The products from runs 9706-102 and 105 and the products from runs 9926-6 and 8 were reduced on a larger scale to give sufficient hydroxyl terminated product for a more quantitative assay of hydroxyl functionality. The reduction of 9706-102 is described below.

"Vitride" Reduction of 9706-102

Into a 5-liter three necked flask fitted with mechanical stirrer, condenser, nitrogen inlet and addition funnel was placed 400 ml (2.9 eq. Al-H) of 70% "Vitride" in toluene, and 500 ml toluene. To this was added, dropwise with stirring over a 2 hr period 1000 g.(0.81 eq. ester) of 9706-102 in 400 ml toluene. The exothermic reaction caused a small amount of reflux to occur. After 15 min an aliquot was removed for infrared analysis. This showed a very weak ester carbonyl absorption. Another 10 ml of 70% Vitride (410 ml in all) was added and stirring continued for an additional 2 hours at which time 30 ml methanol was added cautiously to decompose the excess Vitride (a strong exotherm occured at this point showing the presence of unreacted Vitride). After the exotherm subsided a large excess of water (650 ml) was added and the mixture heated on a steam bath for 2 hours resulting in the

---

*Vitride is a product of Realco, New Brunswick, N. J. and may be purchased in smaller quantities through Eastman Kodak.

TABLE II

Polyisoprene Characterization

	← 9706 →				← 9726 →	
Run No. →	68	102	105	124	6	8
Ester Telechelic Product						
Equivalent Wt. (IR)	1420	1190	1150	3000	1230	1160
Mol. Wt. (V.P.O.)	2780	2468	2290	----	2445	2248
Mol. Wt. (G.P.C.)	2750	2350	2260	5920	----	----
Functionality	1.95	2.02	1.98	1.97	1.99	1.94
Hydroxy Telechelic Reduced Product						
Equivalent Wt. (Acet.)	----	1079	1064	----	1161	1145
Mol. Wt. (V.P.O.)	----	2125	2068	----	2320	2179
Functionality	----	1.98	1.95	----	2.00	1.95

hydrolysis of terminal aluminate groups on the polymer and the formation of a heavy white precipitate (probably sodium aluminate). The supernatant clear toluene solution was decanted and filtered and the toluene removed by evaporation to give 872 grams of a clear colorless liquid product, Brookfield Viscosity 60 poise at 25°C. Analysis (see Table II) indicated that the product was difunctional.

In a similar manner the product from run 9706-105 and runs 9926-6 and 8 were reduced to give hydroxy-telechelic polyisoprene.

To relate the molecular weights attained in these range finding experiments to the polymerization parameters, we make use of the equation relating the number average degree of polymerization, $\overline{X}_n$, to the monomer and initiator concentrations:

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

where $[M]$ is the monomer concentration and $[I]$ is the initiator concentration.

Analog simulation of the 5 gallon reactor and feed system demonstrated that over a wide range of feed rates, the initiator concentration was directly proportional to feed rate and feed solution concentration, and inversely proportional to the initial volume of the polymerization mixture:

$$[I] \propto \frac{R\,[I]_{feed}}{V_o}$$

or:

$$\overline{X}_n = C'\,[M]\sqrt{V_o/R\,[I]_{feed}} = C'\,[M]\;Y$$

Thus for low conversion polymerizations, a plot of $\overline{X}_n$ (or $\overline{M}_n$) against the "run parameter", Y, shown above should be a straight line. At higher conversions deviations from linearity are to be expected since $[M]$ is not a constant under such conditions, however the plot should still remain a useful way of correlating experimental parameters with results.

In Figure 1 is shown a plot of

$$\overline{M}_n \text{ vs. } \sqrt{\frac{V_o}{R\ [I]_{feed}}}$$

for the products described in Tables I and II. For convenience the units of V_o are ml., R in ml/hr and $[I]_{feed}$ in grams per ml. The data approximate a straight line of slope 260 implying that:

$$\overline{M}_n = 260\ Y + 200$$

where:

$$Y = \sqrt{\frac{V_o\ (ml)}{R\ (ml/hr)\ [I]_{feed}\ \ (g/ml)}}$$

Thus to make a 2800 $\overline{M}_n$ polyisoprene Y = 10 is required. If $V_o = 10\ell$ and $[I]_{feed} = 0.5$, a feed rate of 200 ml per hour is appropriate.

Part 2: First Production Attempt

Having completed the rangefinding experiments described in Part 1, we set as a goal the preparation of a uniform composite batch of twenty pounds of difunctional hydroxy-telechelic polyisoprene having a molecular weight between 2500 and 3000.

The correlation between the "run parameter Y" and product molecular weight requires a feed rate of 200 ml/hr of 50% DEAB solution to give a 2800 $\overline{M}_n$ product from a 10 liter initial volume batch polymerization. From Figure 28 page 85 in our previous report[1] we note that a feed rate of 200 ml/hr will lead to a DEAB concentration midway through the run of .0126$\underline{M}$. Accordingly our initial DEAB concentration of .0126$\underline{M}$ was selected for a series of 10 liter batch polymerizations using a feed rate of 200 ml. per hr. This corresponds to 32.44 g DEAB charged initially.

a) Production Schedule

A series of six runs was scheduled to provide ample ester terminated polyisoprene for subsequent reduction to the diol. The sequence of events involved in a polymerization run are outlined below:

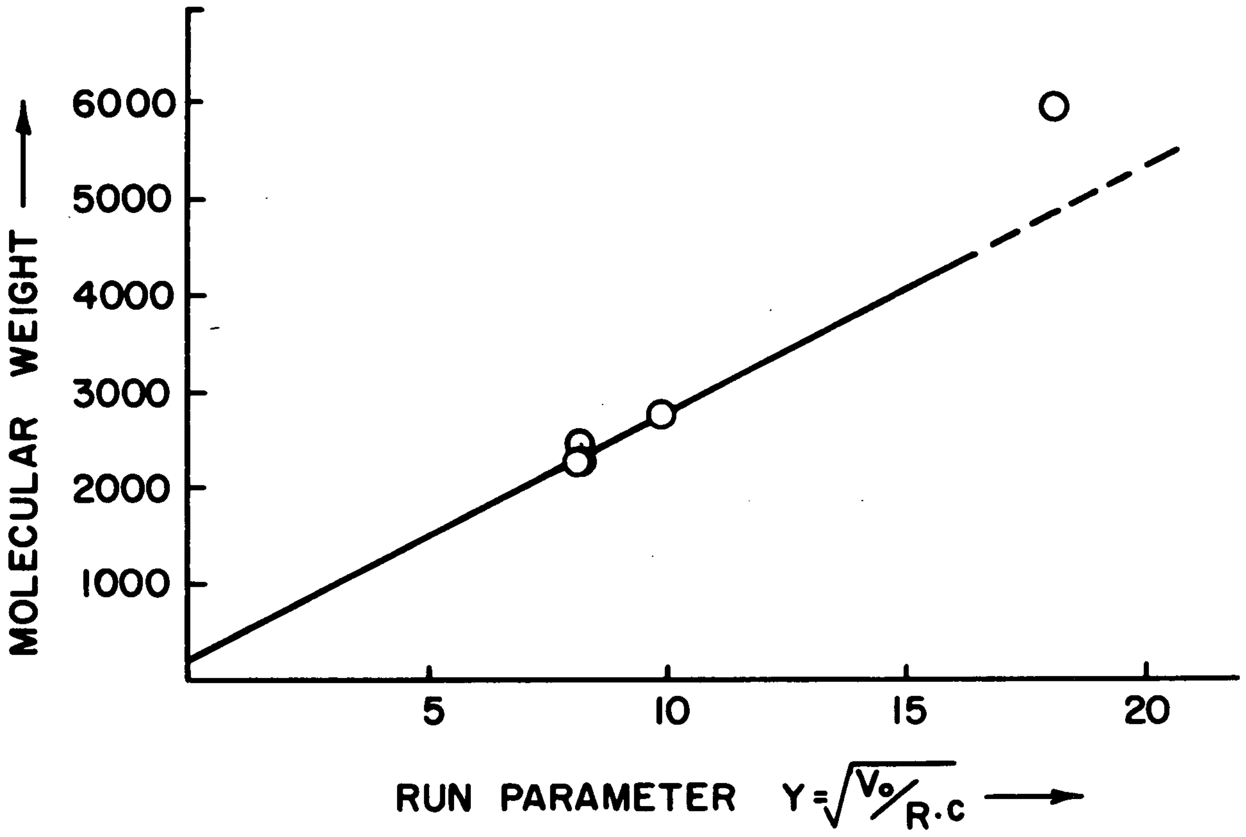


FIGURE I. CORRELATION OF RUN PARAMETER WITH MOLECULAR WEIGHT.

First Day:	A)	Distill Isoprene
	B)	Prepare Reactor
	C)	Prepare Initiator Solution
Second Day:	D)	Charge Pump + Reactor
	E)	Conduct Polymerization
	F)	Discharge Product
Third Day:	G)	Strip off Isoprene
Fourth Day:	H)	Pass through Molecular Still
Fifth Day:	I)	Second Pass through Molecular Still
Sixth Day:	J)	Submit Sample for G. P. G.
	K)	Reduce Small Aliquot with Vitride
	L)	Do T. L. C. Analysis on Reduced Product
Seventh Day:	M)	Evaluate G. P. C. and T. L. C. Results
Much Later:	N)	Composite With other Similar Runs

In order to most efficiently utilize time and manpower, the schedule was set up to work concurrently on several runs at once, i. e., distill isoprene for run 3 while run 2 is being polymerized and run 1 is undergoing devolatilization, etc. (Step C, the preparation of the initiator solution was actually done all at once before the run sequence had started and the benzene solutions stored near 0°C in the cold room until needed.) By this procedure we expected to complete all six runs in under four weeks.

b) Detailed Procedure

Step A Distill Isoprene

The technical grade M. C. & B isoprene is distilled at a reflux ratio of 5:1 through a 32 plate 1 1/4" x 40" Oldershaw column. Only material boiling between 34 and 34.5°C is collected.

Step B Prepare Reactor

The 5-gallon stirred autoclave reactor is rinsed out with hot benzene and flushed with nitrogen and kept under nitrogen atmosphere until the run is made.

Step C Prepare Initiator

Diethyl azobisisobutyrate is dissolved in benzene to give a solution containing 50 grams DEAB per 100 ml of solution. This corresponds to a 1.94M solution. Note: the particular lot of DEAB used in all previous isoprene polymerizations had been exhausted at this point, and the product of five lab scale preparations (notebook reference 9532-PJC-62) composited using the ultraviolet spectrum (showing a λ_{max} at 363 mμ) as an index of purity:

DEAB Prep	ε at 363 mμ
62-1	20.4
62-2	20.8
62-6	20.7
62-7	20.0
62-8	20.2
Standard	20.6

Prior to making up the benzene solutions to be used in the polymerizations, the DEAB was dried over anhydrous sodium sulfate and then filtered through an alumina column. Five 800 ml batches of 50% DEAB/benzene were then made up and stored at 0°C in the cold room until needed.

Step D Charge Pump and Reactor

The 800 ml of 50% DEAB in benzene is charged to the cylinder of the single stroke screw-driven-piston feed pump, and the pump briefly turned on so as to fill all valves and tubing leading to the reactor. At this point the reactor is given a final rinse with benzene (maintaining a nitrogen atmosphere at all times) to wash out the small but unknown quantity of DEAB introduced to the reactor by the "priming" operation described above. The isoprene is then introduced into the reactor by pouring through a large glass column containing 1 lb activated alumina. This step is a precaution against the introduction of peroxides along with the monomer.

The reactor port is then sealed and the feed pump used to introduce 64.7 ml of the 50% DEAB solution into the reactor. This gives an initial DEAB concentration of 0.0126M, and also permits the feed rate to be adjusted close to the 200 ml/hr rate needed for the run.

Step E Conduct Polymerization

At this point the proportional temperature control for the reactor is turned on, set for 100°C. The temperature is carefully monitored and at exactly 90°C the initiator feed pump is turned on. Time, temperature, pressure and initiator feed volume readings are then recorded at about 10 min intervals for the duration of the run. Exotherms if any are manually controlled using internal cooling coils in the reactor.

When all the initiator solution has been fed in the pump is shut off by a limit switch. Simultaneously the heat to the reactor is cut off and the cooling water turned on full force.

Step F Discharge Product

In order to minimize the time spent in the initiator-starved condition at the end of the run, the reactor contents are discharged while still hot into a receiving vessel containing 4 grams di-t-butyl-p-cresol (Ionol). This vessel is maintained with a nitrogen atmosphere and is vented through a heat exchanger to condense isoprene vapors. The flash evaporation resulting from this procedure permits cooling of the polymerization mixture down to about 40°C in under 10 minutes as compared with approximately one hour using the cooling coils alone.

After the discharge into the receiving vessel is complete, the product is drained into 1 gal glass jugs and kept cold and under nitrogen until the next step.

Step G Monomer Removal

The product solution is then continuously fed into a Büchi "Rotovapor" with the evaporation flask heated with a warm water bath, and connected, through condensers and traps, to house vacuum at about 300 mm pressure. After the entire solution has been admitted (originally about 8 liters in volume) and most of the isoprene has distilled off, the pressure is decreased to 30 mm and evaporation continued overnight under a slow stream of nitrogen.

Steps H and I Devolatilization

The product from step G, a clear pale straw syrup, is next passed through a wiped-falling-film molecular distillation apparatus operated at a jacket temperature of 150°C and at a pressure of 300 microns. This results in a yellow distillate (about 1/2 % of the total product) and a colorless clear residue.

The above residue product is again passed through the molecular distillation apparatus at a pressure under 30 microns Hg to give the final devolatilized colorless residue product and an even smaller trace of colorless distillate.

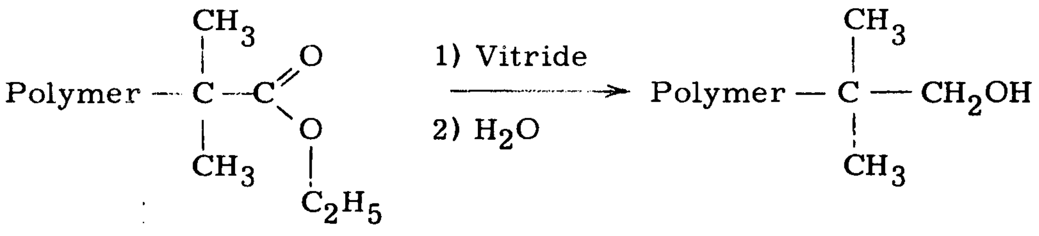
Steps J — M Characterization

Gel Permeation Chromatography gives accurate $\overline{M_n}$ determinations far more easily than vapor pressure osmometry, however it is not an absolute method and must be first calibrated using known $\overline{M_n}$ standards to relate the chromatographically determined $\overline{A_n}$ (number average "extended chain length" relative to polystyrene referrence standards) by a "Q-Factor" to the number average molecular weight.

$$\overline{M_n} = Q \ \overline{A_n}$$

Such a calibration for our current column configuration is shown in Figure 2.

After submitting a sample of the devolatilized product from step I for G. P. C. analysis to give $\overline{M_n}$ and molecular weight distribution, a small sample of a few grams is treated with sodium bis(methoxyethoxy) aluminum hydride ("Vitride") to reduce the ester end groups to methylol groups:



This sample of reduced product may then be analyzed by thin layer chromatography to give a qualitative description of the functionality distribution.

c) Description of Results Obtained

Table III outlines the results obtained when the procedure described in the previous section was carried out in five consecutive polymerizations. Because of the staggered arrangement of the experimental activity, the initial stages of runs 9926-36 and 38 were in progress before the characterization was complete on the earlier runs. Thus some 16 kilograms of product had been prepared or was in process before the first information was obtained which suggested all was not well.

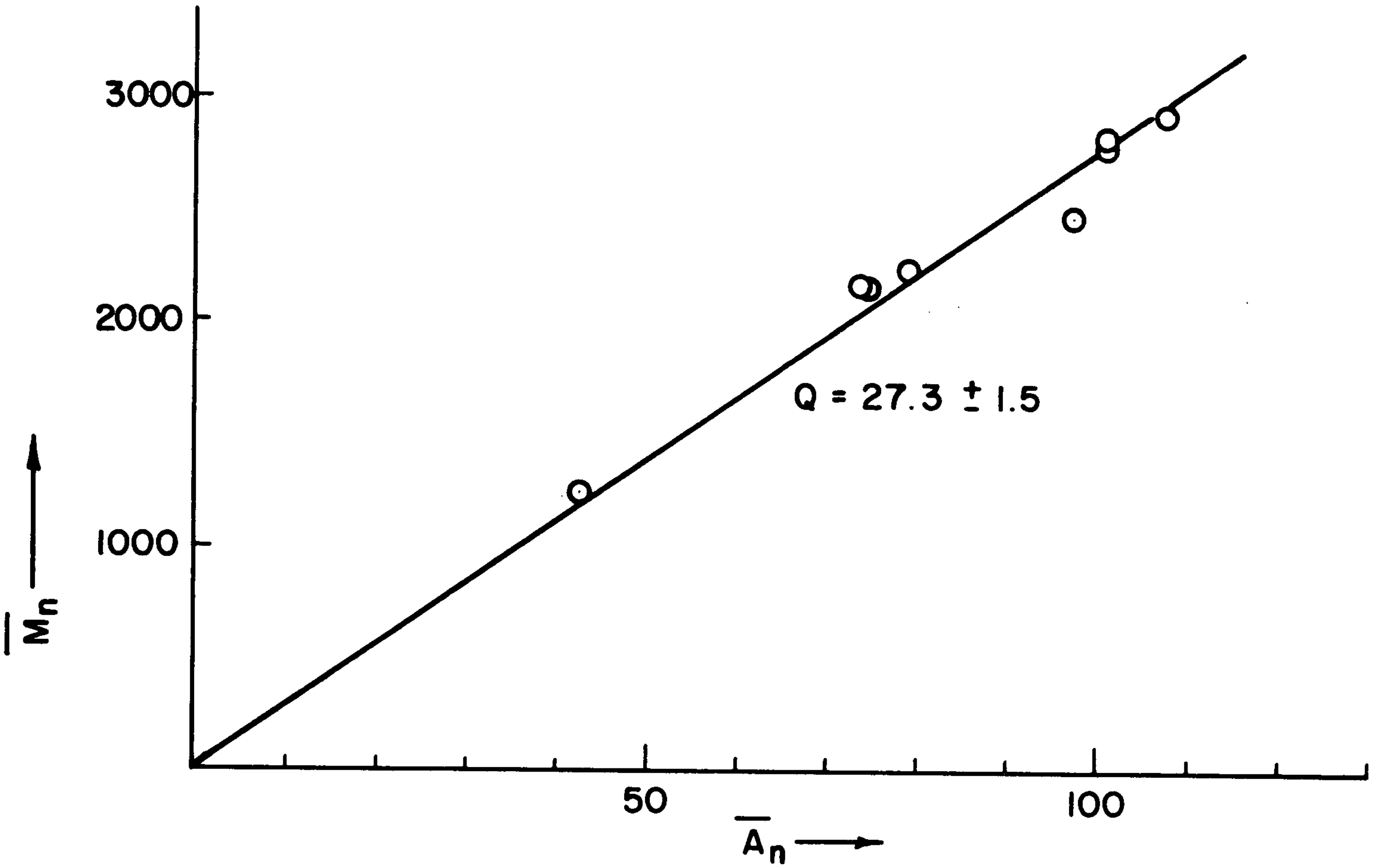


FIGURE 2. CALIBRATION OF GEL PERMEATION CHROMATOGRAPHY FOR MOLECULAR WEIGHT DETERMINATION.

TABLE III

Isoprene Polymerizations for Twenty Pound Composite - First Trial

Run No. 9926 →	28	32	34	36	38
Charged Initially					
Isoprene, gms	6860	→	→	→	→
DEAB, gms	32.45	→	→	→	→
Initial Volume, ℓ	10.073	→	→	→	→
Initial DEAB conc. M	0.0126	→	→	→	→
DEAB Solution Fed in During Run					
DEAB Conc. g/ml	.500	→	→	→	→
Total Vol. Fed, ml	700.4	705.5	717.1	706.4	751.0
Conditions During Run					
Temperature Range, °C	98-101	100-105	100-102	97-107	99-103
Pressure Range, psi	88-122	91-115	98-121	92-117	88-112
Feed Rate, ml/hr	204.4	206.0	206.4	206.8	221.4
Duration Run Hrs.	3.43	3.43	3.48	3.42	3.39
Run Parameter Y	9.93	9.89	9.88	9.87	9.54
Productivity					
Yield, g	2800	2692	3338	3589	3352
Rate, g/hr	816	785	959	1099	989
Conversion, %	40.6	39.1	46.0	49.5	46.1
Conversion Rate %/hr	11.8	11.4	13.2	14.5	13.6

Infrared spectra of the ester-telechelic products 28 and 32 indicated an equivalent weight based upon ester end groups of 2060 and 2050 respectively. If the molecular weight had been 2800 as expected from the 200 ml/hr initiator feed rate employed, this result would have implied an ester functionality of about 1.4. Subsequent thin layer chromatographic analysis of "Vitride" reduced product confirmed this expectation, showing the presence of monofunctional polymer. However an unexpected finding of the T. L. C. analysis was that a significant fraction of the polymer did not migrate at all on the plate under conditions leading to migration of the diol component (2% C_2H_5OH/Benzene). This very highly polar (but apparently not hydroxylic in functionality) fraction amounts to about 10% of the polymer (Estimated from area on the plate).

This same result was obtained with each of the other products: Low ester functionality, low hydroxyl functionality when reduced, and presence of a very polar non-migrating component at $R_f = 0$ on the T. L. C. plate of the reduced product. It was also noted that all of the products obtained, whether ester terminated or hydroxyl terminated were cloudy in appearance, indicating the presence of some incompatible materials.

Table IV summarizes the analysis of these products. All were reduced with "Vitride" on a small scale for T. L. C. anlaysis and runs 32 and 34 were reduced on a 2400 gram scale using the procedure described in part A for 9706-107. These reduced products were analyzed with the results shown. Note that the molecular weights obtained were somewhat higher than the 2800 expected from the initiator feed rate employed.

Part 3: Experiments to Resolve the Functionality Problem

a) Polymerization Run 9924-46

An additional polymerization was conducted in the 5 gallon reactor using a higher initiator feed rate to see if the functionality problem remained when a lower molecular weight polymer was prepared. In runs No. 9926-46 we charged initially 6860 grams of freshly distilled isoprene and 93 ml of 50% DEAB in benzene into the reactor and when the reactor reached 90°C the initiator solution was pumped in at a rate of 302 ml/hr. These conditions were selected to give a mean DEAB concentration of 0.018 M during the run and with a "run parameter Y" of 8.18 were expected to result in a molecular weight of about 2100 to 2300 similar to runs 9706-102, 105 and 9926-6 and 8 described in part 1.

TABLE IV

Ester Telechelic Polyisoprene Characterization

Run No. 9926 ⟶	28	32	34	36	38
Ester Equivalent Wt.	2060	2050	1970	2180	2060
$\overline{M}_n$, Vapor Pressure Osmometry	----	3630	3125	----	----
$\overline{M}_n$, Gel Permeation Chromatography	3180	3140	3100	3510	3220
Ester Functionality	1.54	1.77/1.53	1.59/1.57	1.61	1.56
"Vitride" Reduced Product Characterization					
$\overline{M}_n$, Vapor Pressure Osmometry	----	3595±200	3125±70	----	----
Hydroxyl Equivalent Wt.	----	2055±38	1751±43	----	----
Hydroxyl Functionality	----	1.75±13	1.79±.08	----	----

TLC - All show monofunctional component and a fraction more polar than difunctional component.

During the run of 2.22 hrs duration the reactor temperature was between 100 and 103°C and the pressure between 68 and 118 psi. A yield of 2800 grams of pale straw hazy liquid product resulted after stripping off the monomer on the rotovapor.

Gel permeation chromatography gave a higher molecular weight than predicted of 2650 ± 150 for this product, which was not passed through the molecular distillation apparatus.

Vitride reduction of 2757 grams of 9926-46 gave 2562 grams of a cloudy product 9926-65, showing strong OH bands in the infrared spectrum and no ester. The molecular weight was measured by vapor pressure osmometry in toluene: 2195 ± 50, and the acetylation value for hydroxyl equivalent weight was 1477 ± 62 giving an average hydroxyl functionality of 1.5 ± 1.

b) Polyisoprene Fractionation by Preparative T. L. C.

Examination of 9926-65 by thin layer chromatography using 2% ethanol in benzene as the developing solvent revealed three major components: 1) a spot, the same size as the original area of application of the sample, at $R_f = 0$, estimated to be about 10% of the material visualized on the plate, 2) a streak from R_f ~ 0.05 to about 0.55 containing most of the material and 3) a streak much thinner than (2) trailing from $R_f = 0.55$ to 0.95 and containing about 10 or 15% of the material. Component (2) has an R_f range appropriate for a difunctional component and (3) has an R_f range appropriate for a monofunctional component and component (1) since it did not migrate at all, must be a very high functionality component, low in molecular weight or containing an extremely polar group such as amine or carboxyl.

To test the possibility that component (1) is a low molecular weight and hence quite polar polyol, extractive experiments were done using dimethylformamide, methanol, ethanol, propanol and butanol. DMF, methanol and ethanol did not extract component (1), instead the low R_f (hence low molecular weight) portion of component (2) was extracted. Propanol and butanol did extract part of component (1) but even more of the low molecular weight component of the difunctional fraction. These results suggest that component (1) is not a low molecular weight species.

Preparative thin layer chromatography was then used to isolate a sufficient quantity of these components to permit determination of their molecular weight by gel permeation chromatography: 3/4" from an edge of a 20 x 20 cm x 250 micron silica gel plate was placed a row of 76 applications, 2 μl. each, of a 10% solution of 9926-65 in benzene. The spots were applied to produce a continuous line clear across the plate containing about 15 mg of 9926-65. The plate was developed in 2% ethanol in benzene until the solvent front had moved 12 cm up the plate. The plate was then dried and, except for a 1 cm strip along one side, the layer of silica gel carefully scraped off in five bands across the plate. Fraction (1) includes the origin, from R_f = -.04 to + .04. Fraction (2) includes from R_f = .04 to .27, fraction (3) from .27 to .53, fraction (4) from .53 to .76 and fraction (5) from .76 to the solvent front at R_f = 1.0. These fractions of adsorbent containing the complete functionality and molecular weight distribution of 9926-65 were soaked overnight in 4 ml ethyl acetate. The supernatant liquid was analyzed by spotting 2μl on a T. L. C. plate from each fraction. Development confirmed that a preparative separation had been achieved since each fraction gave developed streaks in R_f corresponding to the region scraped off the preparative plate.

The fractions were recovered by filtering off the silica gel, evaporating to dryness and redissolving each residue in 5 ml tetrahydrofuran, the solvent we use for gel permeation chromatography.

The concentration of the polymer fraction in each of these solutions corresponds approximately to that in a 14.2 mg/5 ml solution of the original polymer or about 0.3% by weight.

The entire 5 ml solution of each fraction was injected onto the column of the gel permeation chromatograph. The five chromatograms obtained are shown in Figure 3 superimposed upon a chromatogram of the starting material. From the relative areas of the chromatograms, fraction (1) comprises 10.5% of the original polymer, and fractions (2) through (5) comprise 29.1%, 46.7%, 12.3% and 1.4% respectively of the original polymer.

Fraction (1), the R_f = 0 component, has distinctly bimodal molecular weight distribution, with the greater portion (~80%) being identical with the molecular weight distribution of the starting material and a minor portion made up of small molecules in the 10 to 20A size range. The non-mobility of the polymeric component of fraction (1) as compared with fraction (3) which has the same molecular weight distribution leads one to the inescapable conclusion that fraction (1) is either of a completely different character with regard to functionality from the other four fractions, that is, it is much greater than 2 in hydroxyl functionality, or else has more highly associative terminal groups such as carboxyl or amine. In the absence of a reasonable mechanism for generating a poly-ol of 3 or greater functionality in 9926-65 and still ending up with a low average functionality, the latter explanation seemed more likely and suggested

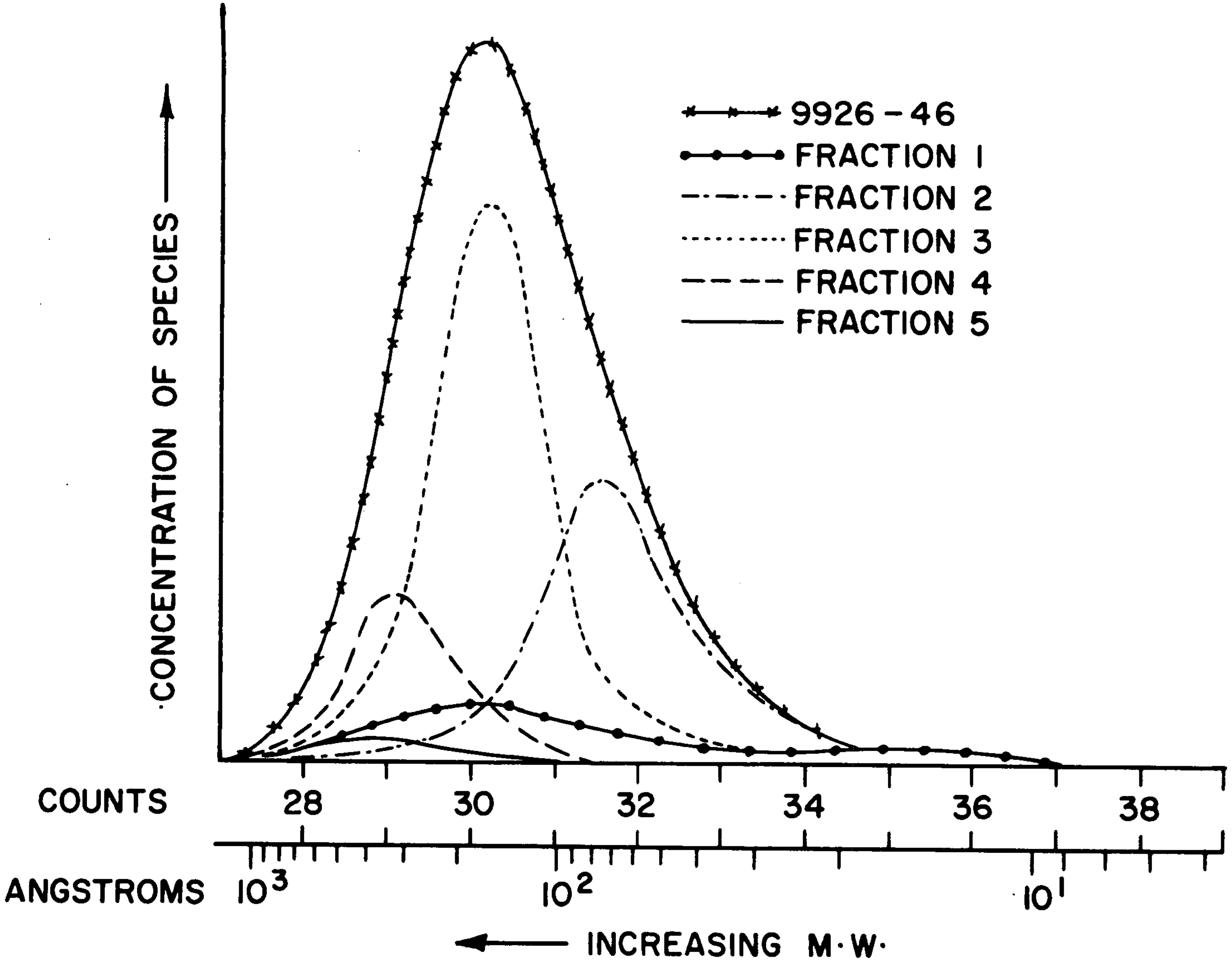


FIGURE 3. GEL PERMEATION CHROMATOGRAMS OF PREPARATIVE T.L.C. FRACTIONS.

that we reexamine our initiator to see whether it contained impurities which could lead to non-hydroxylic, but still highly associative, end groups.

c) Examination of Initiator Purity

An infrared spectrum of the initiator used in the preceding runs (from 9532-PJC-62) was taken in a 0.2 mm cell using no solvent, to accentuate weak absorptions. This spectrum was compared with a spectrum in our file of pure DEAB (Sample 8134-1-2 prepared 2/28/66). Difference between the two spectra were apparent at 6.20, 13.55 and 14.25μ where significant absorptions were present in the spectrum of 9532-PJC-62 that were either weak or absent in the spectrum of authentic DEAB.

Another DEAB sample was on hand which had been prepared at about the same time, 9532-PJC-49-1, 2 & 3 composite. It exhibited an infrared spectrum showing the above absorptions but at a much lower level than the DEAB used in the preceding runs. 3550 grams of this material was cooled with continuous agitation using a bath at -40°C. When the temperature had reached -20°C partial crystallization of the DEAB had occurred, giving a slushy mixture. This mixture was rapidly filtered on a suction funnel to separate the solidified (and presumably purer) portion from the liquor. This resulted in a filtrate of 2890 g (81%) and a solid portion of 652 g (18%) which remelted when it warmed to -17°C.

Infrared spectra in 0.2 mm cells of this solid and liquid fraction of 9532-PJC-49 showed differences at 2.93, 3.02, 3.17, 6.20, 13.55 and 14.25μ. with the latter three differences the most pronounced. These latter three absorptions are the same ones noted when 9532-PJC-62 was compared with an authentic sample of pure DEAB, 8134-1-2.

d) Sealed Tube Polymerization Experiments

Sealed tube isoprene polymerizations were conducted using three different samples of DEAB. In this way other variables such as the condition of the reactor, feed rates etc. would not interfere with the comparison of initiators:

Twenty-five grams of isoprene was placed in each of four glass polymerization tubes along with 2 ml. of DEAB from different sources:

Tube	DEAB Used
1	9532-PJC-62
2	9532-PJC-49
3	Liquor from 9532-PJC-49
4	Solid from 9532-PJC-49

The tubes were then capped and heated at 84°C overnight and the excess isoprene removed by evaporation to give about 9 grams of liquid ester terminated product in each case.

Vitride reduction was then used to convert the above products to hydroxyl terminated prepolymers for comparison by T. L. C. The results were dramatic: The products from the first tube showed the polar but apparently non-hydroxylic component at $R_f = 0$ while the product made with the recrystallized DEAB in tube #4 did not at all, and the products from tubes #2 and #3 showed the $R_f = 0$ component in only trace amounts. Evidently the DEAB sample 9532-PJC-62 contains some impurity responsible for the $R_f = 0$ component. This impurity is present at a greatly reduced level in 9532-PJC-49, and not at all in the recrystallized DEAB prepared from it.

e) Isoprene Polymerization in the Stirred Autoclave Using Purified DEAB

Following the same procedure described in section (2), 10. 2 kg of isoprene and 108 ml of 50% DEAB in Benzene ("Solidified" product from 9532-PJC-49) were placed in the reactor. After the reactor had been heated to 90°C, 610. 1 ml of the same 50% DEAB solution fed in over a period of 1. 69 hrs (corresponding to a feed rate of 361 ml/hr and a run parameter of 9. 09). After discharging the reactor and stripping off the isoprene a yield of 2444 grams of ester terminated clear liquid polyisoprene was obtained.

Infrared analysis gave an equivalent weight of 1173 and gel permeation chromatography gave a molecular weight of 2220 indicating an ester functionality of 1. 9.

Vitride reduction of the above product using 972 grams of 70% Vitride in toluene gave 1939 grams of a clear colorless product having a hydroxyl equivalent weight of 1083±24. T. L. C. analysis shows no $R_f = 0$ component.

Part 4: Second Production Attempt

In part 3 we demonstrated that the initiator batch 9532-PJC-62 was the probable source of the functionality problem encountered in our first production attempt. In the sealed tube experiments of part 3d and the full stirred autoclave run of part 3e, the DEAB batch 9532-PJC-46 was successfully used to prepare difunctional ester-telechelic polyisoprenes from which reduced products were prepared which did not contain the anomalous component at $R_f = 0$. In the sections to follow we will describe the second and successful production attempt using DEAB batch 9532-PJC-46.

a) Changes in Procedure

Compared with the first production attempt the major change in procedure lies in the better batch of initiator used. Other changes in procedure were made designed to improve efficiency and to give an improved product:

Greater Total Volume in Reactor

Previous polymerizations were made using an Isoprene charge of 6860 grams, giving about 10 liters initial volume in the reactor. The reactor actually has room for about twenty liters with the result that we were operating only 1/2 full. If V_O, the initial volume of the polymerization mixture, is made larger, either R, the initiator feed rate, or C, the initiator concentration must be increased to give the same value for Y, the run parameter, and make the same molecular weight polymer.

$$Y = \sqrt{V_O / R\ C}$$

There are advantages to either procedure. Increasing C to maintain the same Y results in an increased yield of product per run (but not an increase in yield based upon the amount of DEAB used). Increasing R on the other hand gives about the same yield but at a lower overall conversion based upon isoprene and with a shorter run time. This results in less change in monomers concentration over the course of the run and should result in a more uniform product.

We chose to increase V_O from 10 to 15 liters and to increase R rather than C.

No Isolation of the Ester Telechelic Intermediate Product

We found that Vitride is quite soluble in isoprene, and that the reduction step could be easily performed directly on the isoprene solution of polymer as it is discharged from the reactor.

Elimination of One of the Molecular Distillation Steps

Comparison of the products obtained at various stages of workup in the first production attempt, using gel permeation chromatography, showed a small but definite downward drift of A_n as more thermal abuse was given to the polymer. To minimize this, the second devolatilization was eliminated.

Filtration of the Final Product

As a final step the neat polymer is filtered under pressure through a filter pad (Columbia F-6) to remove any solid material (such as finely divided sodium aluminate or aluminum hydroxide from the reduction step) and give a perfectly clean product.

b) Description of Results

Isoprene polymerizations 9926-99, 101, 105, 110 and 112 were conducted in the 5-gallon stirred autoclave and the products reduced with "Vitride" to give the results summarized in Table V. The modified procedure used is described in detail for run no. 9926-112 below:

Isoprene Polymerization 9926-112

Into the 5-gallon stirred autoclave was placed 10,200 grams (14.98 liters) isoprene (freshly distilled as described previously and filtered through alumina) and 84 ml of a 50% solution of batch 9532-PJC-46 DEAB in benzene. The reactor was sealed under a nitrogen atmosphere and heated to the polymerization temperature of 100°C. As the temperature of the reactor passed through 90°C the initiator feed pump was turned on and a 50% solution in benzene of the same batch of DEAB was fed in at a rate of 282 ml per hr. This corresponds to a run parameter of 10.30. A total of 640 ml of initiator solution were fed in over a 2.27 hr period. During this time the temperature was maintained between 101-103°C and the internal pressure rose from 58 psi to 114 psi requiring venting of nitrogen to avoid higher pressures as the head space diminished.

At the end of the run, heat was shut off, cooling water turned on full force and the reactor contents discharged through the bottom port into a receiver blanketed with nitrogen, containing 8 grams Ionol and vented through a heat exchanger serving as an isoprene vapor condenser. Approx-

TABLE V

Isoprene Polymerizations for Twenty Pound Composite - Second Trial

Run No. 9926 →	99	101	105	110	112
Charged Initially					
Isoprene, gms	10,200	→			
DEAB, ml 50% solu.	84	→			
Initial Volume, ℓ	14.98	→			
Initial DEAB conc. M	0.011	→			
DEAB Solution Fed in During Run					
DEAB Conc g/ml	.500	→			
Total Vol. Fed, ml	642	654	652	654	640
Conditions During Run					
Temperature Range, °C	100-103	98-104	100-102	101-104	101-103
Pressure Range, psi	57-120	58-122	60-120	55-118	58-114
Feed Rate ml per hr	294	265*	292	286	282
Duration of Run, hrs	2.18	2.47	2.23	2.28	2.27
Run Parameter Y	10.09	10.63	10.13	10.23	10.30
Vitride Reduction					
Initial Amt. used, gms	950	940	950	930	942
Additional Amount Required, gms	0	100	110	196	110
Total Vitride used, gms	950	1040	1060	1126	1052
Productivity					
Overall Yield, gms	1905	2334	2240	2283	2347
Characterization					
Hydroxyl Eq. Wt., acetylation	1426±43	1466±33	1381±23	1390±19	1409±26
$\overline{A}_n$	98.5	103.0	97.4	101.4	100.8
$\overline{A}_w$	172.4	179.7	170.6	174.0	172.3
$R = \overline{A}_w/\overline{A}_n$	1.75	1.74	1.75	1.72	1.71
$\overline{M}_n$, GPC, $Q = 27.33 \pm 1.5$	2690±150	2810±150	2660±150	2770±150	2750±150
Functionality	1.89±.16	1.92±.15	1.93±.14	1.99±.14	1.95±.15
Brookfield Viscosity @ 25°C, poise	94.5	93.4	88.4	93.2	93.3

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*Avg. over whole run. Actually 282 ml/m for 88% of time imately 3000 g isoprene was recovered in this operation which gave 6720 grams of a solution of ester telechelic polyisoprene in isoprene and benzene solvents.

Into a dry argon purged 22 liter glass reaction kettle was placed 942 grams 70% "Vitride" in toluene, and 1000 ml benzene. To this solution was added the polymer solution obtained above over a 1 1/2 hr period, stirring constantly and maintaining a positive argon pressure* all the while. After the addition was complete an aliquot was removed and examined by infrared spectroscopy. A very weak ester carboxyl band was observed, so an additional 110 grams of 70% Vitride was added to the reaction mixture and stirring continued for another 10 min. An aliquot removed at this point showed no carbonyl absorption in the infrared and the reaction was judged to be complete.

The excess "Vitride" was decomposed by cautious addition of 100 ml of water, added dropwise with stirring over a 1 1/4 hr. period. During this time the very viscous, clear colorless reaction mixture first thickened slightly and then became quite fluid. Hydrogen gas was vented during the water addition. Two liters of warm distilled water was then added to the reaction mixture which was stirred vigorously for 20 min. and then allowed to stand overnight. A heavy white precipitate of sodium aluminate formed leaving a cloudy organic layer. The layers were separated and the organic layer washed 4 x 4 liters with distilled water (till pH of wash water is 6-7), then dried over anhydrous magnesium sulfate and filtered. The isoprene and benzene were then stripped off on a rotary evaporator to give a clear nearly colorless hydroxyl terminated product.

This was devolatilized by passage through the molecular distillation apparatus one time only. The wall temperature was maintained at 150°C and the temperature of the devolatilized polymer at the bottom of the still was 80°C. The pressure was 300 microns Hg. during the devolatilization. The product was then filtered under about 20 psi pressure through a 165 mm diam by 5mm thick paper filter pad (Columbia filter grade F-5) to give 2347 grams of final product, having a Brookfield viscosity of 93. 3 poise at 25°C.

The hydroxyl equivalent weight was determined by our acetylation procedure to be 1409±26. When combined with the molecular weight (calculated from the gel permeation chromatogram) of 2750 ±150 this results in a hydroxyl functionality of 1. 95±. 15. When examined by 2-dimensional thin layer chromatography (2% ethanol in benzene *vs.* acetone)

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*Note: an air leak at this stage results in the formation of a yellow to amber product.

one principal component was found on the region of the plate corresponding to the difunctional component. The highly polar material seen at $R_f = 0.0$ in the T. L. C. plates of the products of the first production attempt was also present but at a greatly reduced level. Estimates based upon area indicate 2% or less is present in the final product from run 9926-112.

c) Preparation of the Twenty Pound Composite Sample 9926-115

The uniformity of the products from Runs 9926-99, 101, 105, 110 and 112 can be seen not only from the data in Table V., but also by the comparison of the gel permeation chromatograms. Figures 4, 5 and 6 show the individual chromatograms in both differential and integral forms and Figure 7 shows the superimposition of all of the differential molecular weight distributions onto a single chart. The differences between individual chromatograms are comparable to the differences between successive repeat analyses of the same sample. The virtual identity of the GPC results and the closeness of the other data for all five products gave us confidence that a uniform product would result when the runs were combined.

Into a 12-liter round bottomed reaction kettle having a stopcock on the bottom were placed the following quantities of hydroxy telechelic polyisoprenes from the second (successful) production attempt:

Product	Grams Added
9926-99	1870
9926-105	2254
9926-110	2276
9926-112	2341
9926-101	271
Total	9012 grams (19. 85 lb)

A stream of argon was passed through the bottom inlet. This caused large bubbles to rise in the viscous mixture giving an excellent mixing action. After mixing in this fashion overnight, a 1 gram aliquot was removed and analyzed by ultraviolet spectroscopy to determine the ional content. This was found to be 1000 ppm. To bring the ionol content to 2500 ppm (1/4%) and the total weight over 20 lb, 14. 22 grams of ionol was combined with another 256 grams of 9926-101 and added to the mixture after heating and stirring to dissolve the ionol. Total wt in kettle at this point was 20. 44 lb.

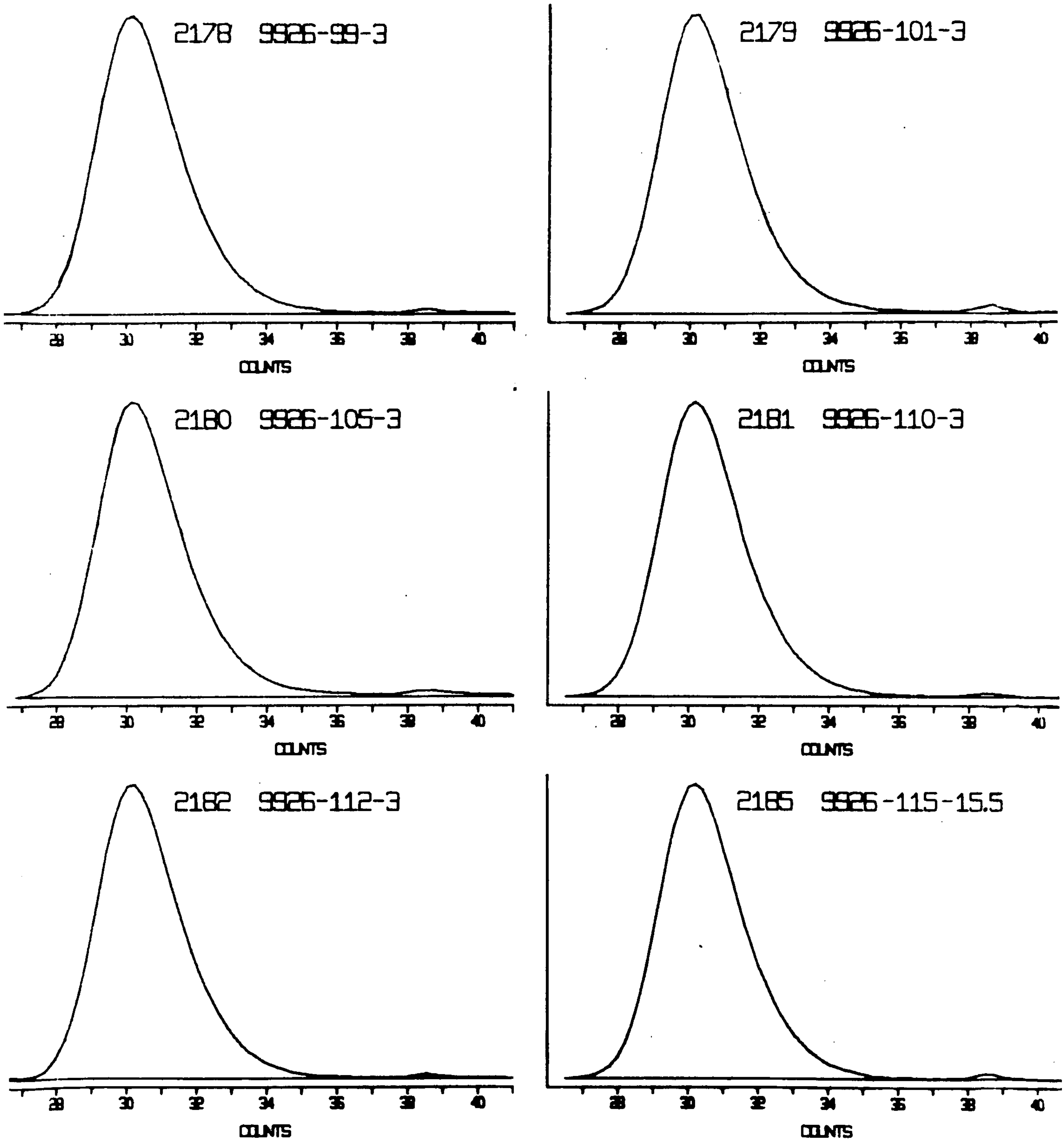


Figure 4 - Gel Permeation Chromatograms of Products From Second Production Attempt

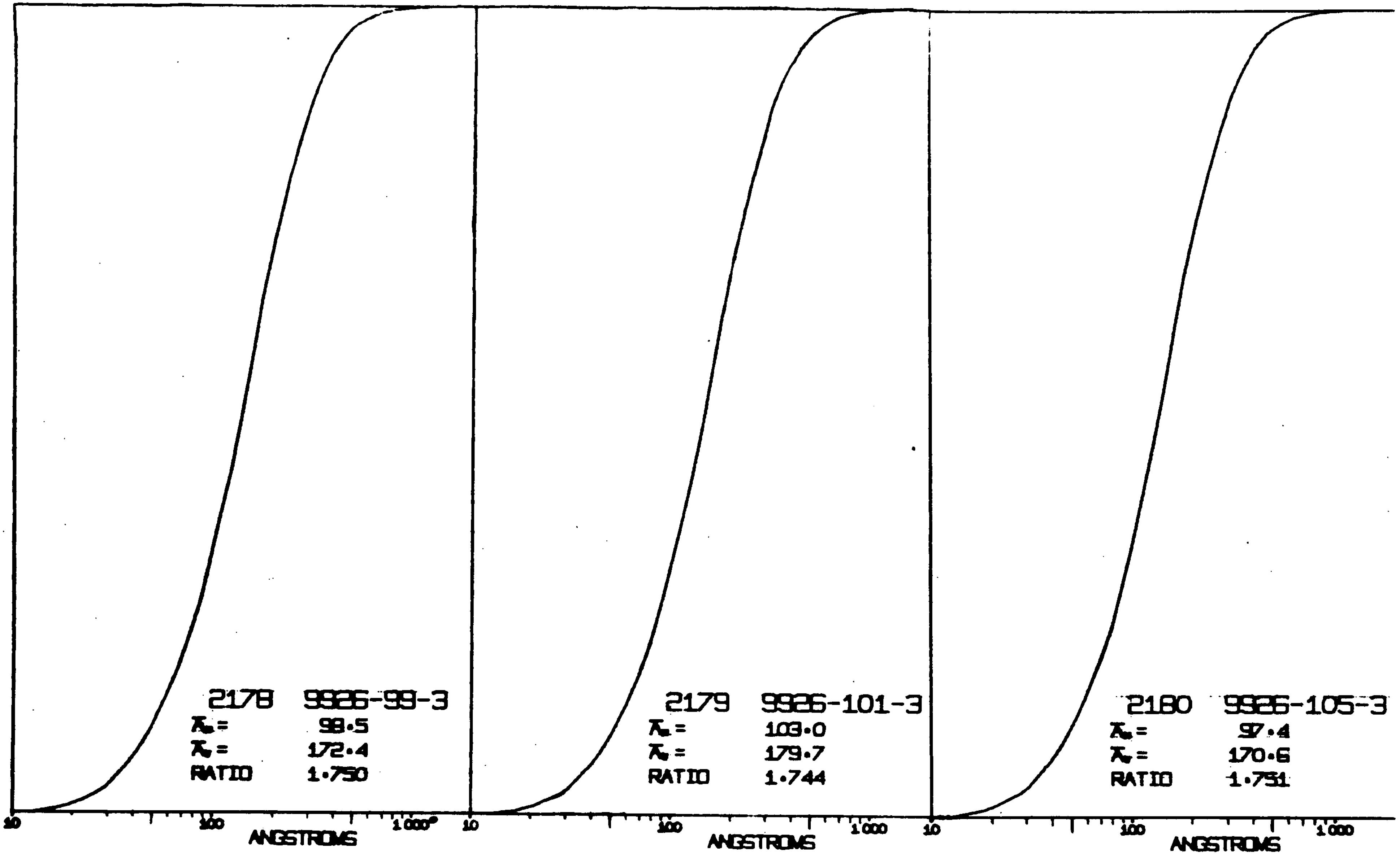


Figure 5 - Integral Gel Permeation Chromatograms

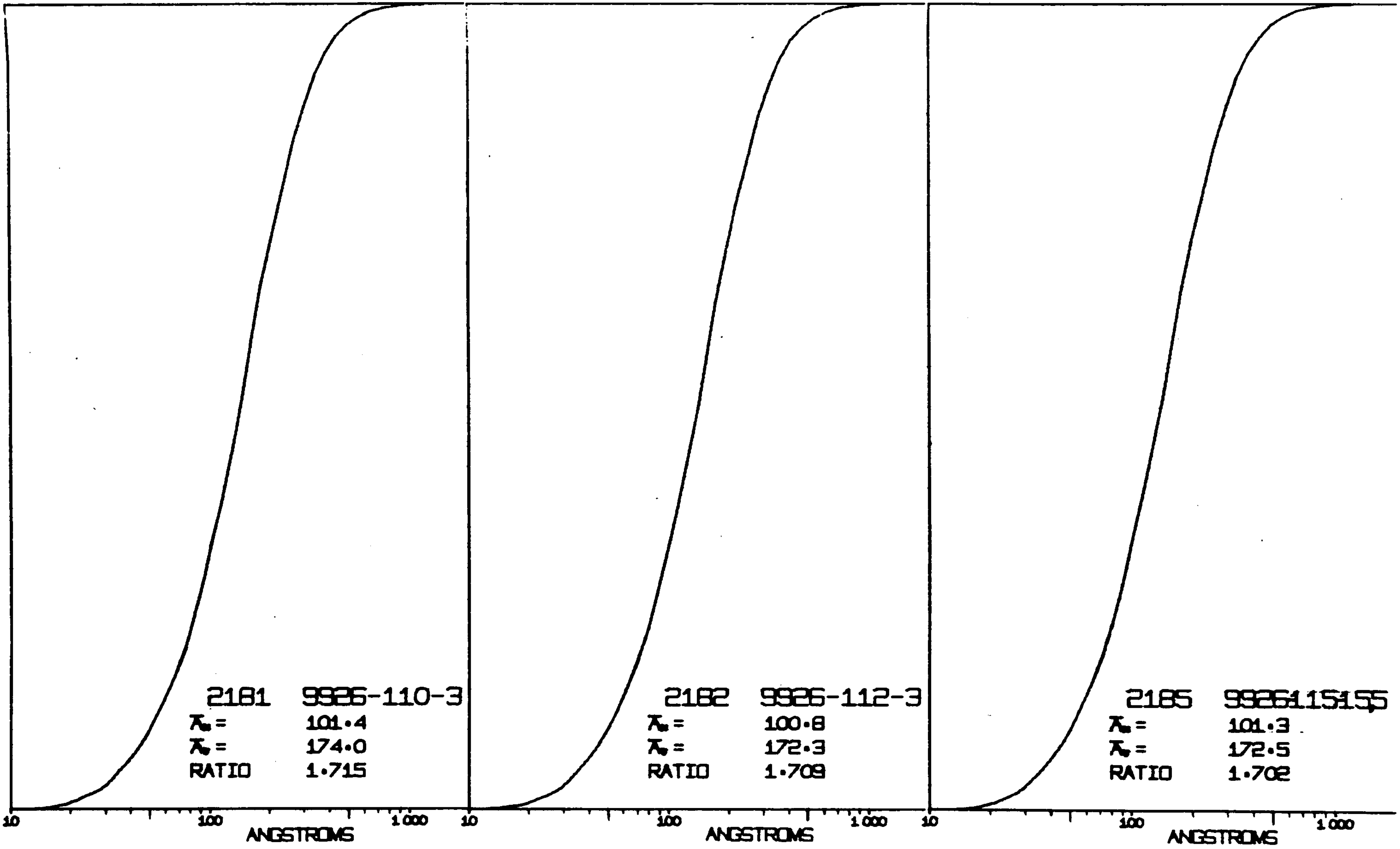


Figure 6 - Integral Gel Permeation Chromatograms

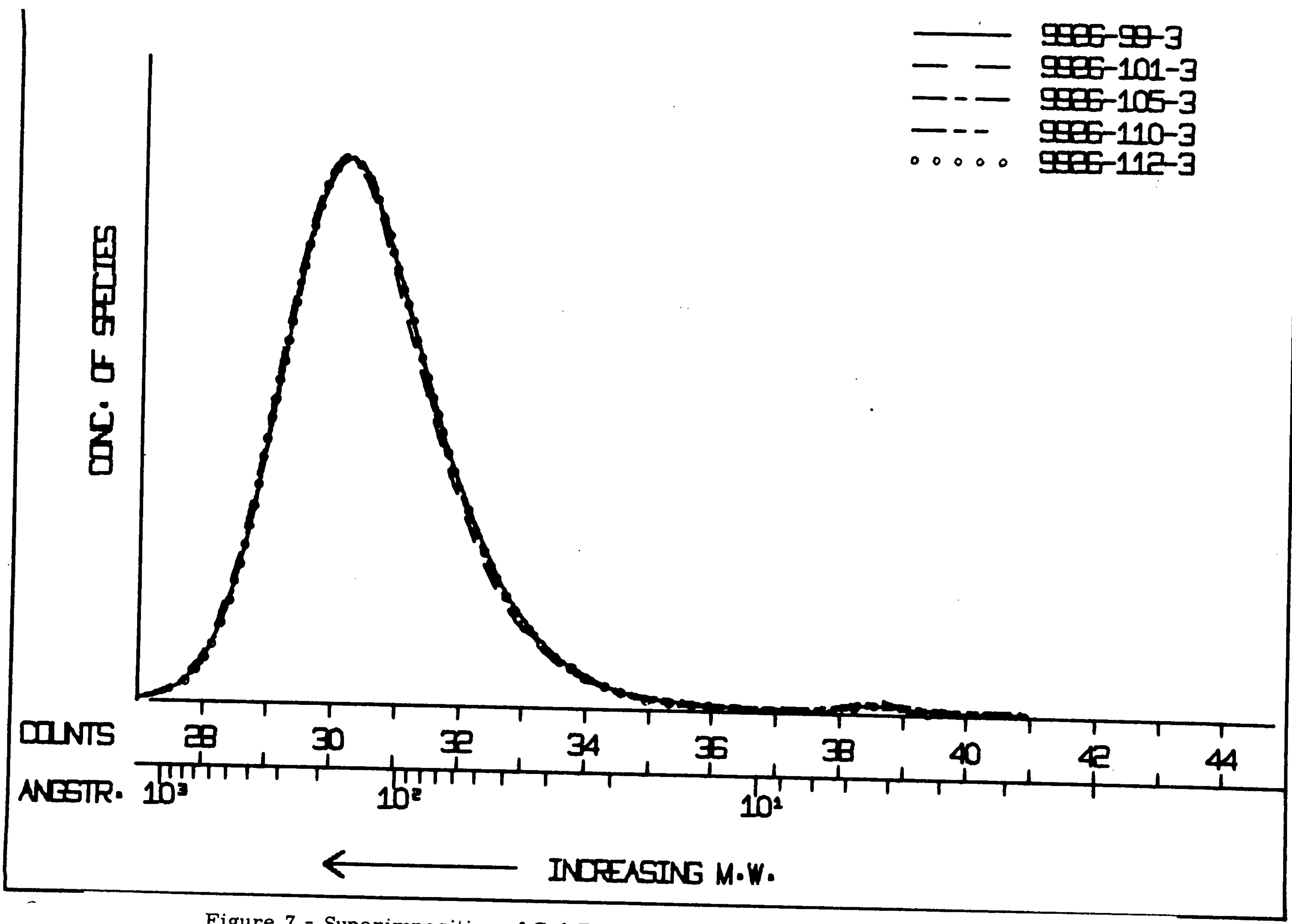


Figure 7 - Superimposition of Gel Permeation Chromatograms of Hydroxy Telechelic Polyisoprenes from The Second Production Attempt

Mixing by argon bubbles was continued overnight again to insure adequate dispersal of the ionol. The contents of the kettle were then heated to 40°C to reduce the viscosity, and discharged through the bottom valve into individual one pint glass jars. Twenty-three jars were filled. A 23 gram sample (designated 9926-115-15 1/2) was withdrawn between jars 15 and 16 to be used as a representative sample to characterize the composite product.

Analysis:

Hydroxyl Equivalent Weight (by acetylation)	1406±11
Number Average Mol. Wt. (V.P.O. in toluene, see Fig. 8)	2786±75
Average Functionality	1.98±06
Ionol Content	2600 ppm
Gel Permeation Chromatography $\bar{A}_n = 101.3$ $\bar{A}_w = 172.5$ $R = \bar{A}_w/\bar{A}_n = 1.70$	
Mol. Wt. from $\bar{A}_n = 27.33 \times 101.3 =$	2766±150
Brookfield Viscosity	62 poise @ 25°C

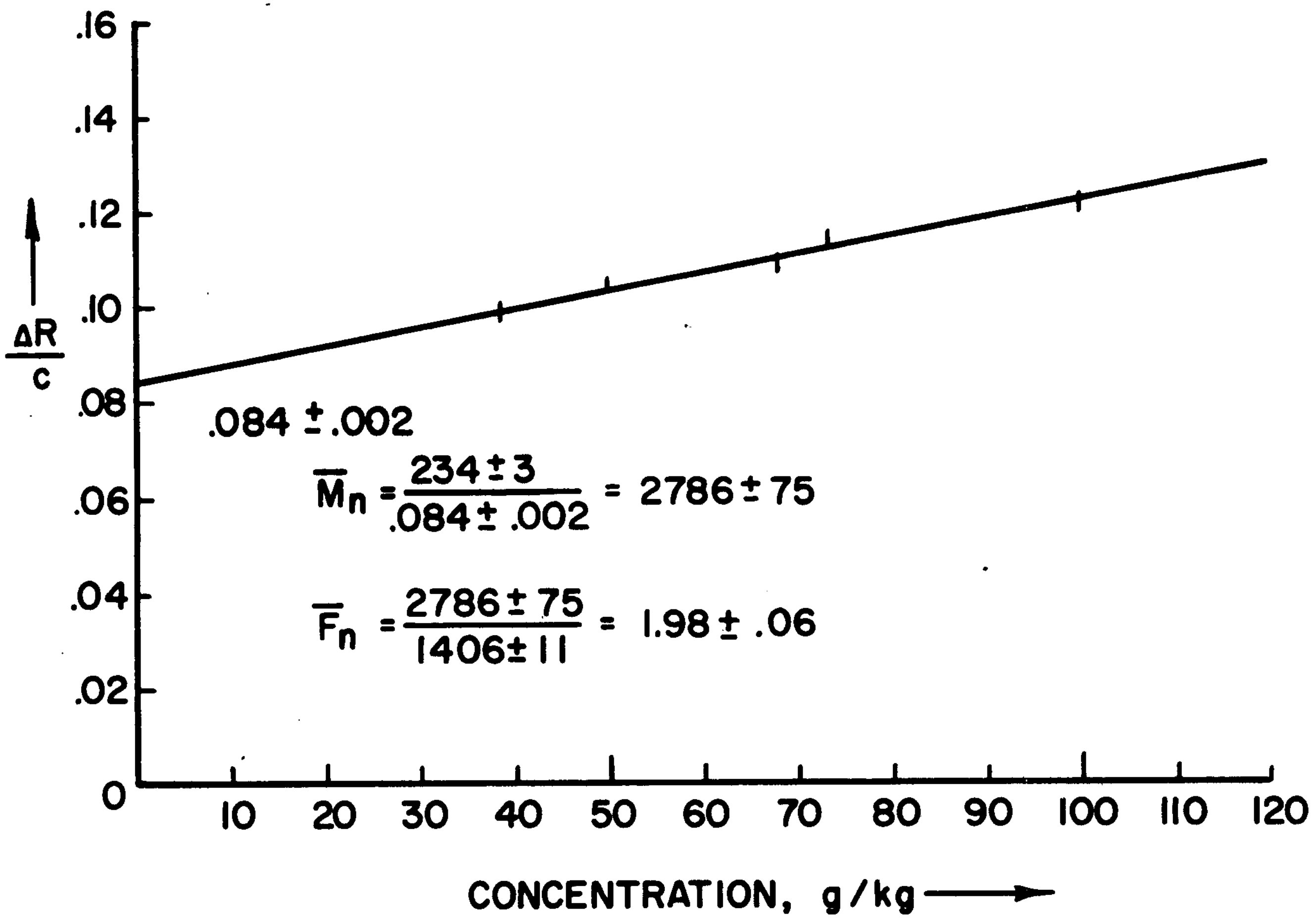


FIGURE 8. V.P.O. DETERMINATION OF MOL. WT. OF COMPOSITE 9926-115

B. Preparation of Saturated Liquid Hydrocarbon Prepolymers based on Other 1, 3-Alkadienes

The preparation of a saturated hydroxy-telechelic liquid hydrocarbon prepolymerby copper chromite hydrogenalysis of ester-telechelic polyisoprene satisfied to a large part the original objectives of our research for the Jet Propulsion Laboratory. The superior chemical inertness of a saturated hydrocarbon prepolymer was necessary if compatibility with the powerful solid oxidant nitronium perchlorate was to be achieved. In addition to this however, a need existed for binder prepolymers which would survive in the presence of conventional oxidants, such as ammonium perchlorate, over extended periods of time or at high temperatures for short periods of time. These characteristics are crucial for binders used in propellant formulations for interplanetary missions involving sterilization, long storage time in transit to the destination or both.

The saturated liquid hydrocarbon prepolymers which we prepared were deficient in two crucial areas which placed limitations upon their usefulness: the viscosity at a given temperature and the glass transition temperature were higher than those of generally used unsaturated hydrocarbon prepolymers or the polypropylene glycol prepolymers.

We proposed a route by which saturated liquid hydrocarbon prepolymers could be prepared having superior low temperature properties and possibly a lower viscosity as well.

Our approach is based upon the observation that glass transition temperatures encountered in poly-1-alkenes decrease in a regular fashion as the alkyl side chain becomes longer in these polyolefins. For example, polybutene-1 has a Tg at -25°C, poly-hexene-1 at -50°C and poly-octene-1 at -65°C (see J. Polymer Sci. 1A, 751 (1963) and J. Appl. Polymer Sci., 1, 121 (1959). These values can be extrapolated to the somewhat controversial value of about -87°C for polyethylene (which corresponds to an infinite length alkyl group). At some point, however, the side chains may themselves crystallize and prevent any further useful effect. This is illustrated in Figure 9.

Our previous experience with ethylene/propylene copolymers and the functionality problems caused by allylic hydrogen chain transfer indicate that an approach based upon the direct polymerization of α-olefins has little chance

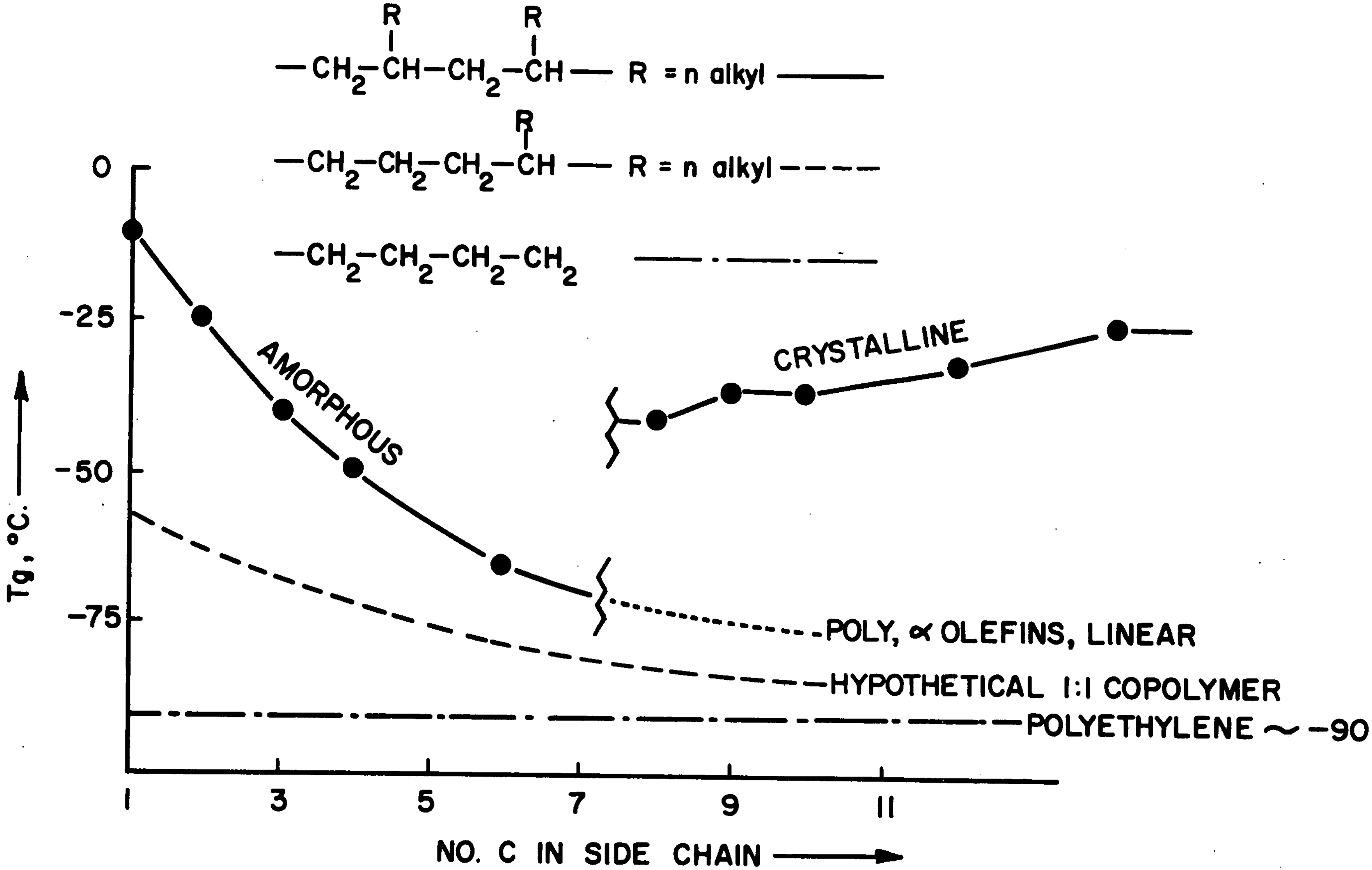
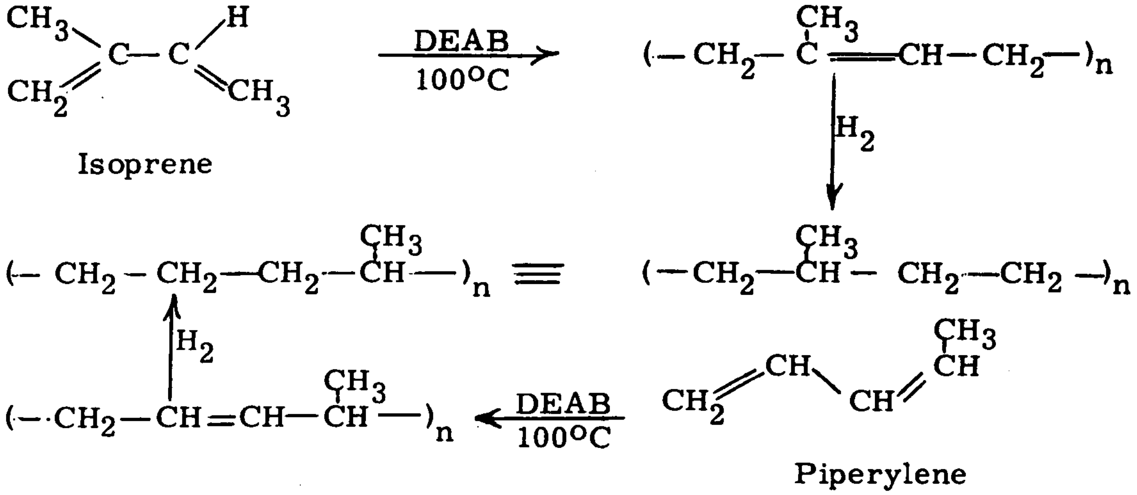


FIGURE 9. GLASS TRANSITION TEMPERATURE OF POLY-∝-OLEFINS WITH LINEAR SIDE CHAINS.

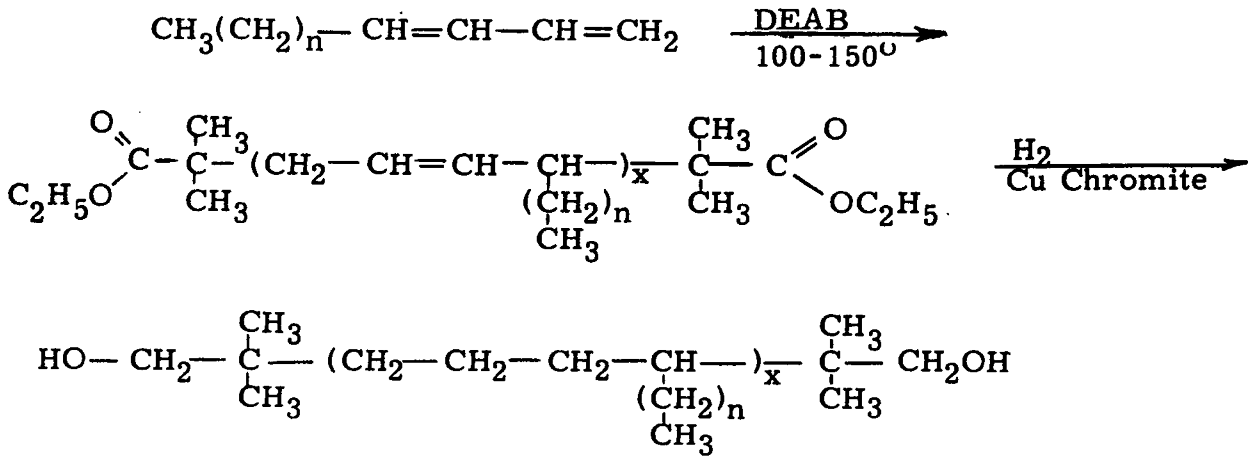
✓

of success. Polymerization of a substituted butadiene, followed by hydrogenation to give the saturated polymer is a more promising route to difuctional hydrocarbon polymers of low Tg.

Our previous work has shown that both isoprene and piperylene polymerize in the presence of diethylazobisisobutyrate to give difunctional polymers which remain liquid upon hydrogenation. It is interesting to note that the 1-4 polymers of these two isomeric dienes are indistinguishable after hydrogenation:



In view of the above equivalence, and the potentially easier synthesis of 1-alkyl substituted butadienes as compared with the 2-alkyl butadienes, we have decided to synthesize a series of 1-n-alkyl butadienes as monomers for polymerization and hydrogenation to give telechelic difunctional ethylene/1-n-alkene copolymers as shown below:



$$CH_3(CH_2)_n-CH=CH-CH=CH_2 \xrightarrow[100-150^{\circ}]{DEAB}$$

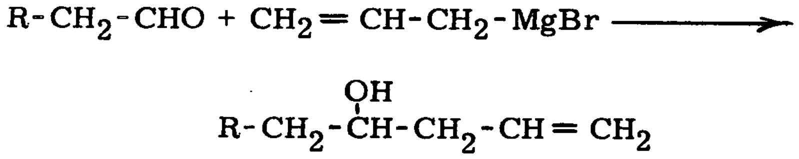
$$C_2H_5O-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-(CH_2-CH=CH-\underset{\underset{CH_3}{(CH_2)_n}}{CH}-)_x-\overset{CH_3}{\underset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[\text{Cu Chromite}]{H_2}$$

$$HO-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-(CH_2-CH_2-CH_2-\underset{\underset{CH_3}{(CH_2)_n}}{CH}-)_x-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH$$

1. Monomer Synthesis

The n-1, 3-alkadienes are generally not available in the quantities required for polymerization studies, so synthetic routes were required for the laboratory scale preparation of these potentially interesting monomers from more readily available starting materials. Two routes were devised for this synthesis. They are outlined in Figure 10.

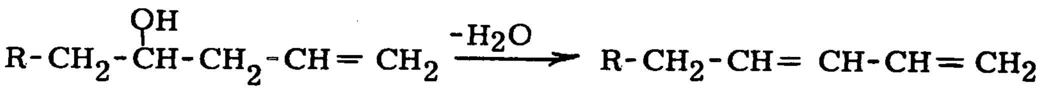
The first route involves the reaction of an allylic Grignard reagent with aldehydes to give a homoallylic alcohol.



$$R-CH_2-CHO + CH_2=CH-CH_2-MgBr \longrightarrow$$

$$R-CH_2-\overset{OH}{CH}-CH_2-CH=CH_2$$

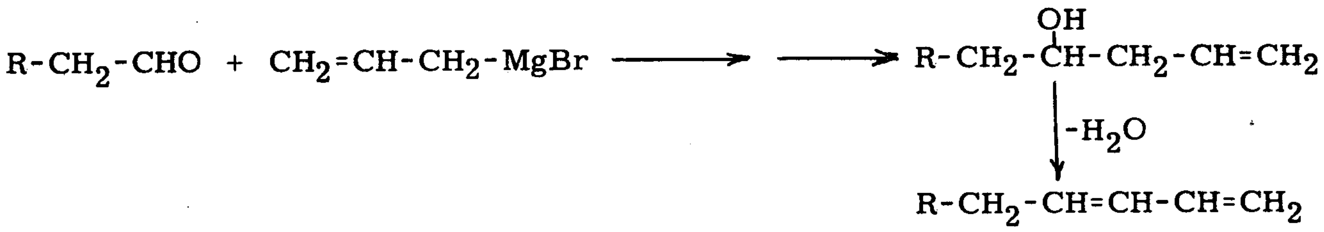
Dehydration of the above alcohol was expected to proceed predominantly to give the conjugated diene rather than the alternate possibility.



$$R-CH_2-\overset{OH}{CH}-CH_2-CH=CH_2 \xrightarrow{-H_2O} R-CH_2-CH=CH-CH=CH_2$$

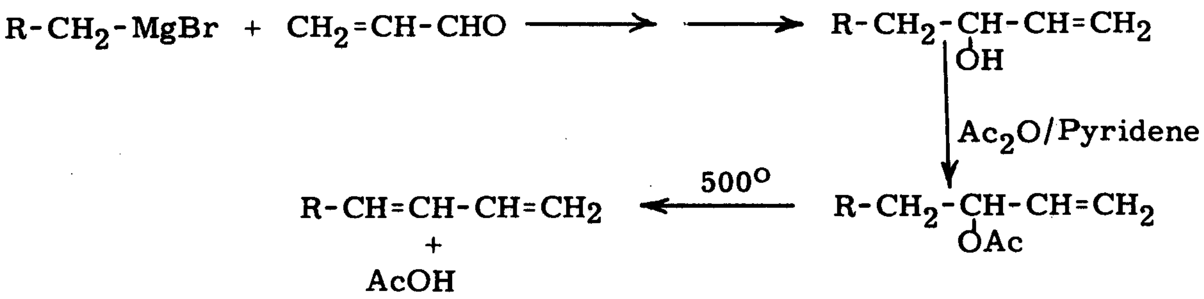
When this route was tried for the synthesis of n-1, 3-heptadiene, we found that the formation of the allylic Grignard reagent went smoothly below 10°C in diethyl ether to give the required reagent in about 60% yield. The major side

1) Allyl Grignard + Aldehydes, dehydration



$$R\text{-}CH_2\text{-}CHO + CH_2{=}CH\text{-}CH_2\text{-}MgBr \longrightarrow \longrightarrow R\text{-}CH_2\text{-}\overset{OH}{CH}\text{-}CH_2\text{-}CH{=}CH_2 \xrightarrow{-H_2O} R\text{-}CH_2\text{-}CH{=}CH\text{-}CH{=}CH_2$$

2) Alkyl Grignard + Acrolein, acetylation, pyrolysis



$$R\text{-}CH_2\text{-}MgBr + CH_2{=}CH\text{-}CHO \longrightarrow \longrightarrow R\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH{=}CH_2 \xrightarrow{Ac_2O/\text{Pyridene}} R\text{-}CH_2\text{-}\underset{OAc}{CH}\text{-}CH{=}CH_2 \xrightarrow{500^{o}} R\text{-}CH{=}CH\text{-}CH{=}CH_2 + AcOH$$

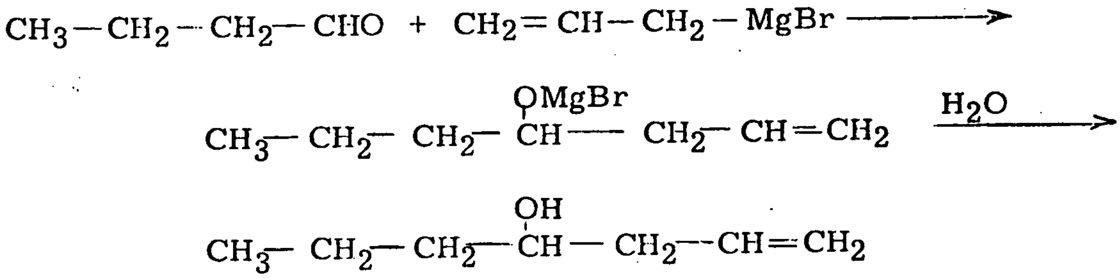
Figure 10. Synthetic Routes to n-1, 3-alkadienes

product was biallyl formed in the coupling reaction:

$$CH_2{=}CH{-}CH_2{-}Br \; + \; CH_2{=}CH{-}CH_2{-}MgBr \longrightarrow$$

$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 \; + \; MgBr$$

Addition of n-butanal to the solution of allyl magnesium bromide afforded allyl propyl carbinol after hydrolysis in a 56% overall yield based on allyl bromide:



$$CH_3{-}CH_2{-}CH_2{-}CHO \; + \; CH_2{=}CH{-}CH_2{-}MgBr \longrightarrow$$

$$CH_3{-}CH_2{-}CH_2{-}\overset{OMgBr}{\overset{|}{CH}}{-}CH_2{-}CH{=}CH_2 \xrightarrow{H_2O}$$

$$CH_3{-}CH_2{-}CH_2{-}\overset{OH}{\overset{|}{CH}}{-}CH_2{-}CH{=}CH_2$$

Three different methods were tried for the dehydration of this homoallylic alcohol:

1) Distillation from potassium hydrogen sulfate

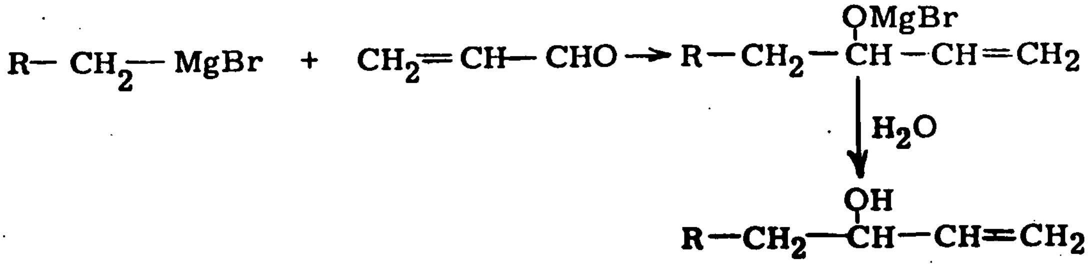
2) Distillation from sulfuric acid

3) Alumina at 200-220°C

Method (1) gave much tar remaining in the distillation pot and the distillate was predominantly the starting alcohol containing a mixture of several dienes. Method (2) was similar in results, however more tar resulted. Method (3) gave mostly unreacted alcohol and a trace of a mixture of dienes.

Because of the above difficulties in dehydration the allyl Grignard route to the n-1, 3-alkadienes was abandoned.

The second route starts with n-alkyl Grignard reagents to which acrolein is added. This results in the formation of allylic rather than homoallylic alcohols:

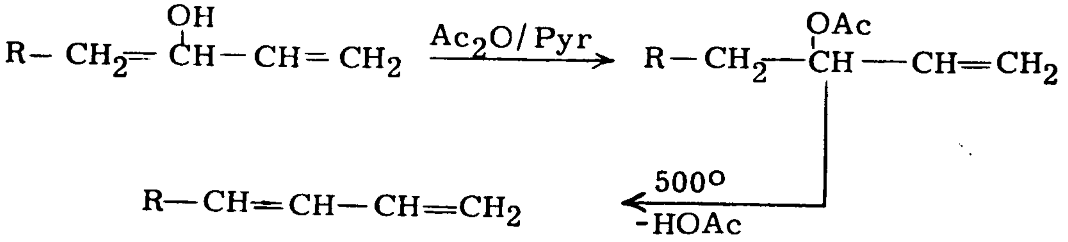


$$R{-}CH_2{-}MgBr \; + \; CH_2{=}CH{-}CHO \rightarrow R{-}CH_2{-}\overset{OMgBr}{\overset{|}{CH}}{-}CH{=}CH_2$$

$$\big\downarrow H_2O$$

$$R{-}CH_2{-}\overset{OH}{\overset{|}{CH}}{-}CH{=}CH_2$$

Acetylation followed by pyrolysis can result in the formation of only one diene:



The above route was first applied to the synthesis of nonadiene. n-Hexyl bromide was reacted with magnesium turning in ether to give hexylmagnesium bromide. To the resulting Grignard reagent solution was added an equimolar quantity of acrolein and the resulting adduct hydrolyzed to give the vinyl hexyl carbinol, bp. 74-79°C @ 6.8 mm, in 67% yield. Treatment of this alcohol with acetic anhydride in pyridine afforded the acetate in 80% yield. The N. M. R. Spectrum and integral (see Figure 11) were consistent with the proposed structure.

Pyrolysis of the acetate, by passage through a Vicor tube packed with glass helices at 500°C, gave a 40% conversion to nonadiene, bp. 50°/12 mm.

Using the same procedure we prepared octadiene and decadiene and found no experimental difficulties in applying this diene synthesis. Because of the approaching end of the experimental program it was decided to concentrate the remaining effort on the polymerization of nonadiene.

2. Diene Polymerization

a) Sealed Tube Polymerization

Into a pyrex tube 18 mm inside diameter and 200 mm long was placed 15 ml nonadiene and 2 ml diethylazobisisobutyrate. The tube was evacuated and then sealed with a flame. The sealed tube was placed in a bath at 100°C for 43 min (3 half lives of DEAB at 100°C). The tube was then cooled and broken open. The resulting polymer solution was evaporated on the rotary evaporator to give 2.9 grams colorless oil.

Infrared spectroscopy showed a strong ester carbonyl band at 1740 cm^{-1} indicating the presence of a trans disubstituted double bond. The

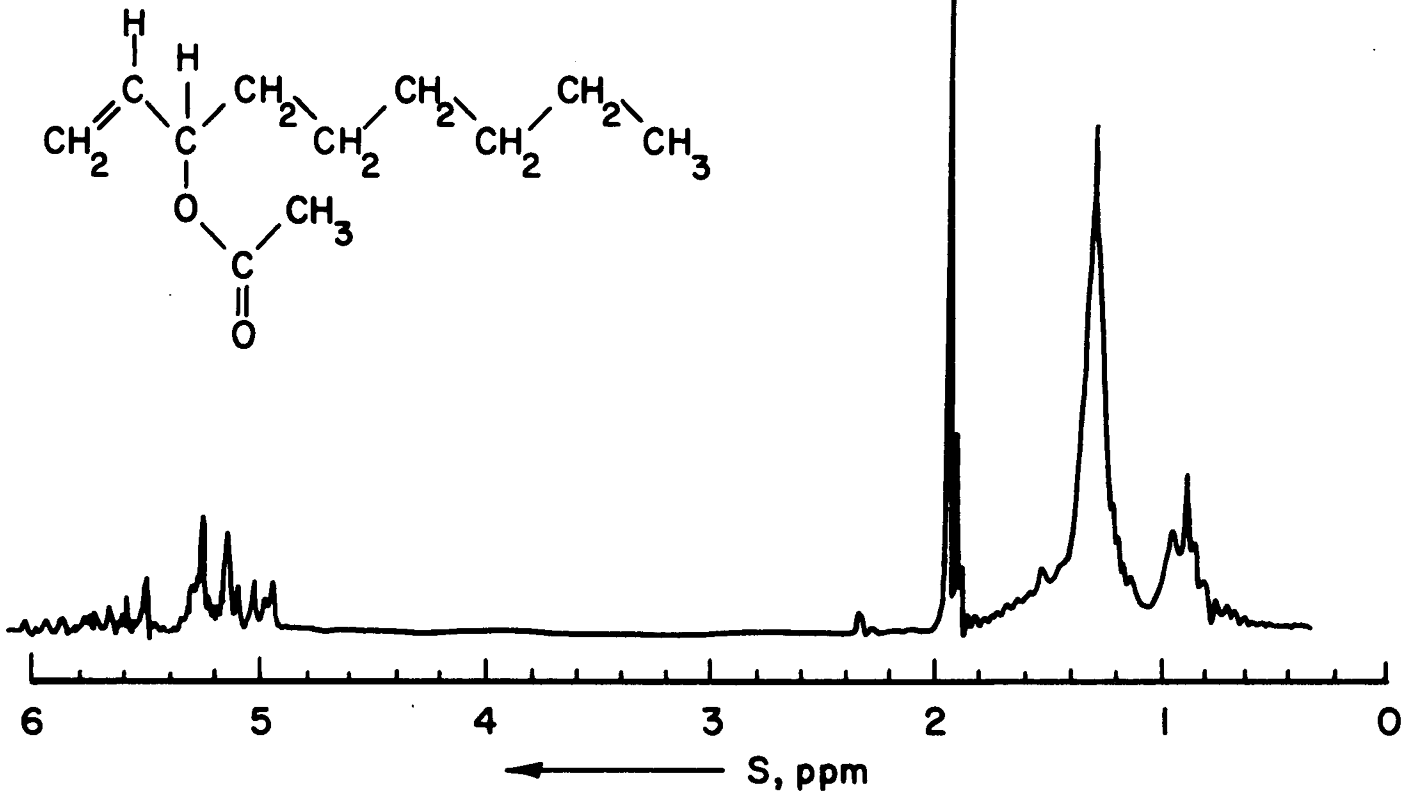
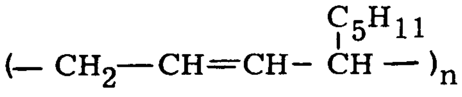


FIGURE 11. VINYL HEXYL CARBINYL ACETATE, N.M.R. SPECTRUM (60mc.)

relative intensities of these absorbances indicated that the product was a relatively low molecular weight polymer.

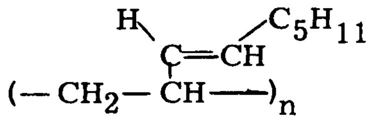
The nuclear magnetic spectrum was consistent with either 1, 2 or 1, 4 polymerization but ruled out 3, 4 as a possibility:



$$(\!-CH_2\!-\!CH\!=\!CH\!-\!\underset{|}{\overset{C_5H_{11}}{CH}}\!-\!)_n$$

1 - 4

or



1 - 2

In both of the above structures the olefinic to allylic hydrogen ratio is 2:3 or 0. 67, whereas in the 3, 4 structure the ratio is 2:1. The actual spectrum showed an olefinic to allylic ratio of 2:3. 2 or 0. 63. In addition to the above information, the ratio of the area of the $-O-CH_2-$ signal at $\delta = 3.95$ ppm to the total spectrum area indicated that, if difunctional, the degree of polymerization of the polymer was 3. 58 corresponding to a molecular weight of 1350.

b) Polymerization with Incremental DEAB Feed

Into a 250 ml three-necked flask fitted with mechanical stirrer, addition funnel thermometer and nitrogen inlet, was placed 50 grams nonadiene 75 grams benzene and 0. 25 ml 50% DEAB in benzene. The polymerization flask was swept out with nitrogen, and then heated with stirring until the internal temperature reached 100°C. Every ten minutes thereafter for a total polymerization time of two hours a 0. 25 ml portion of 50% DEAB in benzene solution was added by syringe. At the end of the addition, the polymerization was stopped by rapidly cooling to room temperature and the unreacted monomer and benzene solvent were removed on the vacuum rotary evaporator. The residue, 16 grams of a straw colored oil, was examined by infrared spectroscopy. This showed a strong ester carbonyl at 1740 cm^{-1} and a band at 970 cm^{-1} due to a trans disubstituted carbon-carbon double bond.

Reduction of three grams of the above product with a large excess (4 ml of 70% Vitride in toluene) of "Vitride" gave the hydroxyl terminated polynonadiene. Examination of this material by two-dimensional thin layer chromatography (2% ethanol/benzene vs. acetone) showed that it was predominantly (over 90%) composed of a single component having R_f and R'_f values appropriate for a low molecular weight difunctional polymer: R_f = .05 to .60, R'_f = .89 to .95. Faint traces of material were also present on the regions of the plate appropriate for mono and nonfunctional polymer, as well as a spot near R_f = O.

Infrared spectroscopic analysis of the reduced polymer using neopentyl alcohol as reference gave a hydroxyl equivalent weight of 388.

c) Polymerization with Slow Continuous DEAB Feed

To facilitate the preparation of a higher molecular weight polymer a device for feeding a dilute solution of DEAB in benzene into a polymerization vessel was constructed by drawing out the tip of a 10 ml burette into a very fine capillary tube having an opening approximately 0. 1 mm diam. The length of the capillary was adjusted by breaking off the tip until a flow rate of 1. 5 ml per hr was obtained from a column of 5% DEAB in benzene 40 cm high. This addition device was fitted into a 100 ml steam jacketed all glass reaction vessel equipped with mechanical stirrer, thermometer and means for sweeping with nitrogen (see Figure 12).

Into this reactor was placed 50 ml (37. 4g) of 1, 3-nonadiene. After sweeping the reactor air space with nitrogen and maintaining a weak positive pressure of nitrogen on the system (approx 0. 5 mm Hg above atmospheric) the steam was turned on and the initiator feed started simultaneously. Over the length of the run of 15 hrs duration at 100°C a total of 19-74 ml of 5% DEAB in benzene was fed in. The rate varied from 1. 7 ml/hr when the burette was full to 0. 9 ml/hr when nearly empty. The average feed rate was 1. 32 ml/hr. Figure 13 shows a plot of volume fed vs. run time. At the end of the run the DEAB feed was terminated and cooling water circulated in the jacket.

The unreacted monomer and the benzene were distilled off on the rotary evaporator at 2 mm pressure. Devolatilization was completed by sweeping the partially evacuated flask containing the polymeric residue overnight with a stream of nitrogen. The residue was 7. 68 grams of a colorless slightly hazy viscous liquid. Infrared spectroscopy showed an ester carbonyl at 1740 cm^{-1} which was considerably weaker than the strong double bond absorption at 970 cm^{-1}. This result showed that the slow continuous feed procedure did result in a higher molecular weight product than had been obtained in the previous experiment. In the spectrum of the product from (b) above the carbonyl absorption was considerably stronger than the double bond absorption.

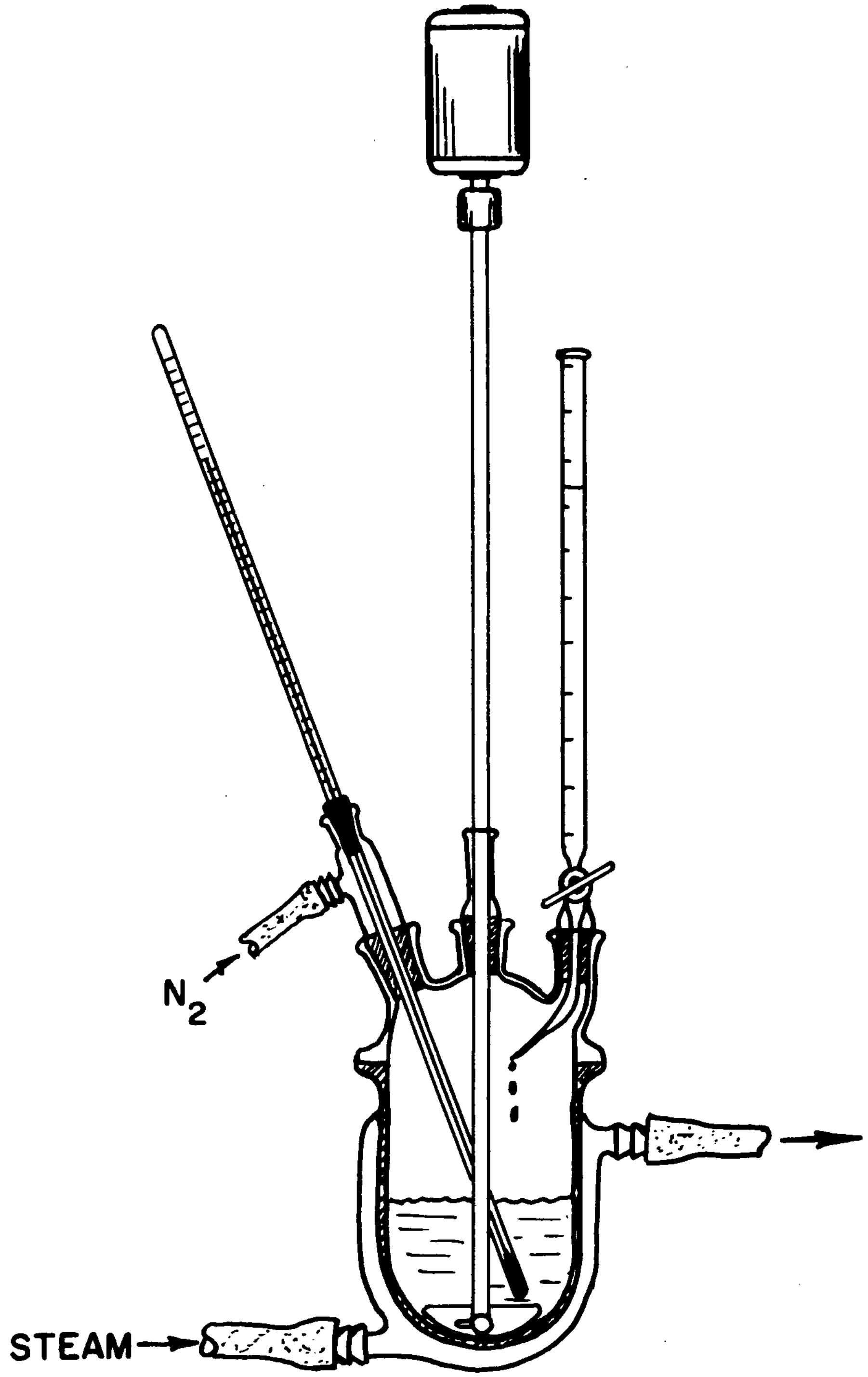


FIGURE 12. MINATURE REACTOR FOR NONADIENE POLYMERIZATION

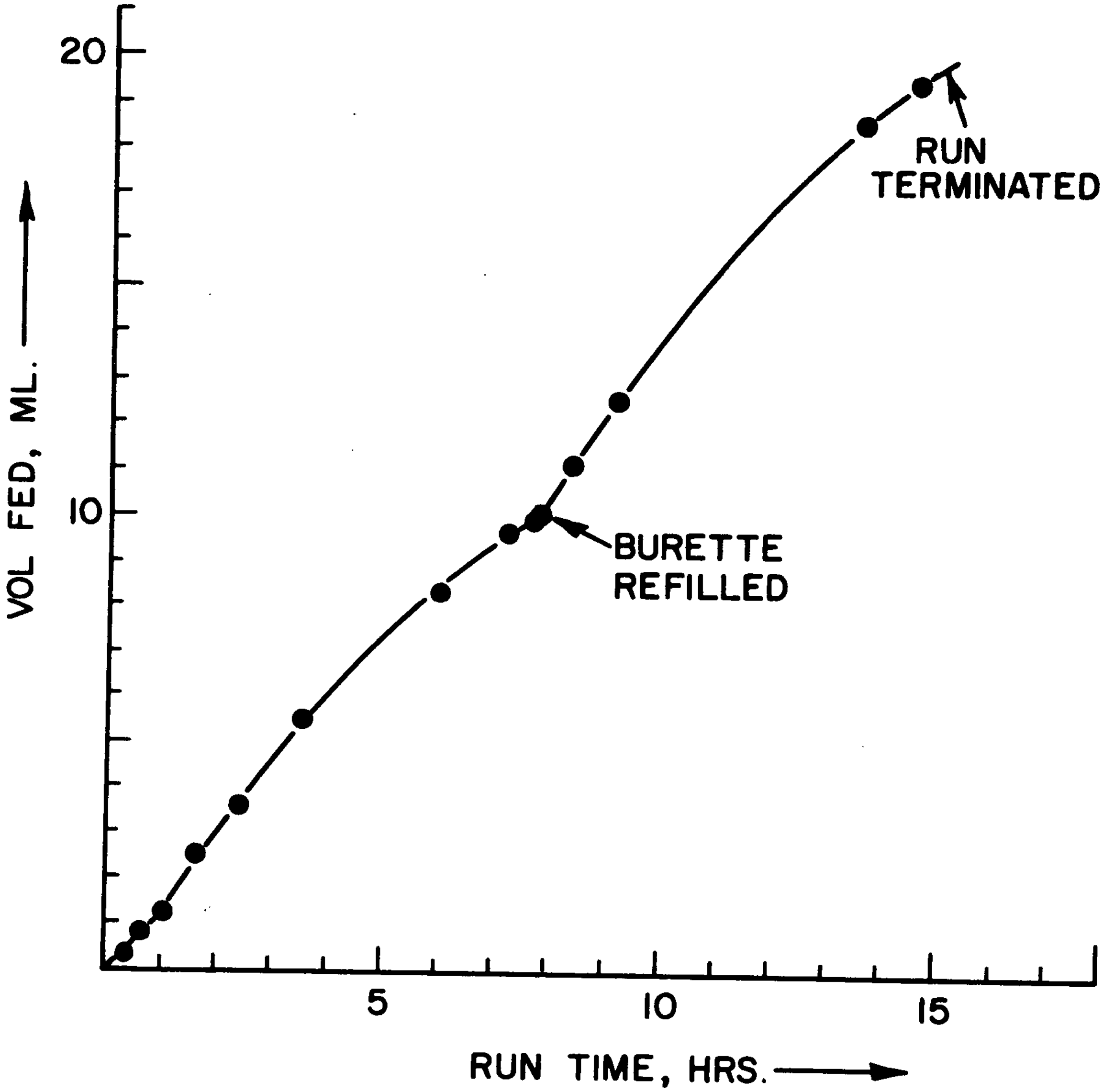


FIGURE 13. INITIATOR FEED TO MINIATURE REACTOR

d) Hydrogenation of Polynonadiene with Copper Chromite Catalyst

All of the product from part (c) was dissolved in 50 ml methyl cyclohexane and placed in a 300 ml stainless steel bomb along with 3 grams Harshaw copper chromite catalyst and another 50 ml methyl cyclohexane solvent. The bomb was then purged three times with hydrogen and pressurized to 2140 psi with hydrogen and heated, while agitating by rocking, to 290°C. During this heating period, which required two hours, the pressure rose to 3500 psi. At this point the pressure was increased to 4040 psi and the heat shut off, allowing the bomb to cool overnight to room temperature while being agitated under a hydrogen atmosphere at 4000 psi.

The reaction mixture was filtered to remove the catalyst and then evaporated to give 7.16 grams (93% recovery) of colorless hazy liquid polymer. Infrared spectroscopy showed that the ester groups and the double bonds had been hydrogenated and that no more than 0.6% of the ester groups and 0.5% of the unsaturation remained. A hydroxyl absorption was present at 3340 cm^{-1}. The $\overline{M}_n$ (by V.P.O. in Toluene at 38°C) was 1623 ± 76.

Since insufficient sample was available to determine the Brookfield viscosity, a 1 ml pipette with .1 and .01 ml divisions was calibrated for use as a viscometer. The pipette chosen had an internal diameter of 3.21 mm. It was used in the inverted position, allowing the liquid to flow from the 1.0 ml mark to the 0.0 ml mark, flowing out of the unconstricted end of the pipette and dripping freely into a vial. Four hydrocarbon diol prepolymers of known Brookfield viscosity were used for the calibration which is shown in Figure 14. Next, the hydrogenated polynonadiene sample was run through the pipette, giving an efflux time of 455 sec. From the calibration curve we read a viscosity of 63 poise.

Figure 15 shows the viscosity molecular weight relationships for hydroxy-telechelic polyisoprene and its saturated derivative. Note that the saturated product has a viscosity of 240 poise at $\overline{M}_n$ = 1623 and the unsaturated product has a viscosity of 40 poise. By comparison the hydrogenated polynonadiene has a much more favorable viscosity than the hydrogenated polyisoprene.

Figure 16 shows the temperature dependance of the viscosity of two different hydrogenated polyisoprenes one of 4025 $\overline{M}_n$ and the other 1500. The 1500 $\overline{M}_n$ product's viscosity does not decrease to 63 poise until it is

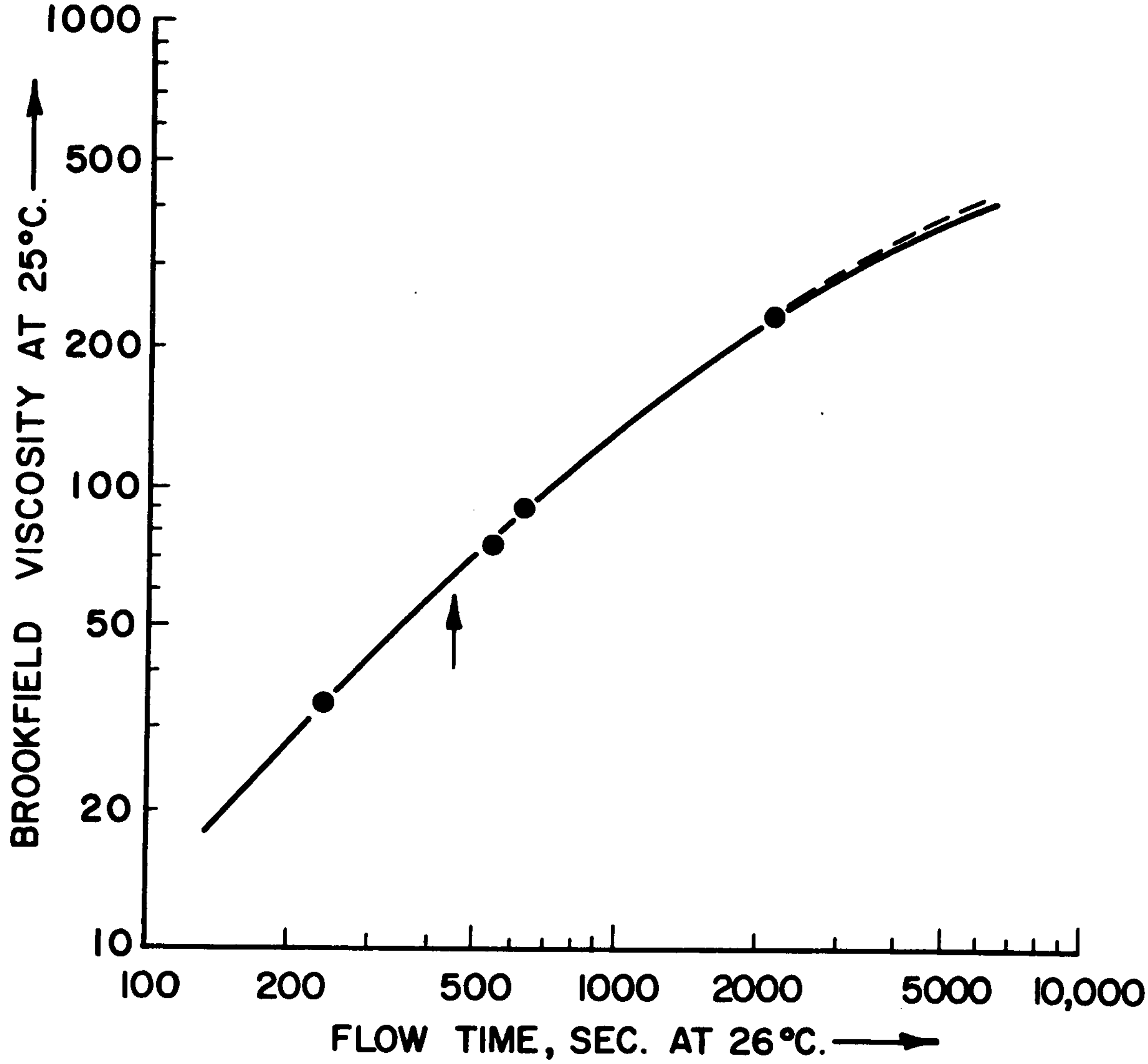


FIGURE 14. CORRELATION OF CAPILLARY FLOW TIME WITH BROOKFIELD VISCOSITY.

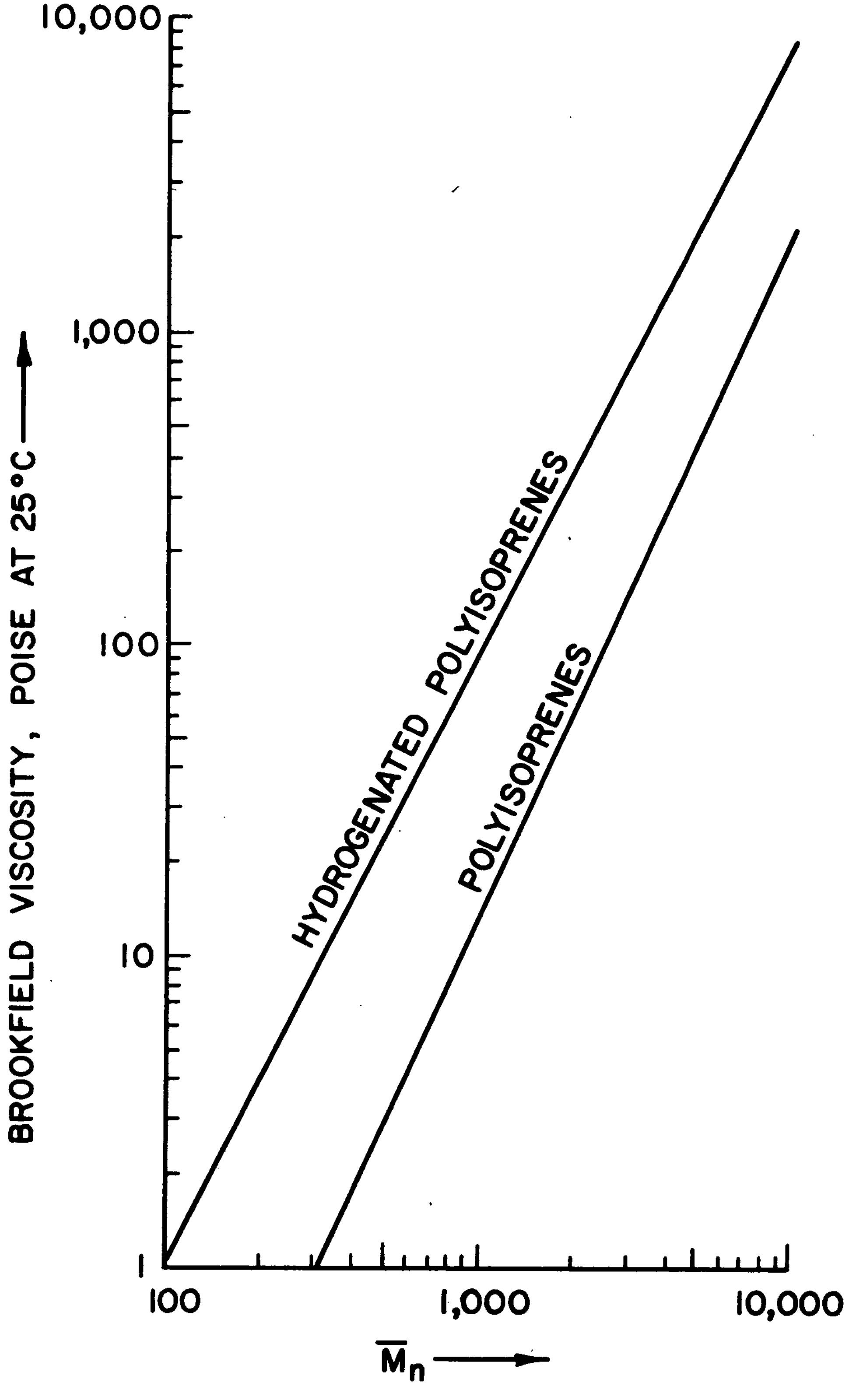


FIGURE 15. VISCOSITY – MOLECULAR WEIGHT RELATIONSHIPS FOR HYDROXY-TELECHELIC POLYISOPRENE AND THE HYDROGENATED DERIVATIVE.

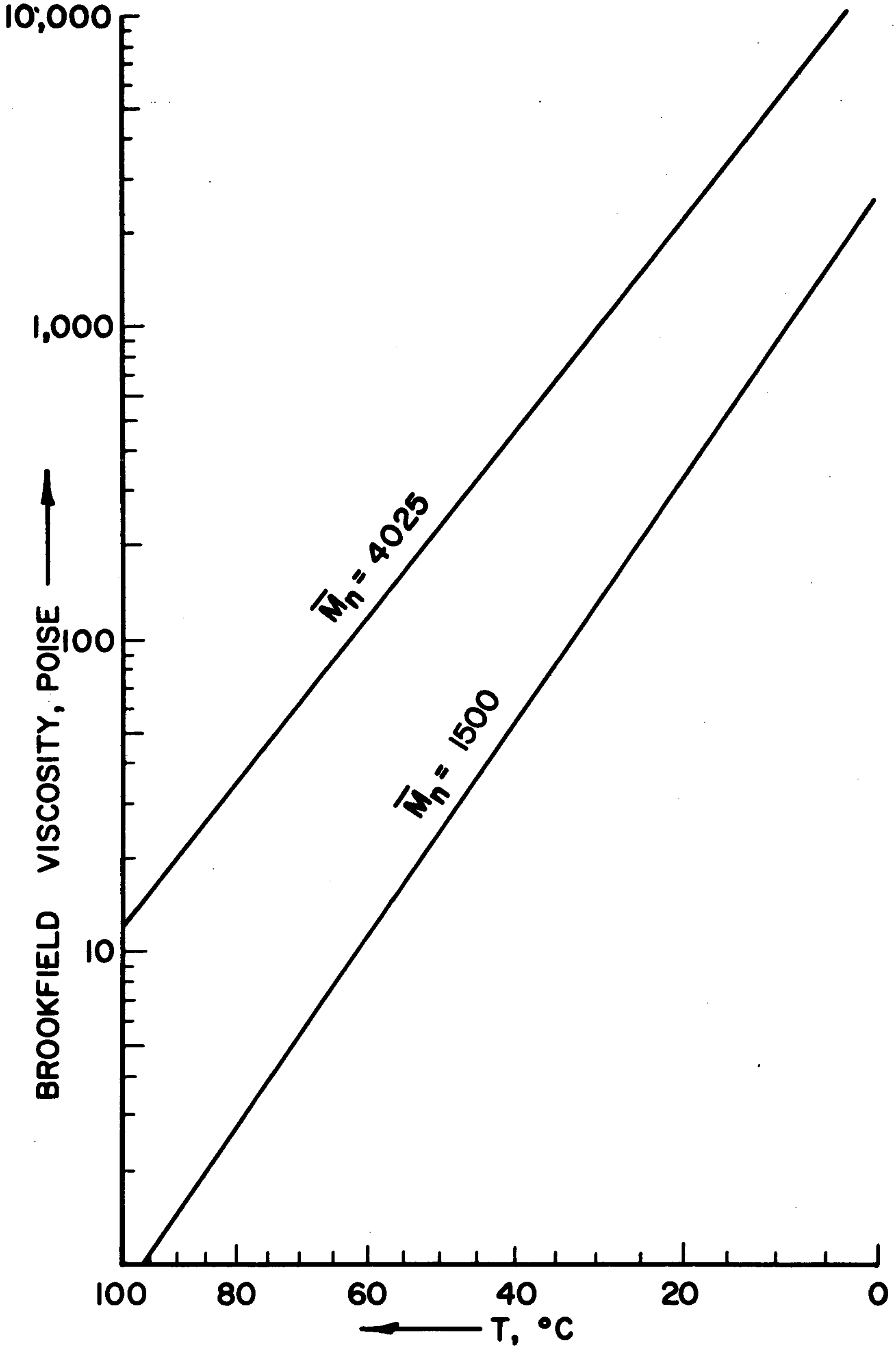


FIGURE 16. TEMPERATURE DEPENDANCE OF VISCOSITY FOR HYDROGENATED POLYISOPRENES.

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warmed to 38°C and the 4025 $\overline{M}_n$ product must be heated to 71°C to reach the same low viscosity.

The torsion pendulum was used to measure the glass transition temperature of the hydrogenated polynonadiene sample. An asbestos cloth strip was impregnated with the liquid sample and the mechanical loss of the composite measured from -130°C to -40°C. Figure 17 shows the results obtained.

The maximum point in the mechanical loss curve at -65°C is the glass transition temperature. The frequency of the torsion pendulum at the Tg was 1.5 cycles per second.

For purposes of comparison a 2000 molecular weight sample of hydrogenated polyisoprene having hydroxyl end groups (29-EMS-39) was also examined with the torsion pendulum. Its mechanical loss curve is shown in Figure 18. The maximum at -47°C is the glass transition temperature, measured at 1.5 cycles per second.

These measurements are to be contrasted with the penetrometer measurements of the glass transition temperature, which correspond to near-zero measurement frequencies. The hydrogenated polyisoprene sample has a Tp of -57.7°C whereas the Tp of the hydrogenated polynonadiene was 17 degrees lower: -74.7°C.

The improvement in room temperature viscosity and the decrease in Tg obtained in the hydrogenated polynonadiene establish polymerization of n-1, 3-alkadienes as a promising route to saturated liquid hydrocarbon polymers of improved processing characteristics and superior low temperature properties.

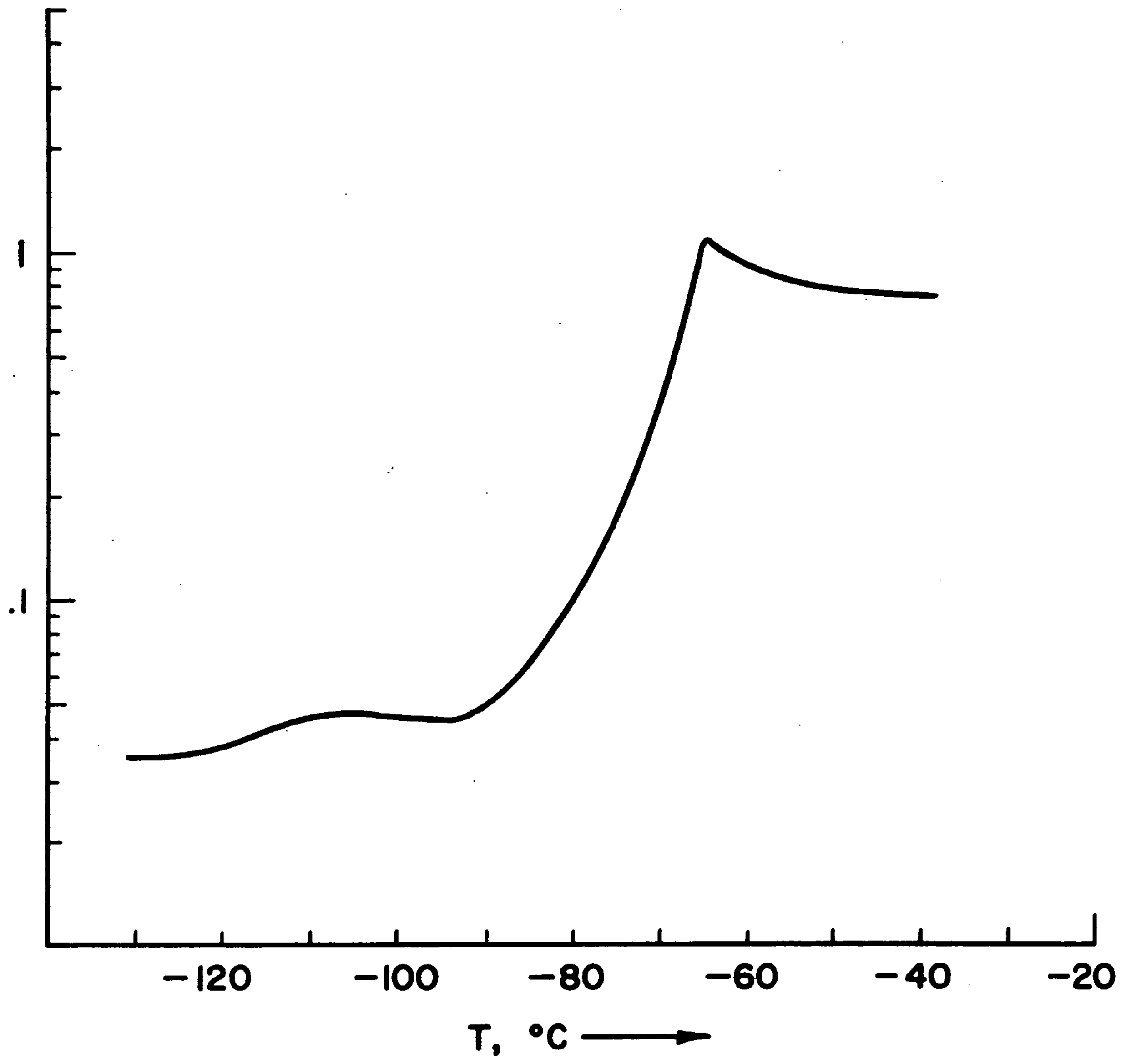

FIGURE 17. MECHANICAL LOSS AS A FUNCTION OF TEMPERATURE, HYDROGENATED POLYNONADIENE TEST FREQUENCY = 1.5 CPS.

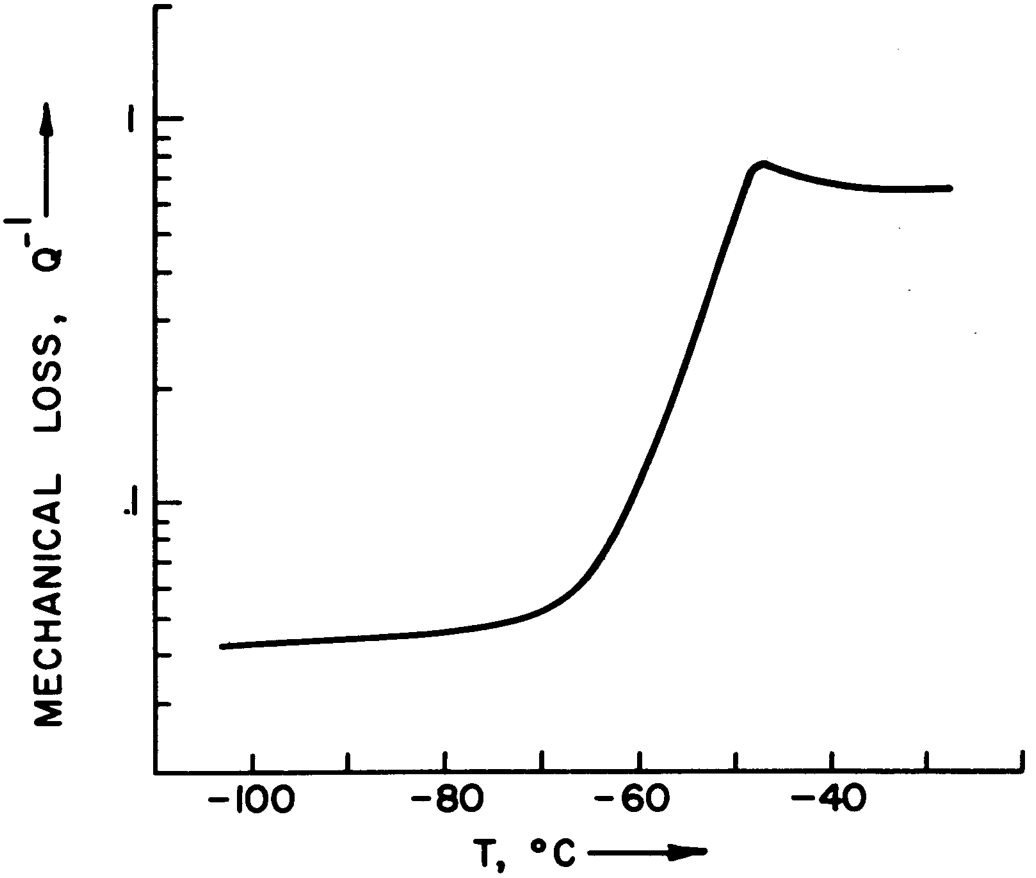

FIGURE 18. MECHANICAL LOSS AS A FUNCTION OF TEMPERATURE FOR HYDROGENATED POLYISOPRENE 29-EMS-39.

C. Linear Urethane Chain Extension Studies

The chain extension reaction of our hydroxyl telechelic hydrogenated polyisoprene prepolymers with hexamethylene diisocyanate was monitored by GPC with two purposes in mind. First, this reaction would help verify the hydroxy-difunctionality of the prepolymer since the presence of higher functionalities leads to gel product, and monofunctional molecules cannot advance past a degree of polymerization of one. Also, the study of the chain extension reaction itself would allow a better understanding of the relationship of molecular weight to urethane elastomer strength.

1. Statistics of Condensation Polymers

It is appropriate to refer to the statistics of linear step reaction polymerizations which have been described by Flory[2]. For a simple polymerization system of two pure bifunctional monomers (undergoing no side reactions) A-A and B-B, the number and weight average degree of polymerization can be shown to be[3].

$$\overline{DP}_n = \frac{1}{1 - 2xa} \tag{1}$$

$$\overline{DP}_w = \frac{1 - x + 4xa - 4x^2a + xa^2}{1 - x - xa^2} \tag{2}$$

Where a is the fraction of A groups reacted and x is the mole fraction of all reactive groups that are of type A where $A < B$, the polydispersity can be described by

$$\frac{\overline{DP}_w}{\overline{DP}_n} = \frac{(1 - x + 4xa - 4x^2a + xa^2)(1 - 2xa)}{1 - x - xa^2} \tag{3}$$

Equations for the cumulative and differential molecular weight distribution have also been derived[3]. These equations are particularly useful since both the extent of reaction a and stoichiometry of the reactants x are variables in the equations. For condensation polymerization of this type where reactants are present in equal stoichiometric amounts, both the number and weight average DPs approach infinity as the reaction approaches completion. However, if the reaction is only slightly less than complete or

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2. P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press. (1957)

3. G. G. Lowry, Macro Chains and Monte Carlo Calculations in Polymer Science, Marcel Dekker (1970)

the stoichiometry of the two reactants not precisely equal, high molecular weight products cannot be obtained. For example, a one mole percent deficiency of a reactant, possibly through a weighing error, volatilization or side reaction, limits the $\overline{DP}_n$ to 100.

2. Linear Extension of Prepolymer with Hexamethylene-Diisocyanate

In the following studies we used a hydroxyl-telechelic hydrogenated polyisoprene, sample 9670-110, having a number average molecular weight of 2370 and a functionality of 1.99.

In the first chain extension experiment, the prepolymer was allowed to react with hexamethylene diisocyanate at 75° C using three different ratios (R) of $[OH]/[NCO]$, 1.20 (A), 1.00 (B) and 0.83 (C). Samples were end capped with methanol and analyzed by GPC to obtain molecular weights and molecular weight distributions after 15, 30, 45, 60, 120 minutes and 48 hours of reaction. The resulting number and weight average chain lengths ($\overline{A}_n$, $\overline{A}_w$), polydispersity ($\overline{A}_w/\overline{A}_n$) and approximate number average molecular weights are presented in Table VI. The number average molecular weights were obtained by multiplication of the average $\overline{A}_n$ values by a constant, 18.0, which was calculated from consideration of the chain lengths of both the polyisoprene and diisocyanate. A constant of 24.7 and 25.7 for saturated and unsaturated low molecular weight polyisoprenes have been used previously with this column configuration.

From these data we found a regular increase in molecular weight in each set of samples as the reaction proceeded. A final number average degree of polymerization of 2.4 for A, 4.2 for B and 2.9 for C was realized, the 1.00 stoichiometric sample B having the greatest extension, as expected (Figure 19). The molecular growth for B after 15,60 minutes and 48 hours of reaction can be seen from the chromatograms displayed in Figure 20. It was also found that the "off" stoichiometry samples A and C exhibited rapid initial chain growth which greatly diminished after 120 minutes of reaction.

The presence of gel in samples B and C and the high molecular weight shoulder in the final B sample in Figure 20 is consistent with either the presence of trifunctional groups in the polyisoprene or allophonate formation. However, sample B does contain soluble molecules which are over one million in molecular weight or degree of polymerization approximately 400, and one third of the sample is over 100,000 molecular weight.

To minimize the occurrence of allophonate formation, another series of urethanes was prepared with $[OH]/[NCO]$ ratios of 1.1, 1.0 and 0.9 in 30 parts of benzene at room temperature. The reaction was terminated after two weeks by addition of methanol. The GPC data are given in

HEXAMETHYLENE DIISOCYANATE AT 75°C

Sample	Reaction Time (Min.)	$\bar{A}_n$	$\bar{A}_w$	$\bar{A}_w/A_n$	$\bar{M}_n$
9670-110-2	Polyisoprene Reactant	98.5	174	1.77	2430
Hexamethylene Diisocyanate	Reactant	15.0	15.0	1.00	168
9670-148-1	15	184	433	2.35	3310
	30	251	645	2.57	4520
$[OH]/[NCO] = 1.20$	45	303	795	2.62	5450
	60	316	941	2.98	5690
	120	347	1100	3.17	6250
	48 hr. (soluble)	343	1055	3.07	6170
9670-148-2	15	139	296	2.14	2500
	30	184	419	2.27	3310
$[OH]/[NCO] = 1.00$	45	229	566	2.48	4120
	60	275	696	2.53	4950
	120	349	1212	3.47	6290
	48 hr. (some insolubles)	607	9180	15.11	10900
9670-148-3	15	164	363	2.21	2950
	30	226	537	2.38	4070
$[OH]/[NCO] = 0.83$	45	279	715	2.57	5020
	60	302	840	2.78	5490
	120	322	1180	3.67	5800
	48 hr. (mostly insoluble) (data on soluble portion only)	419	3190	7.59	7540

FIGURE 19

CHROMATOGRAMS ON FINAL URETHANE PRODUCT PREPARED AT 75°C

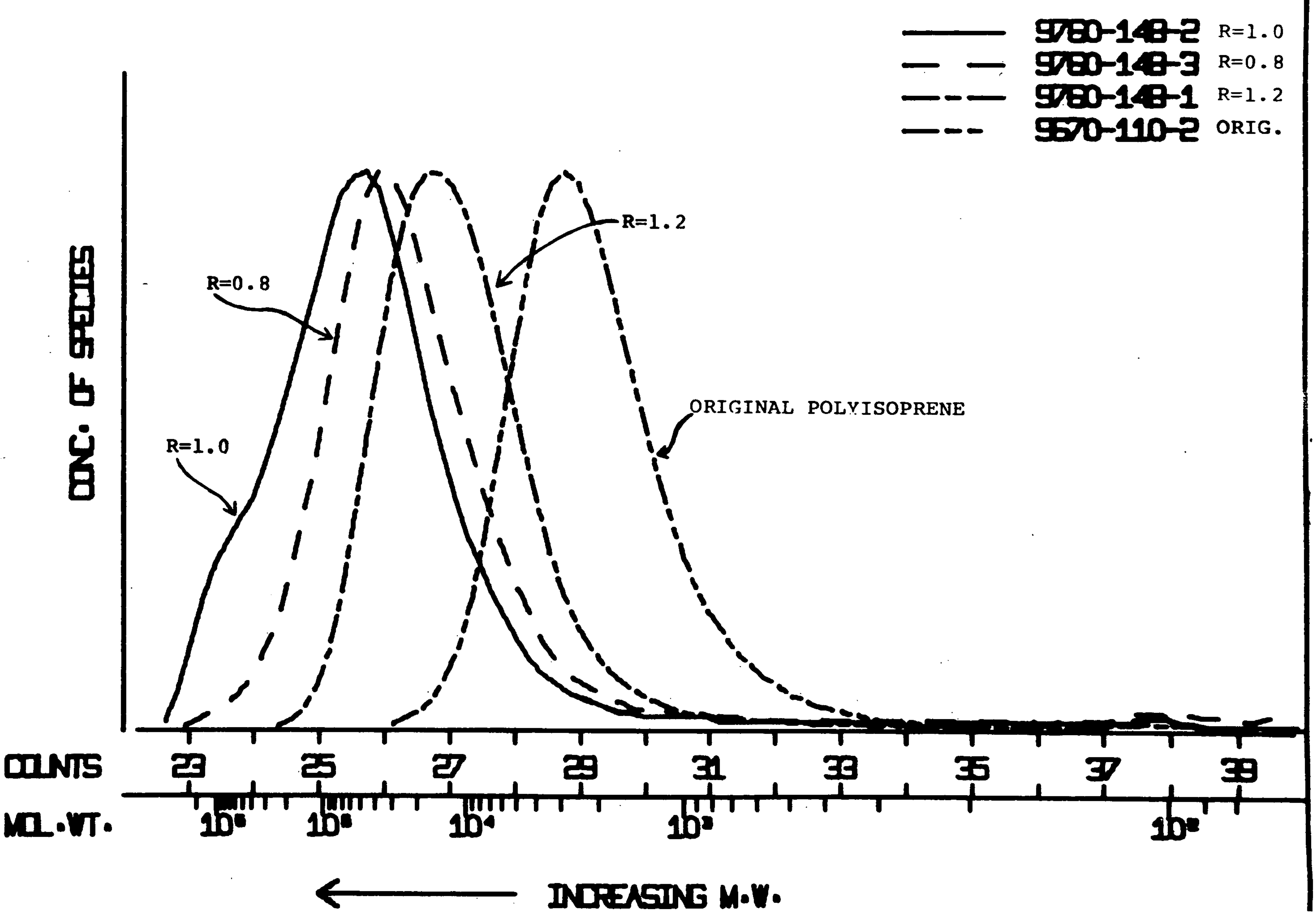

FIGURE 20

CHROMATOGRAMS FOR R=1.0 CHAIN GROWTH WITH TIME

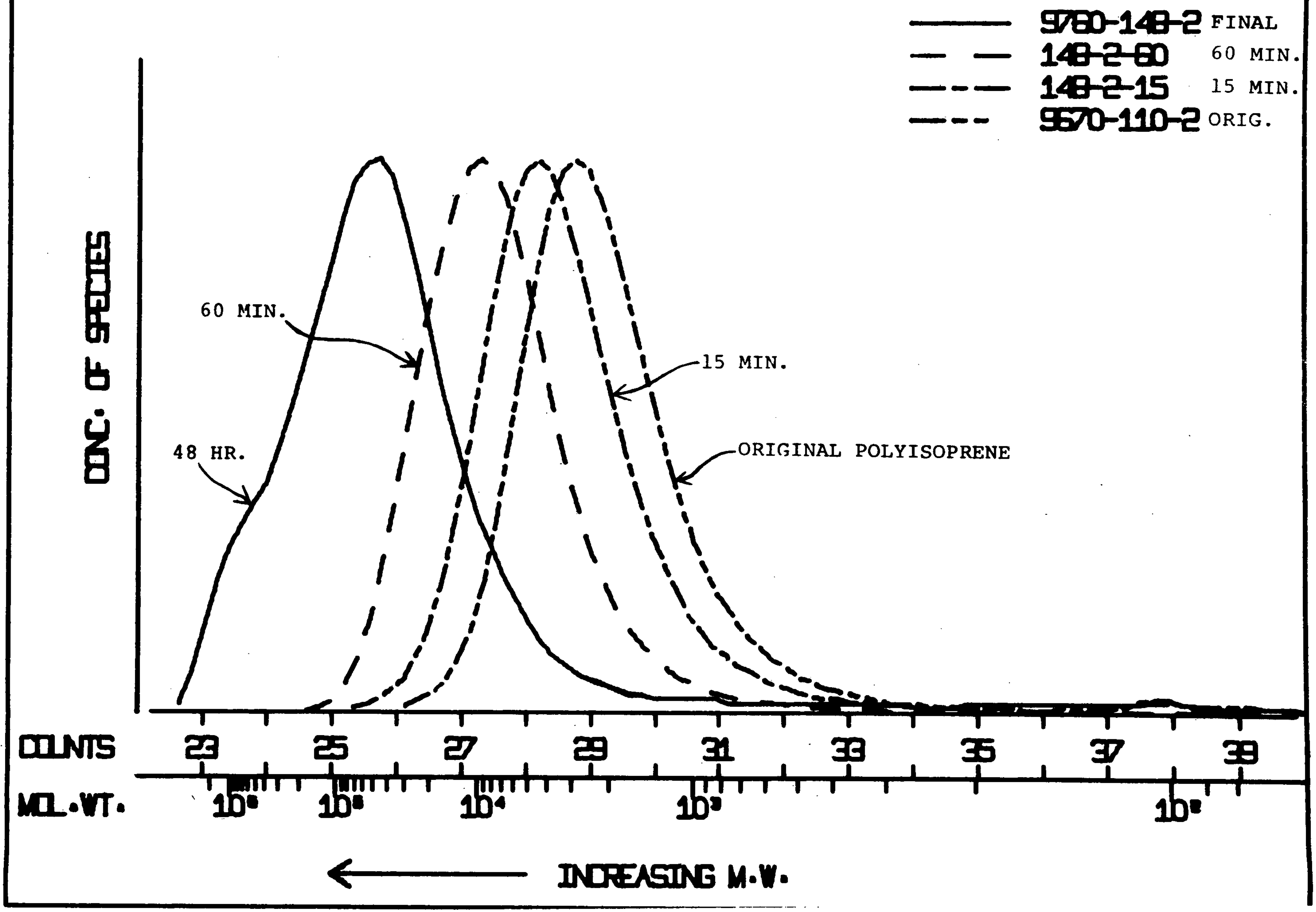

Table VII and the chromatograms of the final products hown in Figure 21. Unfortunately, under these conditions, the reaction of the diol with diisocyanate was extremely slow; the number average molecular weights increased by less than a factor of 2.6, and only 3% of the product was over 100,000 molecular weight.

TABLE VII

GPC DATA ON URETHANES PREPARED FROM POLY(ISOPRENE) DIOL AND HEXAMETHYLENE DIISOCYANATE IN BENZENE AT ROOM TEMPERATURE

SAMPLE	$\bar{A}_n$	$\bar{A}_w$	$\bar{A}_w/\bar{A}_n$	$\bar{M}_n$
9670-110-2	98.5	174	1.77	2430
Hexamethylene Diisocyanate	15.0	15.0	1.00	168
9670-152-1 [OH]/[NCO] = 1.10	293	1040	3.56	5270
9670-152-2 [OH]/[NCO] = 1.00	334	1180	3.52	6010
9670-152-3 [OH]/[NCO] = 0.90	373	1300	3.49	6710

It is informative to compare the theoretically derived degrees of polymerization to those obtained experimentally. These data are shown in Table VIII. As expected, the number average D. P. s are significantly lower than those predicted from Equation 1, most probably due to isocyanate side reactions. However, the weight average D. P. s are not much lower than the theoretical values, especially when an excess of diisocyanate was employed. In fact, the weight average D. P. for 148-3 (R = 0.83) actually exceeded the theoretically predicted value. This again points to isocyanate side reactions, in particular, branching reactions such as allophanate and biruet formation which tend to broaden the distribution and yield high weight average D. P. s or molecular weight species. This reasoning agrees with the gel formation observed in Samples 148-2, R = 1.00 and 148-3, R = 0.83.

FIGURE 21

CHROMATOGRAMS ON FINAL URETHANE PRODUCT PREPARED IN BENZENE AT ROOM TEMPERATURE

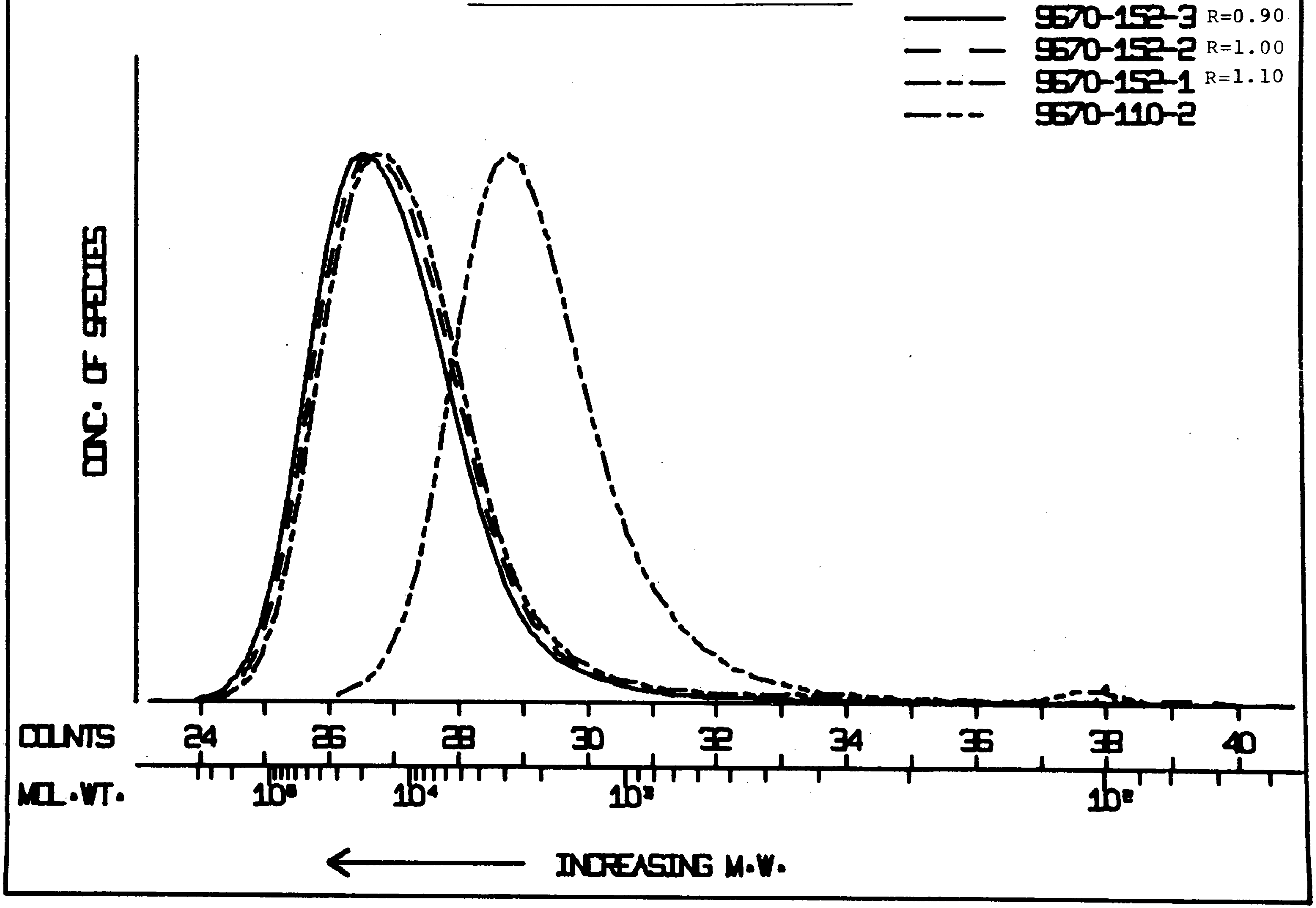

TABLE VIII

COMPARISON OF EXPERIMENTAL AND THEORETICAL DEGREES OF POLYMERIZATION

SAMPLE	[OH]/[NCO]	EXTENT OF NCO REACTION "a"	STOICHIOMETRY A/(A + B)	$\overline{DP}_n$ (EXP.)	$\overline{DP}_n$ (THEO.)	$\overline{DP}_w$ (EXP.)	$\overline{DP}_w$ (THEO.)	$\overline{W}_x/N_x$ (EXP.)	$\overline{W}_x/N_x$ (THEO.)
148-1	1.20	1.00	0.444	2.37	9.00	7.27	17.68	3.07	1.96
148-2	1.00	1.00	0.500	4.20	∞	63.46	∞	15.11	—
148-3	0.83	1.00	0.454	2.90	10.96	22.01	21.65	7.59	1.98
152-1	1.10	0.950	0.474	1.99	10.00	7.08	19.40	3.56	1.94
152-2	1.00	0.854	0.500	2.31	6.85	8.13	12.73	3.52	1.86
152-3	0.90	0.912	0.476	2.58	7.58	9.00	14.29	3.49	1.89