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Part Ia, Summary Report

SYNTHESIS OF ATACTIC AND STEREOREGULAR VINYLAROMATIC POLYMERS AND A STUDY OF THEIR REACTIONS WITH ALKALI METALS

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Approved:

Lionel A. Dickinson

Lionel A. Dickinson, Director
Polymer & Propulsion Sciences Division

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TABLE OF CONTENTS

2

LIST OF ILLUSTRATIONS

3

LIST OF TABLES

I INTRODUCTION

Phase Ia of the present contract was concerned with the synthesis, characterization, and delivery to Jet Propulsion Laboratory of substantial amounts of polymers from 1-vinylnaphthalene, 2-vinylnaphthalene, and 4-vinylbiphenyl.

Because it was agreed that polymers of several different molecular weights would be prepared and that these polymers would have narrow molecular weight distributions, anionic living polymer techniques were used.

In the anionic polymerization of vinylaromatic monomers, the reactive chain-propagating species $[\mathrm{R{-}CH_2{-}CHAr}]^{\ominus}\ \mathrm{M}^{\oplus}$ is a substituted benzylic anion which is stable indefinitely in an inert environment. The macromolecular anions are called "living polymers" because they will resume chain growth in the presence of additional monomer.[1]

In the butyllithium-initiated polymerization of vinylaromatics, each "molecule" of butyllithium generates one chain propagating anion. Polymer molecular weight is therefore determined by the quantities of monomer and initiator, according to the equation

$$M = \frac{\text{grams monomer}}{\text{moles of initiator}}$$

Polymers with predetermined molecular weights can thus be prepared by adjusting the quantities of monomer and initiator.

Since in any homopolymerization all macromolecular anions have equivalent reactivities, chain growth and chain length (molecular weight) distribution are governed by probability considerations. Theory[2] shows that the resulting polymer has a Poisson distribution of chain lengths ($M_w/M_n = 1$).

Any reactive impurities such as protonic compounds, carbonyl compounds, halogen compounds, oxidizing agents, etc., can "kill" some of the growing chains, thereby broadening the molecular weight distribution. Elegant vacuum system techniques[1,3,4] have been developed to attain the scrupulous purities necessary to prepare polymers having M_w/M_n approximating 1. However, by working in an inert atmosphere it is possible to prepare reasonably monodisperse polymers using standard glassware.[4,5] The key to the latter procedure is that deleterious impurities are removed from the polymerization medium and from the monomer by titration, before polymerization (under conditions where polymerization is slow), with the reactive anion which constitutes the initiator. With this procedure it is possible to prepare polymers having molecular weights of about 10^6. Higher molecular weight polymers require such low levels of initiator that unavoidable trace impurities usually seriously interfere with the polymerization.

II SUMMARY

Polymerizations of 1-vinylnaphthalene, 2-vinylnaphthalene, and 4-vinylbiphenyl were carried out using living polymer techniques under an inert atmosphere with butyllithium in benzene. Narrow distribution molecular weight polymers of different molecular weight were prepared and then fractionated. They were characterized by gel permeation chromatography. An improved synthesis of 1-vinylnaphthalene was developed.

III RESULTS AND DISCUSSION

A. Polymerization Procedure

The benzene purification system is illustrated in Figure 1. The argon scrubber A and the solvent reservoir B were assembled ahead of time and flushed with argon. Dry benzene (about 150 and 1500 ml, respectively), 1.6 M butyllithium (20 ml to each) and styrene (2 ml to each) were then added to the scrubber and reservoir, and the exit of B was stoppered until reaction flask C was attached. During several hours both solutions gradually attained the characteristic yellow-orange to red color of the $R\text{-}CH_2CHPh^{\ominus}$ anion. All subsequent operations were performed with a stream of argon moving through the system. Flask C, fitted with a Teflon covered stirring bar, a thermometer (at 3), a 125-ml graduated addition funnel with a Teflon stopcock (at 4), a serum cap (at 6), and an exit tube (at 7) leading to a mineral oil U-bubbler (D), was attached via the condenser (at 2). Flask C and the addition funnel were flamed and cooled under argon, and the addition funnel was sealed with a serum cap (at 5) The tube connecting the exit 7 to D was arranged so that any condensing vapors could not drain back into C. About 600 ml benzene were distilled from B to C. During the latter stages of the distillation, 125 ml benzene was transferred from C to the addition funnel with a 100-ml syringe having a 6-inch needle (via caps at 6 and 5). When the distillation was finished B was brought to room temperature, removed from the system, stoppered, and set aside for future use so long as the anion survived. Flask C was quickly reattached to the argon supply at 7 and the exit bubbler D attached at 1 (Figure 2).

The initiator solution was prepared by adding to the addition funnel with syringes 0.80 ml 1.6 M butyllithium and 0.5 ml monomer, giving an initiator concentration of about 0.01 meg. per ml. Warming with a heat gun hastened the formation of the colored anion. The benzene in C was then heated to reflux and titrated with the initiator solution until a yellow color persisted. The refluxing and titrations should be continued for about 2 hours and may consume 10 to 30 ml initiator solution. After reactor C was cooled to 5-10°, addition of the freshly purified monomers (with a syringe via serum cap at 6 if liquid, or as a benzene solution if solid) dissipated the yellow color. Impurities in the monomer were titrated at 5-10° by adding initiator until the colored anion persisted for 0.5 hour. After C was brought to 50° with a warm water bath, the required amount of initiator was added. In 5-15 minutes an exotherm was observed; within 30 minutes the solution sometimes became quite viscous. The temperature was kept at about 50° for 6 hours with a heat lamp, then the polymerization was terminated by adding a few drops of isopropanol. The polymer was precipitated by slowly adding the viscous

7

solution to 2 to 3 liters of methanol stirring in a 1-gallon Waring Blendor. Conversion was usually of the order of 90%.

B. Polymer Fractionation

Although many of the polymers prepared using the procedure just described were of reasonably narrow molecular weight distribution (see Table IV, V, and VI), all samples submitted to the Jet Propulsion Laboratory were fractionated to further narrow the molecular weight distribution.

The fractionations were carried out in two 14-gallon constant temperature baths, each with a special 5-liter 3-necked flask with a well on the bottom.

The usual procedure was to make up a 3% solution of polymer in benzene (about 30 g in 1000 ml), heat this solution with stirring and under nitrogen to 50°C, and then slowly add methanol until the solution becomes cloudy. This ordinarily required from 260 to 300 ml of methanol. The cloudy solution was then slowly cooled to room temperature and the gel allowed to settle to the bottom of the well. The supernatant liquid was decanted and the gel added to a Waring Blendor with methanol. After thorough blending, the solid was filtered, washed with fresh methanol, and dried in a vacuum oven at 80°C for 24 hours.

C. Monomer Purification

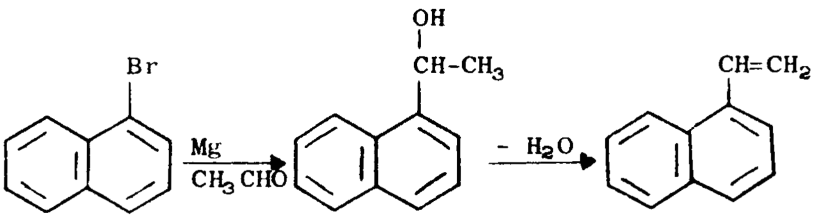
The monomers used in this research were purchased from the Research Organic Chemical Co. and from the Aldrich Chemical Co. They were quite impure and required extensive purification. Indeed, the most difficult aspect of this work has been the acquisition of the monomers and their refinement to the high purity necessary for good anionic polymerization.

1-Vinylnaphthalene, as obtained commercially, was a mixture of 30 to 40% monomer in low molecular weight polymer. The yellow viscous mass was dissolved in benzene and added slowly to a large volume of 65° ligroin to precipitate the polymers. The solution of monomer in ligroin was then passed through a column with silicic acid and alumina in alternating layers until no more color was removed. After concentration on a rotary evaporator, 1-vinylnaphthalene was distilled in vacuo (b.p. 55°C, 0.2 torr.). The distilled product had a faint yellow color. Crude 1-vinylnaphthalene prepared at SRI by dehydration of 1-naphthylethanol was dissolved in ligroin, separated from water, and purified by the silicic acid-alumina treatment as already described. While the initially distilling product was faintly yellow, much of the distilled product was colorless.

The yellow commercial 2-vinylnaphthalene and 4-vinylbiphenyl were dissolved in ligroin and a benzene-ligroin mixture, respectively, and passed through a column of silicic acid and alumina until no more color was removed. Then the solutions were concentrated on a rotary evaporator. The recovered monomers were recrystallized from methanol and then sublimed in vacuo. 2-Vinylnaphthalene sublimed at 50-60°, 4-vinylbiphenyl at 90-100°. In some purifications the recrystallized monomer was dissolved in benzene and treated with the organolithium polymerization initiator until the characteristic color of the carbanion began to form. The mixture was then rapidly cooled with ice, the benzene stripped off in vacuo, and the monomer sublimed without exposure to air. The purified 2-vinylnaphthalene usually melted at 66-67°, but occasionally began to melt as low as 60°. The purified 4-vinylbiphenyl usually melted at 120-122°, but occasionally began to melt as low as 105°. Both monomers were colorless after sublimation.

D. Synthesis of 1-Vinylnaphthalene

Because of delays in receiving this monomer and the fact that it was usually received as 60-70% polymer, it was decided to synthesize this monomer here. The following synthetic route was used



A typical procedure is given below. It is described in some detail because it represents a considerable improvement over those reported in the literature.[6,7]

Magnesium turnings (24.3 g, 1 mole) were placed in a 2-liter 3-necked flask equipped with a mechanical stirrer, a reflux condenser, and a 1-liter addition funnel. A nitrogen atmosphere was maintained in the flask. After the entire apparatus was flamed, 207 g(1 mole) of freshly distilled 1-bromonaphthalene (Eastman Kodak, b.p. 100°C, 1 torr.) and 500 ml of dried tetrahydrofuran were placed in the addition funnel and a small portion added to the stirred magnesium turnings. The mixture was stirred and heated gently until the reaction began. The remaining solution was then added slowly so as to maintain gentle reflux. On completion of this reaction, 44 g (1 mole) of acetaldehyde (Eastman Kodak, used as received) dissolved in 300 ml of tetrahydrofuran was slowly added from the addition funnel. Next, 150 g of ammonium chloride in 500 ml of water were added with rapid stirring, the mixture transferred to a separatory funnel, and the aqueous layer separated. After washing twice with tetrahydrofuran, the combined extracts and the original organic layer were combined and the tetrahydrofuran removed by distillation. The remaining brown solid was refluxed with 750 ml of petroleum either (65-110°C) and the cooled solution filtered and washed twice with 50 ml of petroleum either. The yield was 72.0 g (41.9%) m.p. 65°C.

The dehydration was performed as follows: 2-foot-long, 1-inch-diameter Pyrex column provided with a thermocouple well was packed to a length of 14 inches with 4-mesh Alcoa activated alumina and topped with a 1-inch height of glass beads. A dropping funnel containing the carbinol was placed on top of the column and a receiving flask cooled to -76°C at the bottom. A 0.5-torr vacuum was established, the column was heated to 300°C, and the carbinol was melted in the dropping funnel by means of an infrared lamp and allowed to degass for one hour. The molten carbinol was next slowly allowed to drop through the column and the product collected in the receiving flask. The yield

10

of 1-vinylnaphthalene was usually of the order of 90%.

E. Polymer Characterization

The bulk of the polymer characterization was performed using a Waters Associate gel permeation chromatograph equipped with one 10^6 Å, two 10^5 Å, and two 10^4 Å polystyrene gel columns. Toluene was used as the carrier and the instrument was operated at 70°C.

A typical gel permeation chromatograph is shown in Figure 3. In Figure 4 is shown a calibration plot obtained with compounds of known chain-length, supplied by Waters Associates. This calibration can then be used to determine the chain length of unknown molecular weight compounds by measuring curve heights on the gel permeation trace for each count, thus determining the number of chains for each particular chain length. These data can then be converted to A_n and A_w, which are essentially number average and weight average molecular weights in Angstroms. Table I shows this calculation for the chromatograph depicted in Figure 3.

In order to obtain actual molecular weights it is necessary to multiply these quantities by a factor Q such that;

$$M_n = Q_n A_n \quad \text{and} \quad M_w = Q_w A_w$$

The quality Q is defined as the molecular weight per Angstrom length considering only valence angles and bond lengths in a fully extended molecule. In vinyl polymers this repeat distance in an extended chain is 2.55 Å, and therefore Q values should be obtainable by dividing the molecular weight of the repeat unit M_o by 2.55.

In actual practice, Q values are obtained from the slope of plots of molecular weights obtained from light scattering and osmometry measurements against A values obtained from gel permeation date.

Table II shows the results of molecular weight measurements for poly-2-vinylnaphthalene and poly-4-vinylbiphenyl.* Plots of these

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*The light scattering and osmometry measurements shown in Table II were carried out at JPL by Dr. Jovan Moacanin and Mr. R. Landenslager.

values vs. corresponding A values are shown in Figures 5, 6, 7, and 8. Table III shows Q values actually obtained and those calculated. Polystyrene and polyacenaphthalene have been included for the sake of interest.

It will be noted that the values of Q_w and Q_n, while similar, are not identical so that the molecular weight distribution of an unknown polymer cannot always be obtained from a ratio of A_w/A_n. It will also be noted that the calculated Q values are very close to the measured Q_w values. This excellent agreement is to a large measure due to the fact that the initial calibration was performed with polystyrene where an extended chain configuration was assumed, and thus indicates that these vinyl-aromatic polymers in solution have the same effective size.

Detailed characterization of all polymer samples delivered to the Jet Propulsion Laboratory are shown in Tables IV, V, and VI. In calculating the data for poly-1-vinylnaphthalene, it was assumed that Q_w and Q_n would be identical to those obtained for poly-2-vinylnaphthalene.

ACKNOWLEDGEMENT

We wish to acknowledge the assistance of Mr. Fred J. Martinelli and C. B. Kingsley who carried out the large-scale preparation of 1-vinylnaphthalene and Mr. Richard Won who did the gel permeation and molecular weight measurements.

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13

Table I

CALCULATION OF A_n AND A_w FOR SAMPLE 8080-60-1

Counts	Height Hi = MiNi	Chain Length Ai	Hi/Ai	HiAi
17.5	0	–	–	–
18.5	7	8.4×10^3	0.00083	58,800
19.5	45	4.9×10^3	0.00918	220,500
20.5	139	2.8×10^3	0.04964	389,200
21.5	133	1.6×10^3	0.08312	212,800
22.5	53	9.6×10^2	0.05520	50,880
23.5	15	5.6×10^2	0.02679	8,400
24.5	3	3.6×10^2	0.00833	1,080
25.5	0	–	–	–
Totals	395		0.23309	941,660

$$A_n = \frac{M_n}{Q} = \frac{1}{Q} \frac{\Sigma \text{ MiNi}}{\Sigma \text{ Ni}} = \frac{395}{0.23309} = 1694.6$$

$$A_w = \frac{M_w}{Q} = \frac{\Sigma \text{ Mi}^2\text{Ni}}{Q \; \Sigma \text{ MiNi}} = \frac{941,660}{395} = 2383.9$$

$$A_w/A_n = \frac{2383.9}{1694.6} = 1.41$$

Table II

LIGHT SCATTERING AND OSMOMETRY DATA FOR POLY-2-VINYLNAPHTHALENE AND POLY-4-VINYLBIPHENYL

Code No.	Polymer	M_w x 10^{-3}	M_n x 10^{-3}	M_w/M_n
8036-16	P2VN	240	104	2.31
8036-18	P2VN	152	84	1.81
8080-44-1	P2VN	694	489	1.42
8080-45-1	P2VN	686	352	1.95
8080-46-1	P2VN	345	135	2.56
8080-48-1	P2VN	–	128	–
8080-48-2	P2VN	–	124	–
8080-57-1	P2VN	–	223	–
8080-41-1	P4VB	735	459	1.60
8080-42-1	P4VB	704	379	1.86
8080-51-1	P4VB	74	69	1.07
8080-52-1	P4VB	78	68	1.15
8080-56-1	P4VB	94	62	1.52
8080-63-1	P4VB	1670	510	3.27
8080-64-1	P4VB	–	420	–
8080-71-1	P4VB	140	105	1.33
8080-72-1	P4VB	–	86	–

Table III

CALCULATED AND OBSERVED Q-VALUES FOR VARIOUS VINYLAROMATIC POLYMERS

Polymer	M_o	Q_w	Q_n	$M_o/2.55$
P1VN	154	—	—	60.4
P2VN	154	63.1	75.0	60.4
P4VB	180	74.6	68.1	70.6
PS	104	41.9	46.9	40.8
PAcN	159	59.8	69.4	59.6

P1VN	Poly-1-Vinylnaphthalene
P2VN	Poly-2-Vinylnaphthalene
P4VB	Poly-4-Vinylbiphenyl
PS	Polystyrene
PAcN	Polyacenaphthalene

Table IV

CHARACTERIZATION OF POLY-1-VINYLNAPHTHALENE BY GEL PERMEATION CHROMATOGRAPHY

$Q_n = 75.0; \quad Q_w = 63.1$

Code No.	A_n	A_w	A_w/A_n	M_n	M_w	M_w/M_n
8036-64	1273	2076	1.63	95,500	131,000	1.37
8080-59-1	1813	2461	1.36	136,000	155,300	1.14
8080-60-1	1695	2384	1.41	127,100	150,400	1.18
8036-71	1533	2611	1.70	115,000	164,800	1.43
8080-65-1	1676	2836	1.69	125,700	179,000	1.42
8080-66-1	1326	2335	1.76	99,500	147,300	1.48
8036-81	1499	3779	2.52	112,400	238,500	2.12
8080-73-1	2414	4477	1.85	181,000	282,500	1.56
8080-74-1	2840	5012	1.76	213,000	316,300	1.48
8036-89	1180	1512	1.28	88,500	95,400	1.08
8080-87-1	1213	1488	1.23	91,000	93,900	1.03
8080-88-1	1319	1638	1.24	98,300	103,400	1.05
8036-90	1697	4592	2.70	127,300	289,800	2.28
8080-89-1	2244	4701	2.09	168,300	296,600	1.76
8036-98	658.8	827.3	1.26	49,400	52,200	1.06

Table V

CHARACTERIZATION OF POLY-2-VINYLNAPHTHALENE BY GEL PERMEATION CHROMATOGRAPHY

$Q_n = 75.0; \quad Q_w = 63.1$

Code No.	A_n	A_w	A_w/A_n	M_n	M_w	M_w/M_n
8036-23	3862	8921	2.31	289,700	562,900	1.94
8080-44-1	6342	11666	1.84	475,700	736,100	1.55
8080-45-1	5048	10178	2.02	378,600	642,200	1.70
8036-18	1265	2262	1.79	94,900	142,700	1.50
8080-48-1	1878	2892	1.54	140,900	182,500	1.29
8080-48-2	1451	2021	1.39	108,800	127,500	1.17
8080-46-1	1479	2290	1.45	110,900	144,500	1.30
8036-16	1840	4225	2.30	138,000	266,600	1.93
8080-57-1	2794	4958	1.77	209,600	312,800	1.49
8080-58-1	2887	4851	1.68	216,500	306,100	1.41
8036-45	636	776	1.22	47,700	49,000	—
8080-61-1	681	775	1.15	51,100	48,900	—
8080-62-1	737	848	1.14	55,300	53,500	—
8036-19	917	976	1.06	68,800	61,600	—
8080-67-1	938	1038	1.11	70,400	65,500	—
8080-68-1	934	1014	1.08	76,100	64,000	—
8036-66	2492	7661	3.07	186,900	483,400	2.59
8080-69-1	4039	9184	2.27	302,900	579,500	1.91
8080-70-1	4002	8929	2.23	300,100	563,400	1.88

Table VI

CHARACTERIZATION OF POLY-4-VINYLBIPHENYL BY GEL PERMEATION CHROMATOGRAPHY

$Q_n = 68.1$; $Q_w = 74.6$

Code No.	A_n	A_w	A_w/A_n	M_n	M_w	M_w/M_n
8036-30	3952	10100	2.56	269,100	753,500	2.80
8080-41-1	5036	9471	1.88	343,000	706,500	2.06
8080-42-1	4719	9820	2.10	321,400	732,600	2.28
8036-27	828	1031	1.24	56,400	76,900	1.36
8080-51-1	943	1083	1.15	64,200	80,800	1.26
8080-52-1	986	1125	1.14	67,100	83,900	1.25
8036-38	659	935	1.42	44,900	69,800	1.55
8080-53-1	855	1141	1.33	58,200	85,100	1.46
8080-56-1	995	1381	1.39	67,800	103,000	1.52
8036-35	3646	13600	3.73	248,300	1,014,000	4.08
8080-63-1	7533	14800	1.96	513,000	1,104,000	2.15
8080-64-1	6080	11100	1.82	414,000	828,000	2.00
8036-73	1279	2060	1.61	87,100	153,700	1.76
8080-71-1	1714	2271	1.32	116,700	169,400	1.45
8080-72-1	1606	2206	1.37	109,400	164,600	1.50
8036-91	4871	6773	1.39	331,700	505,300	1.52
8080-90-1	4237	6326	1.49	288,500	471,900	1.63
8080-91-1	4473	6559	1.47	304,600	489,300	1.61

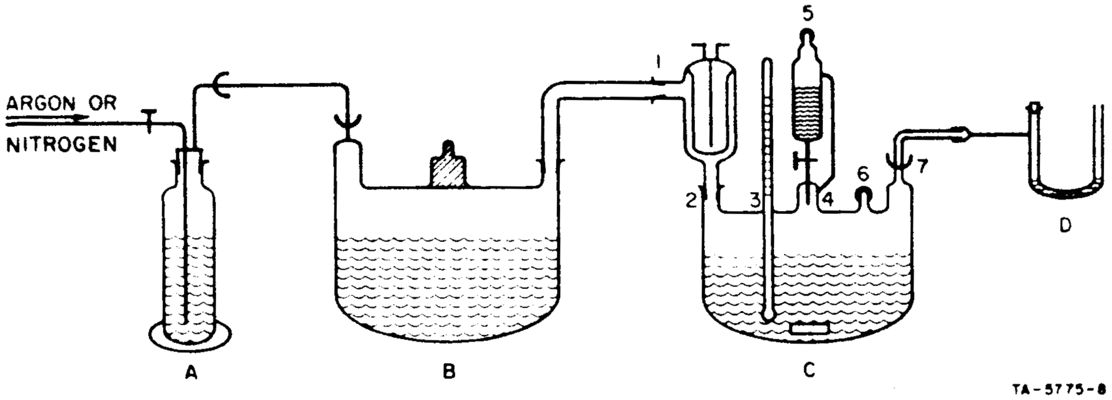

FIG. 1 APPARATUS FOR SOLVENT PURIFICATION AND DISTILLATION

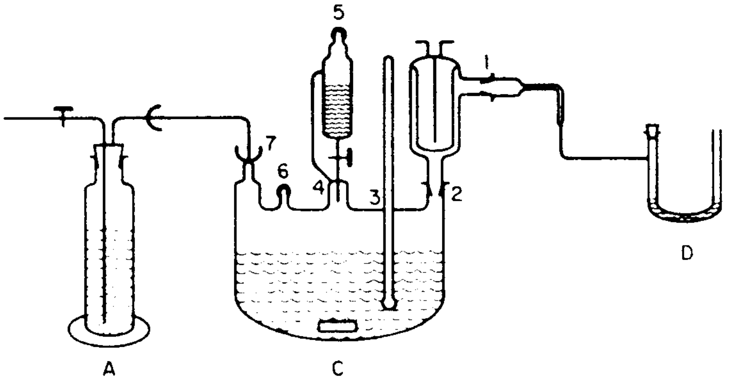

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FIG. 2 APPARATUS FOR MONOMER POLYMERIZATION

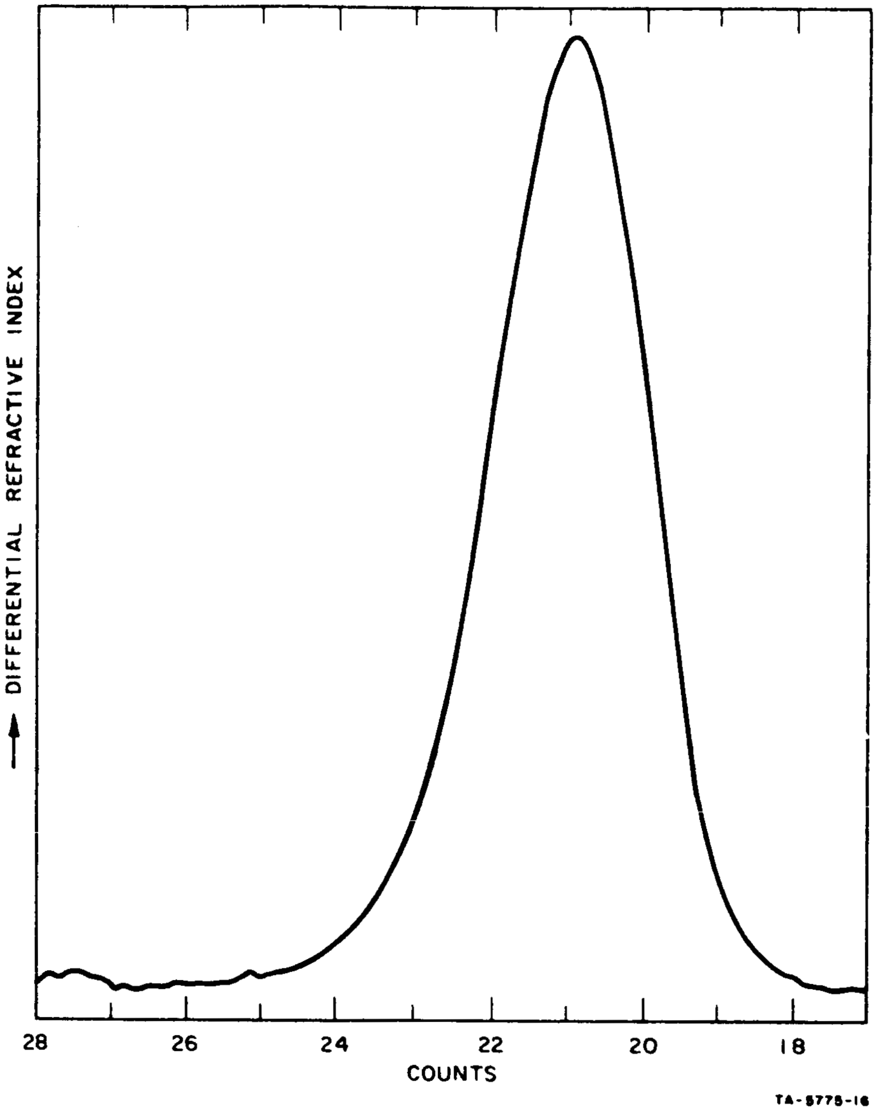

FIG. 3 GEL PERMEATION TRACE FOR SAMPLE 8080-60-1

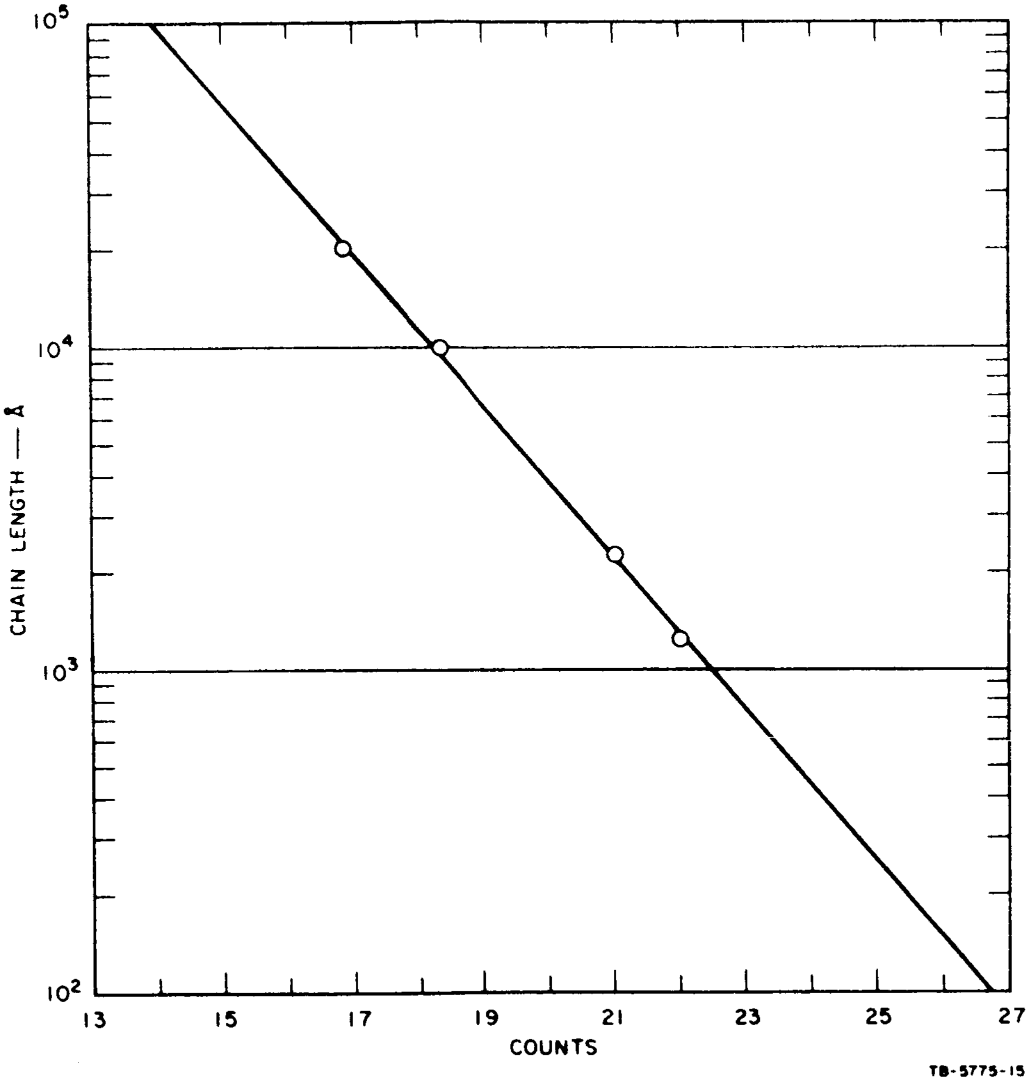

FIG. 4 CALIBRATION PLOT FOR GEL PERMEATION CHROMATOGRAPH USING COMPOUNDS OF KNOWN MOLECULAR DIMENSIONS

23

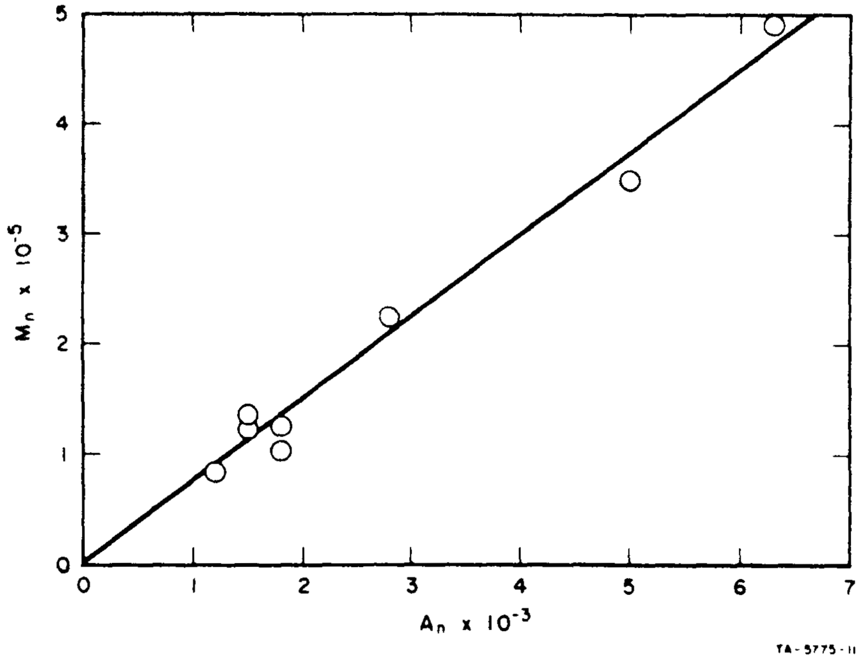

FIG. 5 POLY-2-VINYLNAPHTHALENE, PLOT OF NUMBER AVERAGE MOLECULAR WEIGHT DETERMINED BY OSMOMETRY vs. A_n

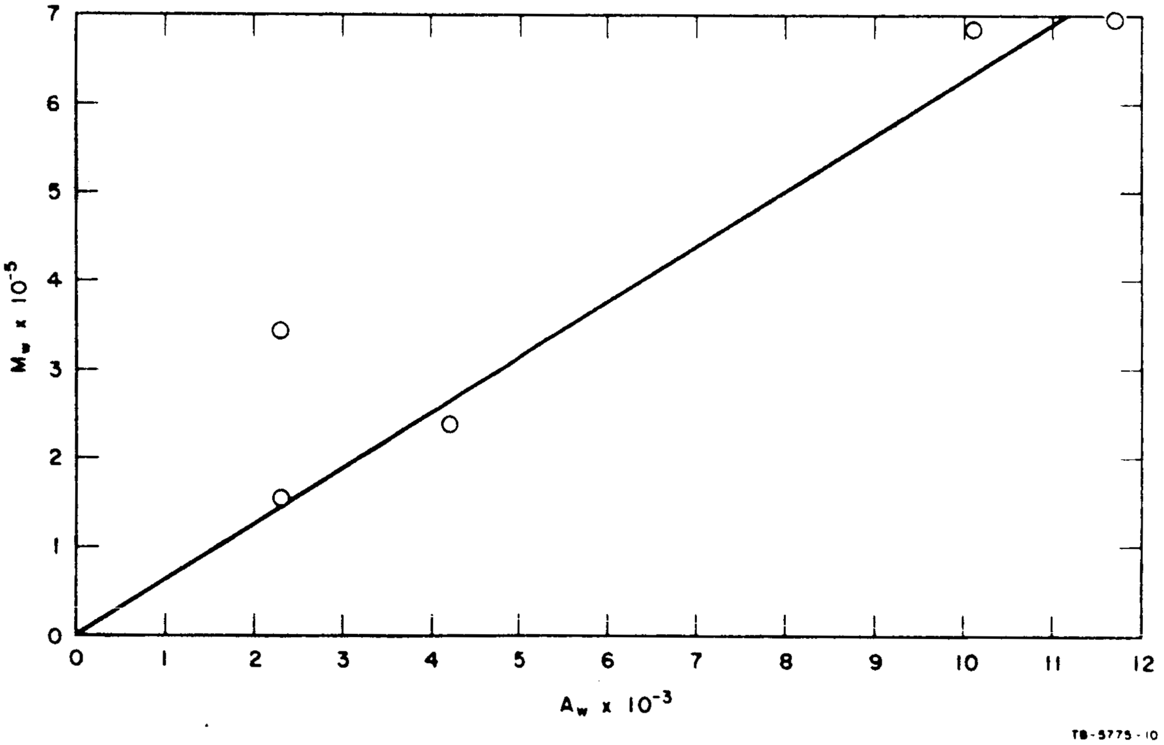

FIG. 6 POLY-2-VINYLNAPHTHALENE, PLOT OF WEIGHT AVERAGE MOLECULAR WEIGHT DETERMINED BY LIGHT SCATTERING vs. A_w

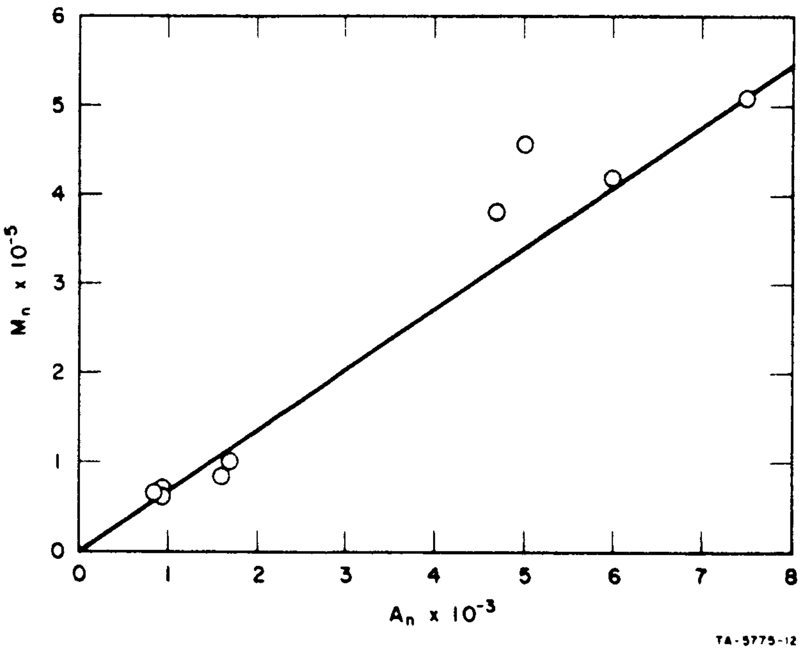

FIG. 7 POLY-4-VINYLBIPHENYL, PLOT OF NUMBER AVERAGE MOLECULAR WEIGHT DETERMINED BY OSMOMETRY vs. A_n

26

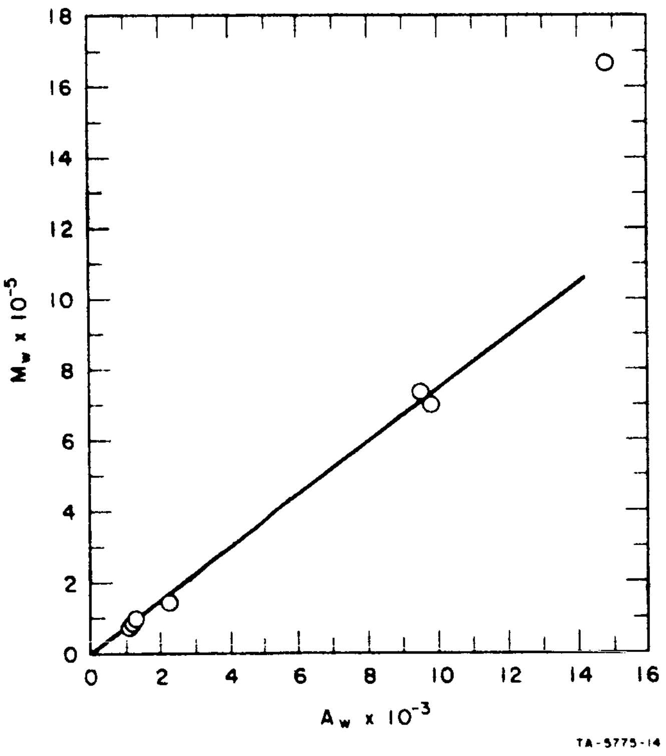

FIG. 8 POLY-4-VINYLBIPHENYL, PLOT OF WEIGHT AVERAGE MOLECULAR WEIGHT DETERMINED BY LIGHT SCATTERING vs. A_w

27