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Final Report

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

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GENERAL INTRODUCTION

Work performed during this project was divided into three phases. The first was concerned with the synthesis, characterization, and delivery to Jet Propulsion Laboratory of substantial amounts of narrow molecular weight distribution polymers from 1-vinylnaphthalene, 2-vinylnaphthalene, and 4-vinylbiphenyl. The second phase was concerned with synthesis, characterization, and delivery to the Jet Propulsion Laboratory of substantial amounts of stereoregular polymers from 1-vinylnaphthalene, 2-vinylnaphthalene, 4-vinylbiphenyl, and 9-vinylcarbazole. The third phase consisted of a study of the reaction of these vinylaromatic polymers with alkali metal atoms.

Summary reports for the first two phases (Ia and Ib) containing a detailed description of all work performed under these phases have already been issued. They are included in this report for the sake of completeness. Summary report Ib has been somewhat modified to include new data recently obtained on isotactic poly-4-vinylbiphenyl.

Phase Ia

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 $[\text{R-CH}_2\text{-CHAr}]^\ominus \text{M}^\oplus$ 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. Theory² 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 $R-CH_2CHPh^{\ominus}$ 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 $5-10^{\circ}$, 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 $5-10^{\circ}$ 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

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.

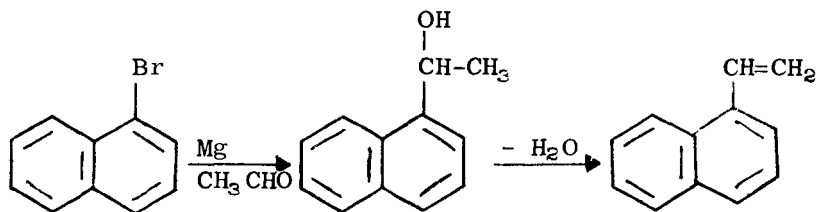
1-Vinylnaphthalene, as obtained commercially, was a mixture of 30 to 40% monomer in low molecular weight polymer. The yellow viscous mass was dissolved in benzene and added slowly to a large volume of 65° ligroin to precipitate the polymers. The solution of monomer in ligroin was then passed through 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°C, 4-vinylbiphenyl at 90-100°C. 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°C, but occasionally began to melt as low as 60°C. The purified 4-vinylbiphenyl usually melted at 120-122°C, but occasionally began to melt as low as 105°C. 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 ether (65-110°C) and the cooled solution filtered and washed twice with 50 ml of petroleum ether. 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

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;

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

The quantity 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_0 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 data.

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

*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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7. S. Loshaek and E. Broderick, *J. Polymer Sci.*, 39, 241 (1959).

Table I

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

Counts	Height $H_i =$ $M_i N_i$	Chain Length A_i	H_i/A_i	$H_i A_i$
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

$$A_n = \frac{M_n}{Q} = \frac{1}{Q} \frac{\sum M_i N_i}{\sum N_i} = \frac{395}{0.23309} = 1694.6$$

$$A_w = \frac{M_w}{Q} = \frac{\sum M_i^2 N_i}{Q \sum M_i N_i} = \frac{941,660}{395} = 2383.9$$

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

Table II

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

Code No.	Polymer	M_w $\times 10^{-3}$	M_n $\times 10^{-3}$	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

$$Q_n = 75.0; Q_w = 63.1$$

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

$$Q_n = 75.0; Q_w = 63.1$$

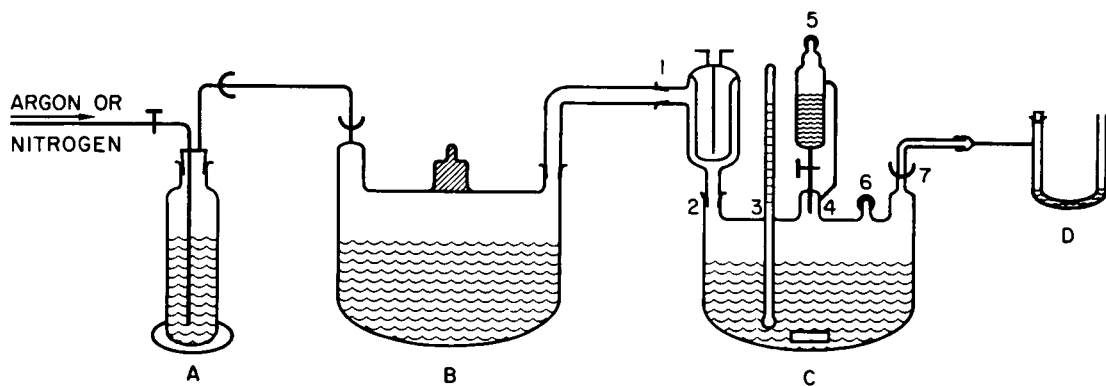
Code No.	A_n	A_w	A_w/A_n	M_n	M_w	M_w/M_n
8036-23	3862	8921	2.31	289,700	562,900	1.94
8080-44-1	6342	11666	1.84	475,700	736,100	1.55
8080-45-1	5048	10178	2.02	378,600	642,200	1.70
8036-18	1265	2262	1.79	94,900	142,700	1.50
8080-48-1	1878	2892	1.54	140,900	182,500	1.29
8080-48-2	1451	2021	1.39	108,800	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

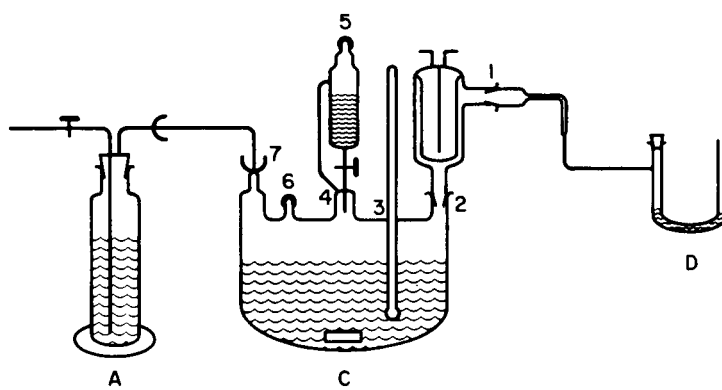
$$Q_n = 68.1; Q_w = 74.6$$

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



TA-5775-8

FIG. 1 APPARATUS FOR SOLVENT PURIFICATION AND DISTILLATION



TA-5775-9

FIG. 2 APPARATUS FOR MONOMER POLYMERIZATION

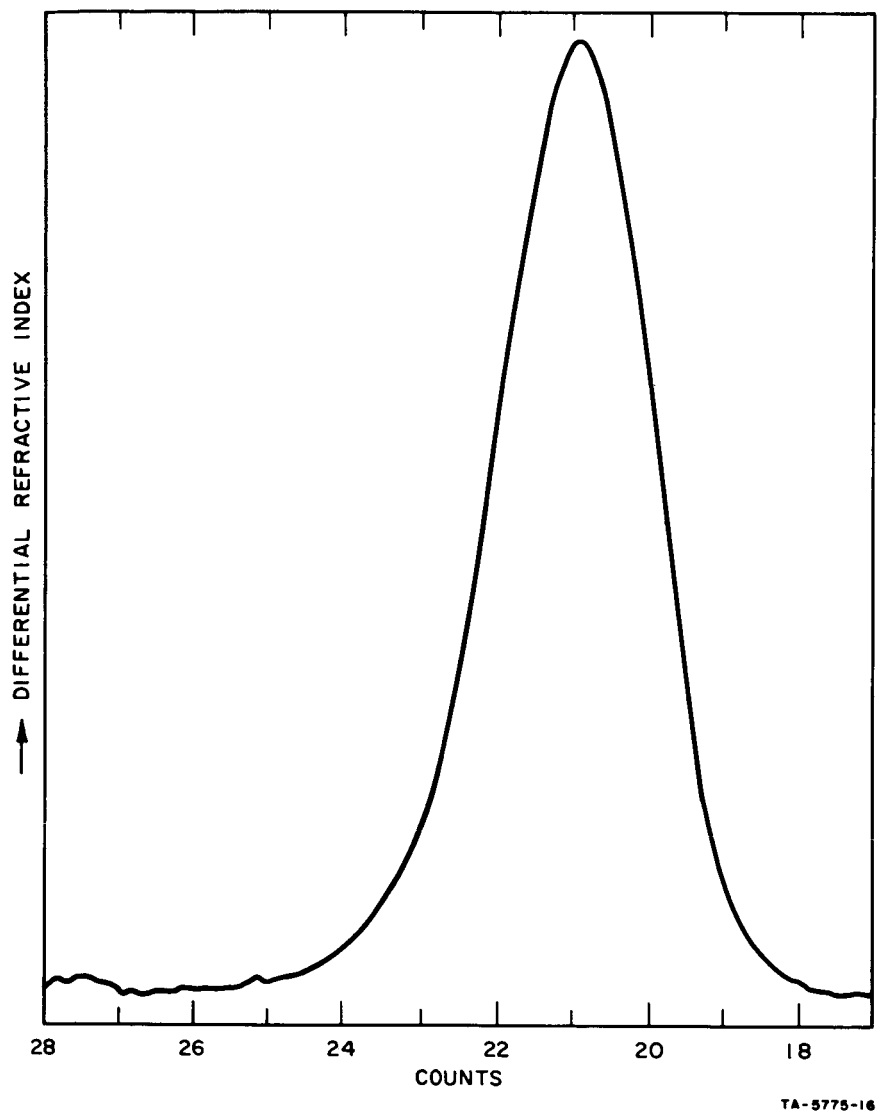
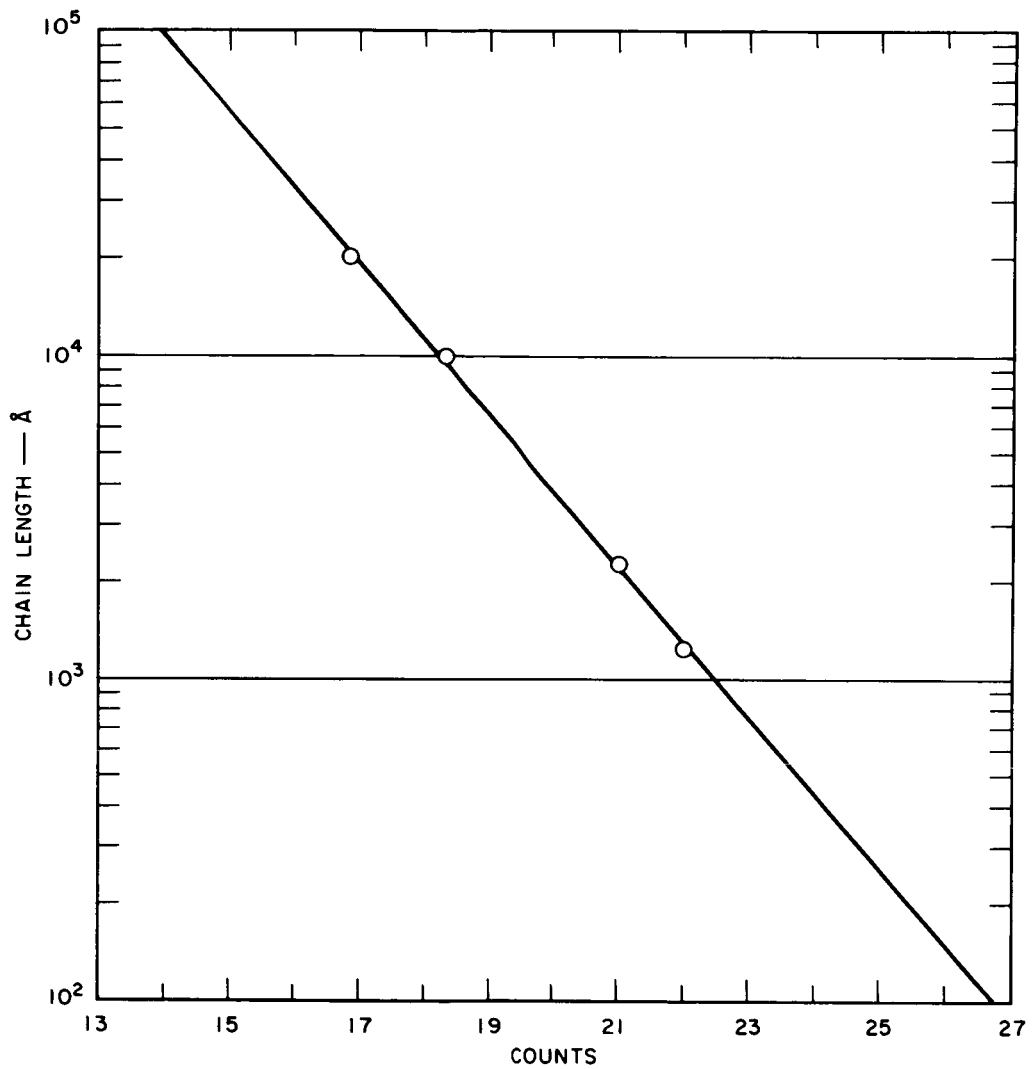


FIG. 3 GEL PERMEATION TRACE FOR SAMPLE 8080-60-1



TB-5775-15

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

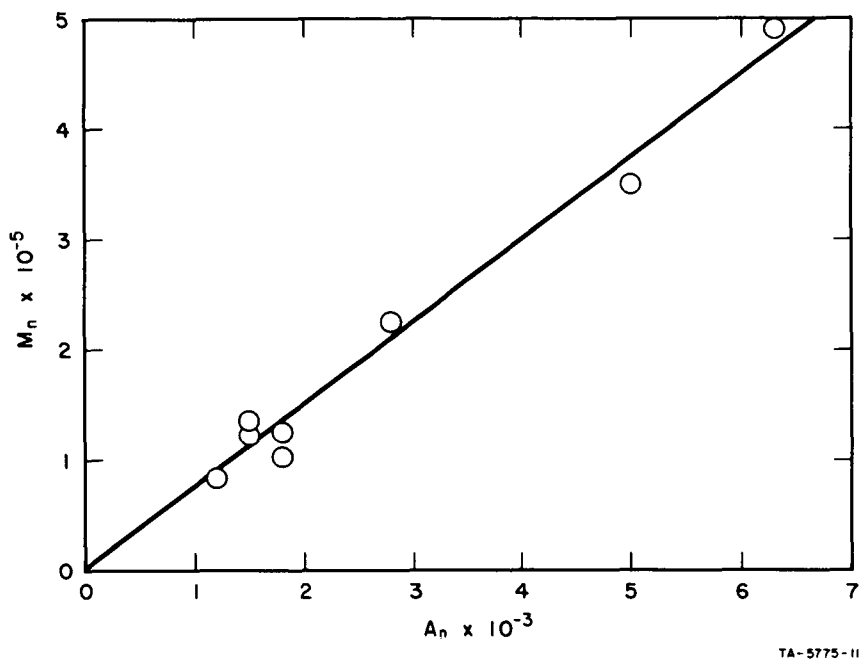
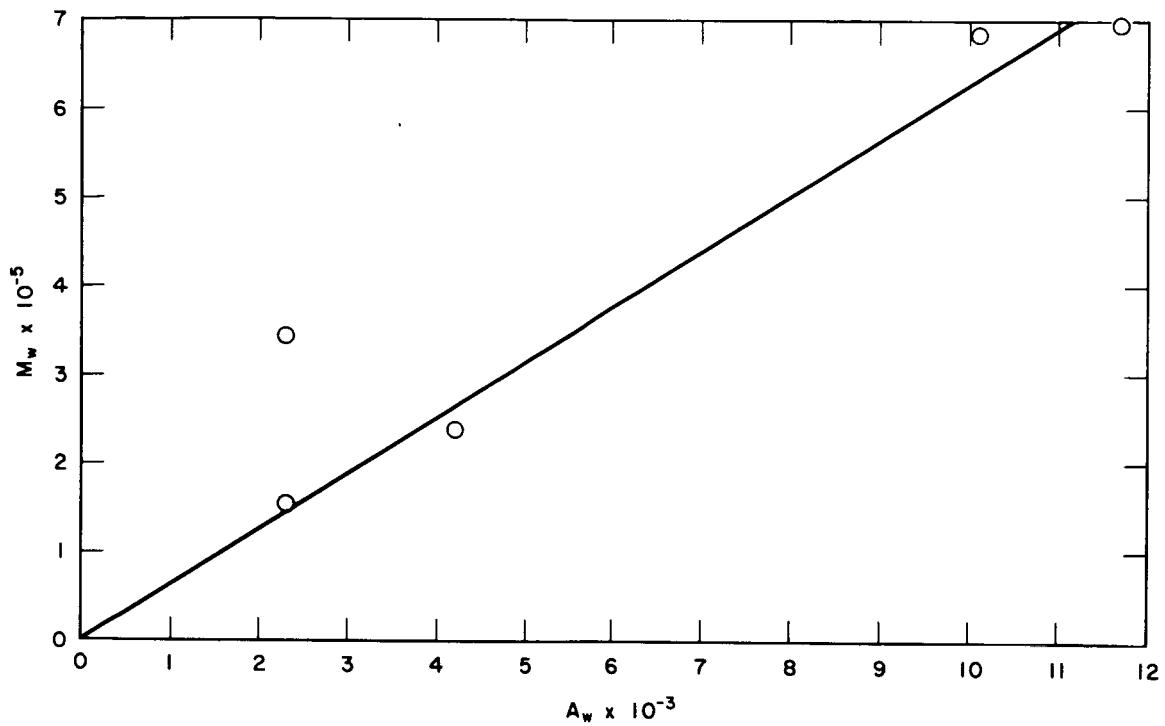
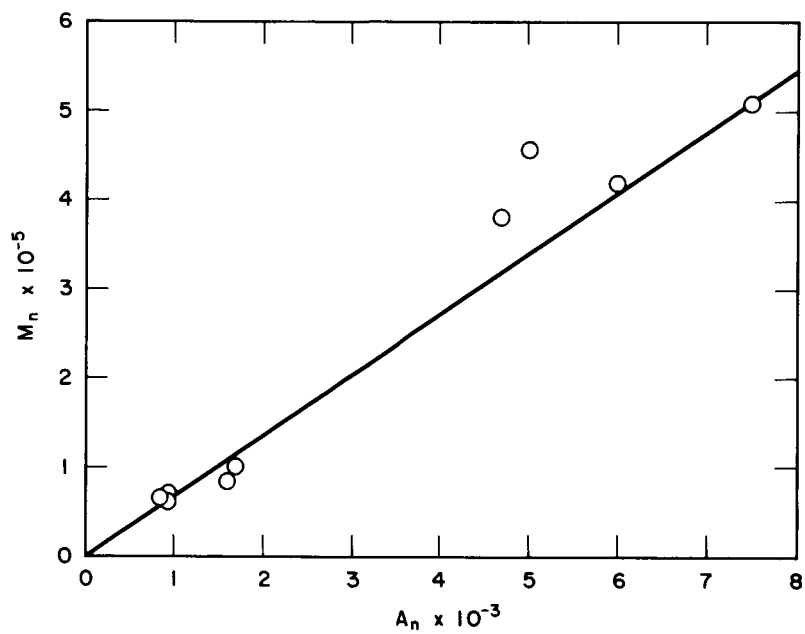


FIG. 5 POLY-2-VINYLNAPHTHALENE, PLOT OF NUMBER AVERAGE MOLECULAR WEIGHT DETERMINED BY OSMOMETRY vs. A_n



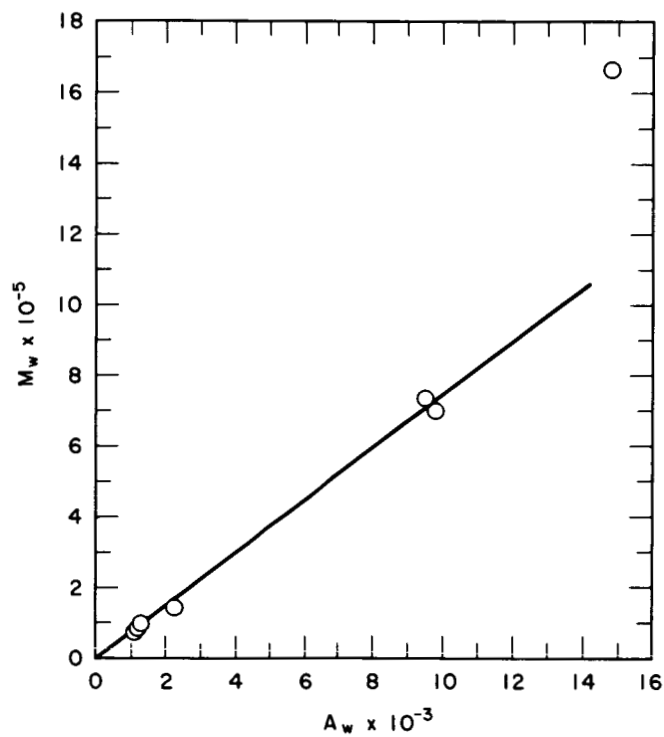
TB-5775-10

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



TA-5775-12

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



TA-5775-14

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

I INTRODUCTION

Phase Ib of the present contract was concerned with the synthesis, characterization, and delivery to the Jet Propulsion Laboratory of substantial amounts of stereoregular polymers from 1-vinylnaphthalene (1VN), 2-vinylnaphthalene (2VN), 4-vinylbiphenyl (4VB), and 9-vinylcarbazole.

Though a considerable number of papers have been published on the stereoregulated polymerization of styrene, very little has been reported on the stereoregulated polymerization of other vinylaromatics. In fact, the only known mention of the stereoregular polymerization of the vinylnaphthalenes and 4VB is by Natta, Danusso, and Sianesi, who surveyed the polymerization of more than 20 vinylaromatic monomers.¹ Relevant material from their paper is excerpted in Table I.

The polymerizations were reported to give polymers which were not separable by solvent extraction into fractions of different steric order. Furthermore, while in the polymerization of vinylalkanes, catalyst systems based on $TiCl_3$ are known to give higher isotaxy than those based on $TiCl_4$, surprisingly, Natta et al. have reported that with vinylaromatics both catalyst systems behave similarly. No detailed characterization of stereoregular vinylaromatic polymers, could be found in the literature; however, it was reported that differences could be noted in their IR spectra.¹

On the other hand, literature dealing with the stereoregular polymerization of styrene, the prototype vinylaromatic, was quite extensive,² but even here reported procedures and results were not completely satisfactory. Two of the better synthetic procedures were reported to produce only about 44% conversion¹ and 4 grams isotactic polymer³ per gram $TiCl_3$, respectively. A third procedure using monomer as the polymerization medium was limited to about 20% conversion by handling and work-up problems.⁴

Since fairly large samples of stereoregular polymers were to be prepared from rather expensive monomers, some effort was devoted to

Table I

DATA ON POLYMERIZATION OF VINYLAROMATIC MONOMERS
OBTAINED BY NATTA ET AL.

Monomer	Physical State of the Polymer ^a	Melting Temperature ^b (°C)	$[\eta]^c$	Conversion Yield ^d (%)
Styrene	Crystalline	240	3.5	43.7
1-Vinylnaphthalene	Crystalline	~ 360	2.3	12.9
2-Vinylnaphthalene	Amorphous	—	3.4	38.9
4-Vinylbiphenyl	Amorphous	—	0.7	39.2

^aThe crystalline polymers have been characterized by x-ray and polarizing hot-stage microscope examinations. Many polymers achieve the crystalline state during preparation; sometimes, they become crystalline only after suitable thermal treatments. We have considered as amorphous those polymers whose x-ray diagrams did not show sharp diffraction peaks after several attempts of crystallizing them by thermal treatments at temperatures higher than that of glass transition.

^bTemperature of complete disappearance of the crystallinity, determined by polarizing hot-stage microscope, with heating rate of 1-2°C/min.

^cIntrinsic viscosity in tetralin at 100°C, in 100 cm³ g⁻¹, determined on samples obtained as specified in footnote d.

^dPolymerization conditions: 2.0·10⁻³ mole TiCl₄, 6.0·10⁻³ mole Al(C₂H₅)₃, 80·10⁻³ mole monomer; reaction volume, 35 cm³; solvent, benzene; 7 hours of reaction at 70°C.

developing a polymerization procedure which afforded high yield conversions.

The polymerization of 9-vinylcarbazole was carried out as described in a Montecatini patent.⁵

II SUMMARY

Catalyst systems based on $TiCl_3$ and $TiCl_4$ were studied in stereoregular polymerizations of 1-vinylnaphthalene, 2-vinylnaphthalene, 4-vinylbiphenyl, and, for comparison, styrene. Conversions of 75 to 95% were obtained with the $Et_3Al-TiCl_3$ system. This represents a significant improvement over reported procedures. Extraction with 2-butanone removes polymer having low stereoregularity (<10%) and leaves the insoluble isotactic polymers. Isotactic P1VN and P2VN are at least partly soluble in toluene, but isotactic P4VB is insoluble in toluene. The isotactic polymers are also distinguishable from the corresponding atactic polymers by their IR and NMR spectra.

Polymerization of 9-vinylcarbazole was carried out with $EtAlCl_2$ in toluene at $-76^\circ C$ as described in the literature. Insoluble, high melting polymers were obtained, which showed no differences (IR and X-ray) from free radical poly-9-vinylcarbazole.

III RESULTS AND DISCUSSION

A. Polymerization

In all, about 40 polymerizations were conducted with Ziegler-Natta catalysts. The polymerizations were conducted in pop bottles, and the polymer was isolated by washing with isopropanol. Extraction with 2-butanone (MEK) is known to remove atactic polystyrene from the insoluble isotactic polymers.³ It was found, similarly, that atactic P2VN and P4VB were readily extracted with refluxing MEK. Atactic P1VN, however, was peculiar in that extraction with hot MEK soon rendered it a

fluid viscous mass, and long extraction periods were necessary to wash the polymer from the extraction thimble.

The stereoregular polymers could be differentiated from their atactic analogs by their insolubility in MEK, by their infrared spectra, and, when soluble, by their NMR spectra. Polymerization data are shown in Table II. Figures 1-7 show IR and NMR spectra.

Preliminary polymerizations of styrene conducted in cyclohexane indicated that the $\text{Et}_3\text{Al-TiCl}_3$ catalyst system gave much higher conversion to isotactic polymer than either the $\text{Et}_3\text{Al-TiCl}_4$ or the $\text{Et}_2\text{AlCl-TiCl}_3$ systems (runs 32-1 to 32-4). Only low conversions were obtained, however, when 2VN and 4VB were polymerized in cyclohexane with the $\text{Et}_3\text{Al-TiCl}_3$ system (runs 43-2 and 50). Changing from cyclohexane to benzene, the solvent used by Natta et al., resulted in high conversions (>90%) of these monomers to isotactic polymers (runs 55-4 and 55-6). The stereoregular polymerization of 4VB and 1VN were found to be appreciably slower than the polymerization of 2VN, and even though 4VB ultimately gave high conversion to polymer, the best conversion obtained with 1VN was about 75% (runs 63-4, 101-3, and 101-4). The fact that better conversions were obtained in benzene than in cyclohexane suggests that the stereoregular polymerization of vinylaromatics is facilitated by solvents which can dissolve or swell the polymer.

As already mentioned, Natta et al. found that the use of TiCl_3 or TiCl_4 gave similar results in the polymerization of vinylaromatics. Our results with the $\text{Et}_3\text{Al-TiCl}_3$ system are better than those of Natta et al., while our results with the $\text{Et}_3\text{Al-TiCl}_4$ systems (runs 94-4 and 95-6) are somewhat poorer than theirs.

Although $\text{Et}_2\text{AlCl-TiCl}_3$ is an outstanding catalyst for the stereoregulated polymerization of propene, with vinylaromatics this catalyst gave only low conversions and the resulting product contained considerable amounts of atactic polymer (runs 32-4 and 87-1). It is likely that the $\text{Et}_2\text{AlCl-TiCl}_3$ system polymerizes vinylaromatics so slowly that cationic polymerization catalyzed by the Et_2AlCl becomes significant. In a control run (95-8), Et_2AlCl alone caused 2VN to polymerize.

Table II
POLYMERIZATION OF VINYL AROMATIC COMPOUNDS WITH ZIEGLER-NATTA CATALYSTS (a, b)

Run	Monomer	g	Alkyl-Aluminum ^(c)		Ti-halide		Al/Ti ^(d)	M. Wt. Regulator		Hours	Conv.	% MEK Insol.	% PhMe Insol.
			Compd.	Mmole	Compd.	Mmole ^(d)		Agent ^(e)	Mmoles				
8036-32-1	Styrene	10	TEAL	12	TiCl ₄	4	3	-	-	20	20	44	23
8036-32-2	Styrene	10	TEAL	6	TiCl ₄	4	1.5	-	-	20	41	51	11
8036-32-3	Styrene	10	TEAL	8	TiCl ₃	2.5	3	-	-	20	79	93	41
8036-32-4	Styrene	10	DEAC	8	TiCl ₃	2.5	3	-	-	20	24	44	14
8036-43-2	2VN	5	TEAL	4	TiCl ₃	1.3	3	-	-	40	20	70	nil
8036-43-3	2VN	5	TEAL	3.7	TiCl ₄	2	1.8	-	-	40	48	6	-
8036-50	4VB	5	TEAL	4	TiCl ₃	1.3	3	-	-	40	13	66	53
8036-54-1	2VN	5	TEAL	1.8	TiCl ₃	0.2	-	-	-	40	52	-	-
8036-54-2	2VN	5	TEAL	2	TiCl ₃	0.7	3	-	-	20	90	-	-
8036-54-3	2VN	5	TEAL	6	TiCl ₃	2	3	-	-	20	56	94	-
8036-55-4	2VN	5	TEAL	1.3	TiCl ₃	2	1.5	-	-	20	96	97	large
8036-55-6	4VB	5	TEAL	3	TiCl ₃	2	1.5	-	-	60	96	96	94
8036-57-1	2VN	5	TEAL	3	TiCl ₃	2	1.5	H ₂	4	20	72	68	16
8036-57-2	2VN	5	TEAL	3	TiCl ₃	2	1.5	VCl	4	20	38	9	-
8036-62-1	4VB	5	TEAL	3	TiCl ₃	2	1.5	VCl	1.3	40	58	8	-
8036-63-4	1VN	4.5	TEAL	3	TiCl ₃	2	1.5	-	-	40	76	90	26
8036-63-5	1VN	4.5	TEAL	3	TiCl ₃	2	1.5	VCl	1.3	40	9	-	-
8036-67-1	2VN	5	TEAL	2	TiCl ₃	3	1.5	VCl	0.4	20	30	32	nil
8036-67-2	2VN	5	TEAL	2	TiCl ₃	3	1.5	VCl	0.13	20	82	70	nil
8036-77	2VN	36.4	TEAL	10	TiCl ₃	7	1.5	VCl	0.3	40	79	42	nil
8036-82	1VN	35.3	TEAL	12	TiCl ₃	10	1	VCl	0.04	40	60	-	-
8036-83	2VN	35	TEAL	10	TiCl ₃	7	1.5	VCl	0.03	40	91	93	51
8036-84	2VN	30	TEAL	10	TiCl ₃	7	1.5	VCl	0.1	40	90	95	(40)
8036-86-1	2VN	32	TEAL	10	TiCl ₃	7	1.5	VCl	0.1	20	79	96	nil
8036-86-2	2VN	32	TEAL	10	TiCl ₃	7	1.5	VCl	0.2	20	55	94	nil
8036-87-1	2VN	5	DEAC	6	TiCl ₃	2	3	-	-	40	64	18	-
8036-87-2	2VN	5	DEAC	6	TiCl ₃	2	3	VCl	0.12	40	64	21	-
8036-92 (4x)	4VB	25	TEAL	10	TiCl ₃	7	1.5	-	-	70	67	95	93
8036-94-1	Styrene	5	TEAL	3	TiCl ₃	2	1.5	VCl	0.12	20	92	94	11
8036-94-2	Styrene	5	TEAL	3	TiCl ₃	2	1.5	VCl	0.4	20	88	95	10
8036-94-3	Styrene	5	TEAL	3	TiCl ₃	2	1.5	-	-	20	90	95	11
8036-94-4	2VN	5	TEAL	9	TiCl ₄	3	3	-	-	20	26	67	nil
8036-95-5	4VB	5	TEAL	6	TiCl ₄	2	3	-	-	7	7	10	-
8036-95-6	4VB	5	TEAL	9	TiCl ₄	3	3	-	-	40	13	11	-
8036-95-7	2VN	5	TEAL	3	TiCl ₃	2	1.5	-	-	20	91	96	58
8036-95-8	2VN	2	DEAC	6	-	-	-	-	-	40	25	-	-
8036-99-1	1VN	19.7	TEAL	10	TiCl ₃	7	1.5	-	-	90	67	95	73
8036-99-2	1VN	20.8	TEAL	10	TiCl ₃	7	1.5	-	-	90	64	95	-
8036-100-1	1VN	20.3	TEAL	10	TiCl ₃	10	1	-	-	70	49	-	24
8036-100-2	1VN	20.3	TEAL	10	TiCl ₃	10	1	-	-	70	49	-	24
8036-101-3	1VN	21.2	TEAL	10	TiCl ₃	10	1	-	-	70	75	-	43
8036-101-4	1VN	20.3	TEAL	10	TiCl ₃	10	1	-	-	70	75	-	43

(a) Polymerizations were run at 60° in benzene except for runs 32-1 to 50 which were in cyclohexane.

(b) A different batch of TiCl₃ was used beginning with run 86-1.

(c) TEAL = Triethylaluminum; DEAC = diethylaluminum chloride.

(d) Approximate values.

(e) VCl = Vinyl chloride.

The solubility behavior of the isotactic polyvinylaromatics is somewhat peculiar and is not yet entirely understood. P2VN varied from largely insoluble to largely soluble in toluene. Polymerization conditions yielding high conversions seemed to give the least soluble polymer (of runs 43-2 and 55-4). Much of the P2VN which was soluble in hot toluene came out of solution when the solution was cooled. Isotactic P1VN appeared to be completely soluble at the conditions of polymerization (benzene at 60°), and the polymerization mixtures gradually became very viscous but did not gell if the temperature was kept at 60°. On cooling to room temperature the solutions gelled irreversibly; warming for an extended period at 75° did not redissolve the polymer. Isotactic P4VB appeared to be only slightly swollen in its polymerization mixtures, and was invariably insoluble in hot toluene.

Since extremely high molecular weights could account for the insolubility of some of the polymers, some polymerizations were run in the presence of hydrogen or vinyl chloride which are known molecular weight regulators in Ziegler-Natta polymerizations. Since vinyl chloride was far more active than hydrogen (runs 57-1 and 57-2), it was used in most runs. It was found that large amounts of vinyl chloride seriously reduced the polymerization rates and the isotaxy of the resulting polymers (runs 57-2, 62-1, and 63-5). However, small amounts gave acceptable conversions to isotactic P2VN which was largely soluble in toluene (run 67-2). For reasons that are not understood, larger-scale polymerizations were not entirely successful (runs 77, 82). Attempts to produce a soluble P4VB using vinyl chloride were not successful.

When heated at about 300°, atactic PS gradually decreases in molecular weight with only minimal volatilization or carbonization.⁶ It was found that the toluene solubility of insoluble or only partially soluble isotactic PS and isotactic P2VN is significantly increased after 4 hours at 300° (Table III), even though the P2VN had become quite dark and the toluene-soluble extracts gave IR spectra characteristic of the isotactic polymers. However P4VB remained insoluble in toluene even after 15 hours at 300°. When heated one hour at 350°, P4VB underwent considerable

Table III

SOLUBILITY OF STEREOREGULAR POLYVINYLAROMATICS BEFORE AND AFTER
HEATING IN VACUO 4 HOURS AT 300°

	PS		P4VB		P2VN	
	<u>Before</u>	<u>After</u>	<u>Before</u>	<u>After</u>	<u>Before</u>	<u>After</u>
Sample Number	32-2	74-1	55-6	74-2	55-4	74-3
% insoluble in 2-butanone	93	69*	96	100	97	92
% insoluble in toluene	41	8.5	94	100		11

*2-Butanone extract was 94% insoluble in hexane. This hexane insoluble extract appeared (IR spectrum) to be largely isotactic PS.

volatilization, partly to monomer, and partly to a higher boiling liquid. The fact that the polymer melt flowed fairly readily during the heating at 350° suggests that the P4VB is not crosslinked and that its molecular weight has been considerably reduced. After cooling, however, the recovered P4VB remained insoluble in toluene and showed an IR spectrum typical of isotactic P4VB. It can thus be concluded that isotactic P4VB is inherently insoluble in toluene, even though it can be molded readily at 200°.

It is possible that the toluene solubility of vinylaromatic polymers is influenced by the kind of $TiCl_3$ used in the polymerization. In later runs in this project (beginning with run 86-1), a different batch of $TiCl_3$ was used, and the polymerizations gave PS and P2VN with greater solubility in toluene. (Cf. runs 32-3, 55-4, 94-1, and 95-7.) However, the P4VB obtained with the new $TiCl_3$ remained insoluble.

Since Natta et al. have reported a viscosity datum for isotactic P4VB in tetralin at 100° (Table I), attempts were made to dissolve samples of isotactic P4VB as obtained and after pyrolysis at 350° in tetralin. Both samples were found to be completely soluble at 150°,

but both samples came out of solution when cooled to 140°. It is not understood why the isotactic P4VB produced by Natta et al., was soluble in tetralin at 100°.

The polymerization of 9-vinylcarbazole was carried out at -78°C in toluene, using EtAlCl₂ as catalyst, as described in a Montecatini patent.⁵ It was claimed that polymers produced under these conditions had a crystallinity of 35-50% (by x-ray) and softening points between 300 and 400°C.

Polymers produced under these conditions in the present work had softening points around 290°C, but showed no increased crystallinity over polymers produced by high temperature free radical initiation or polymers produced by cationic initiation.

No differences could be detected in infrared spectra of the EtAlCl₂ or free radical-produced polymers. Since the polymers were insoluble, no NMR studies could be carried out. Thus, it is not known whether stereoregular polymers were produced.

B. IR, NMR, and X-Ray Characterization

The infrared spectra of the isotactic P1VN, P2VN, and P4VB were obtained as pressed films and compared with the spectra of the atactic polymers prepared in Part Ia. (See Fig. 1-4; note that the spectra include both the NaCl and KBr regions.) The spectral differences between the atactic and isotactic polymers were small but real, and were usually found in the 7-11 μ region (cf. Fig. 3) and in the KBr region.

NMR spectra of the isotactic and atactic polymers in deuteriochloroform are shown in Figs. 5-8. Since isotactic P4VB is insoluble in deuteriochloroform, it was measured in naphthalene-d₈ at 130°C. It will be noted that the spectral differences between the atactic and isotactic polymers are quite pronounced. The fact that the aromatic H signals of the isotactic polymers are more complex (better resolved) than the corresponding signals of the atactic polymers suggests that the rotation of the aromatic rings in the isotactic polymers is restricted. As can be seen in Figs. 5-8, the aliphatic H signals of the HCH and the ArCH

groups of the polymer chain are relatively broad. The chemical shifts exhibited by these hydrogens (Table IV) show some interesting trends and anomalies. The trends are exhibited by isotactic and atactic PS, P2VN, and P4VB; for each polymer the isotactic ArCH signal is shifted significantly downfield from the corresponding atactic signal. The HCH signals are very little affected by the isotaxy of the polymers. The signals for the ArCH of P1VN (isotactic and atactic) are shifted far downfield from the signals of the other three polymers, while the isotactic HCH signal is shifted far upfield. The shifts shown by P1VN probably arise from interaction of the chain hydrogens with the naphthalene rings. Downfield shifts may signify proximity to the naphthalene ring in the plane of the ring, while upfield shifts indicate proximity to the π cloud of the ring system.

In the stereoregular polymerization of vinylaromatics, some MEK soluble polymer usually is formed along with the MEK insoluble (isotactic) polymer. The MEK soluble fraction from a stereoregular polymerization of 2VN gave the NMR spectrum shown in Fig. 7c. The poorly resolved signals of this spectrum suggest that the fraction has an intermediate steric order.

Table IV
NMR SIGNALS OF CHAIN PROTONS IN ISOTACTIC AND
ATACTIC POLYVINYLAROMATICs

Polymer	ArCH		HCH	
	Isotactic	Atactic	Isotactic	Atactic
PS	7.96	8.17	8.54	8.59
P1VN	7.52	7.24	9.02	8.57
P2VN	7.84	8.16	8.54	8.55
P4VB	—	8.13	—	8.49
<u>P4VB*</u>	7.68	7.98	8.45	8.54

Data are τ values with tetramethylsilane as internal standard.

* In naphthalene- d_8 .

Natta et al. found (Table I) that P1VN is crystallizable, while P2VN and P4VB did not crystallize. Our findings agree: P1VN crystallized without difficulty (m.p. 330-335°C; see Table V for X-ray data), but P2VN and P4VB were found to be amorphous by X-ray and optical birefringence examination.

Table V

LATTICE SPACINGS FOR CRYSTALLINE P1VN^a

<u>d</u>	<u>Intensity</u> ^b
6.02	S
4.760	S
4.330	M
3.747	S
3.528	M
3.130	M

^aCu K α radiation (1.541 Å); specimen was annealed film.

^bS, strong; M, medium.

IV EXPERIMENTAL

A. Preparation of Isotactic Poly(vinylaromatics)

Triethylaluminum, a "1 M" cyclohexane "suspension" of TiCl₃(AA), and monomer were transferred, in an inert atmosphere, to an argon flushed pop bottle containing dry benzene and a magnetic stirring bar. After the bottle was capped with a Buna-N septum, vinyl chloride gas, if used, was added with a syringe, and the bottle was agitated at about 60° in a water bath on a stirring hot plate. The polymerization was continued 20 hours or longer. At the end of a 4VB polymerization, the reaction mixture was a very fine dispersion of only slightly swollen polymer particles.

A 1VN polymerization gave a viscous mass which gelled on cooling, and polymerization of 2VN gave a mixture which was a gel even at 60°. The polymerization mixture was transferred to a blender and washed twice with isopropanol. If the polymer was not colorless it was then washed once or twice with 2-butanone and finally dried overnight in vacuo. Polymer of low stereoregularity was removed by continuous extraction with 2-butanone for 20-40 hours.

Infrared spectra were made from pressed films. P2VN and P4VB were pressed at 200-250°. P1VN was pressed at 315° and annealed by allowing it to cool in the press. NMR spectra were made at 100 mc using tetramethylsilane as an internal standard.

B. Pyrolysis of Isotactic Poly(vinylaromatics)

The polymer sample (1 to 2 g) was placed in a tube which was continuously evacuated while the sample was immersed in a Woods metal bath at 290-310°. After 4 hours, when the heating was stopped, P2VN was very dark, while PS and P4VB remained light colored. The recovered polymers were characterized by extraction with 2-butanone and toluene, and by their IR spectra. Since the recovered P4VB was still insoluble in refluxing toluene, it was heated an additional 10 hours at 300° (still toluene insoluble) and finally for one hour at 350°. During the final heating some monomer crystallized onto the cool upper surface of the pyrolysis tube, and a liquid slowly refluxed just above the surface of the bath. The polymer melt was observed to flow when the hot tube was tilted. The recovered P4VB was insoluble in toluene (110°), dichloromethane, o-dichlorobenzene, dimethylsulfoxide, tetrahydrofuran, and benzene (all at 60°). The IR spectrum of the recovered P4VB was unchanged.

C. Polymerization of 9-Vinylcarbazole with EtAlCl₂

A solution containing 50 g (0.26 mole) of 9-vinylcarbazole in 225 ml of toluene was added dropwise over a 2-hour period to a solution of

12.7 ml of a 20% solution of EtAlCl_2 in 150 ml of toluene at -78°C while stirring rapidly. The polymers separated out of solution as formed and usually wrapped around the stirrer. After the addition was completed, stirring was continued for 15 minutes, and then approximately 10 ml of methanol was added to decompose the catalyst.

The product was collected into methanol, blended twice in a Warring Blendor, and then dried in a vacuum oven at 60°C for 24 hours. Conversion was quantitative.

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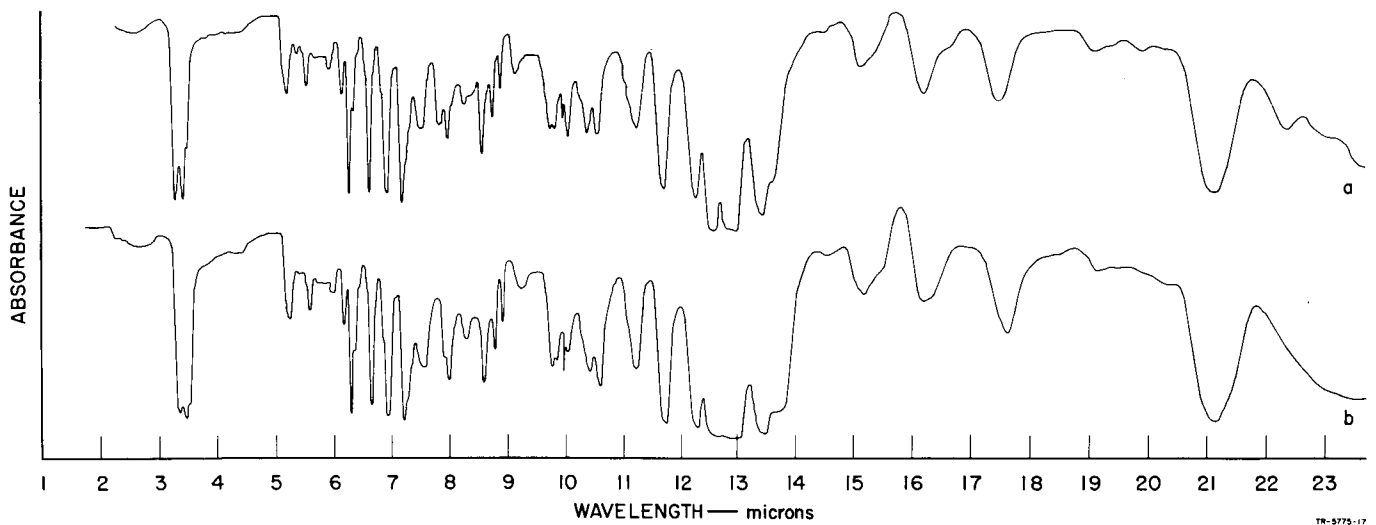


FIG. 1 INFRARED SPECTRA OF (a) ISOTACTIC AND (b) ATACTIC POLY-1-VINYLNAPHTHALENE

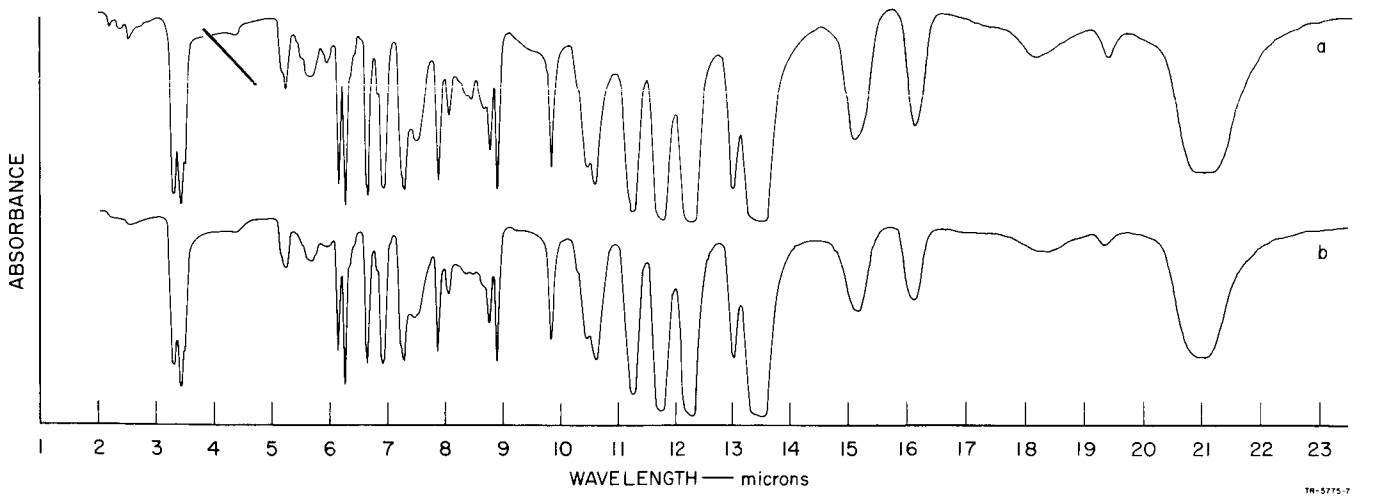


FIG. 2 INFRARED SPECTRA OF (a) ISOTACTIC AND (b) ATACTIC POLY-2-VINYLNAPHTHALENE

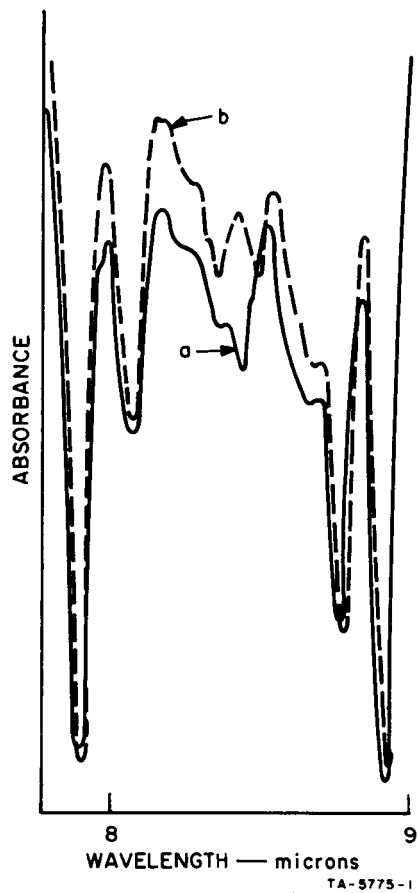


FIG. 3 DETAIL OF INFRARED SPECTRA OF (a) ISOTACTIC AND (b) ATACTIC POLY-2-VINYLNAPHTHALENE

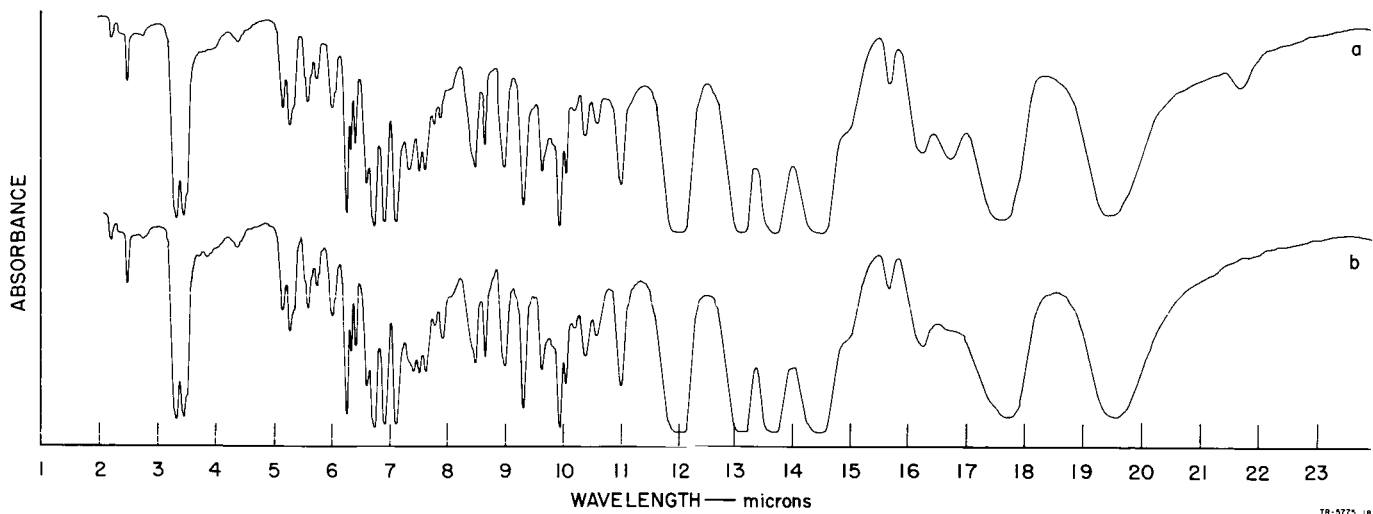


FIG. 4 INFRARED SPECTRA OF (a) ISOTACTIC AND (b) ATACTIC POLY-4-VINYLBIPHENYL

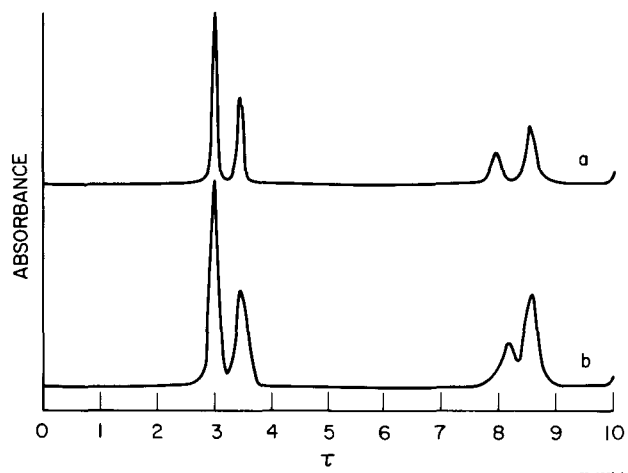


FIG. 5 NMR SPECTRA OF (a) ISOTACTIC AND (b) ATACTIC POLYSTYRENE

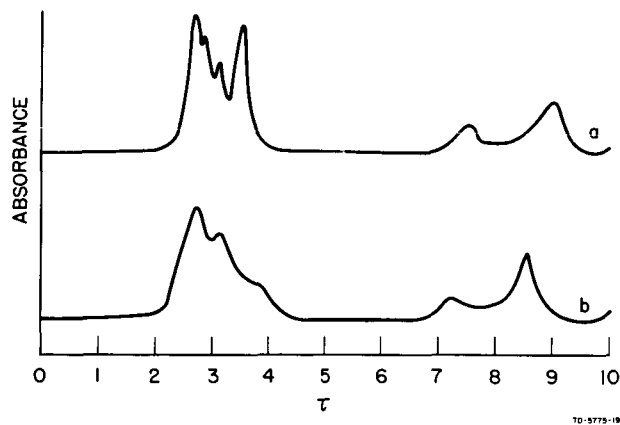


FIG. 6 NMR SPECTRA OF (a) ISOTACTIC AND (b) ATACTIC POLY-1-VINYLNAPHTHALENE

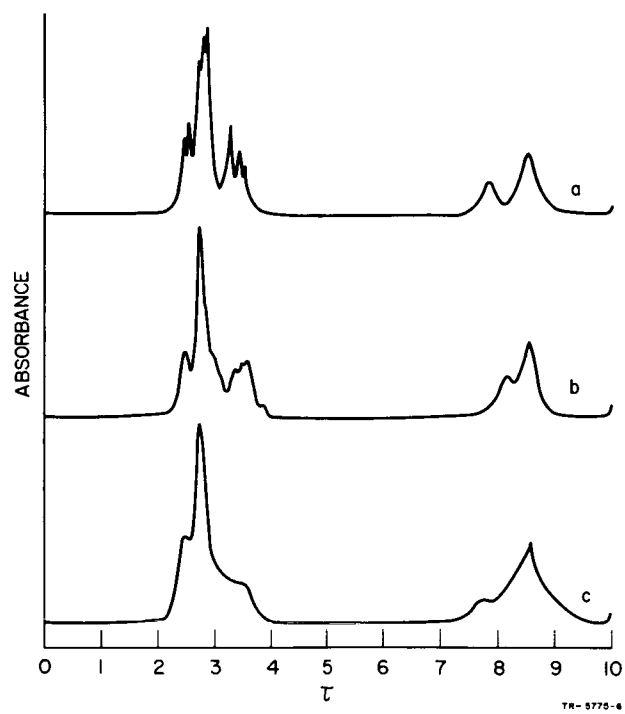
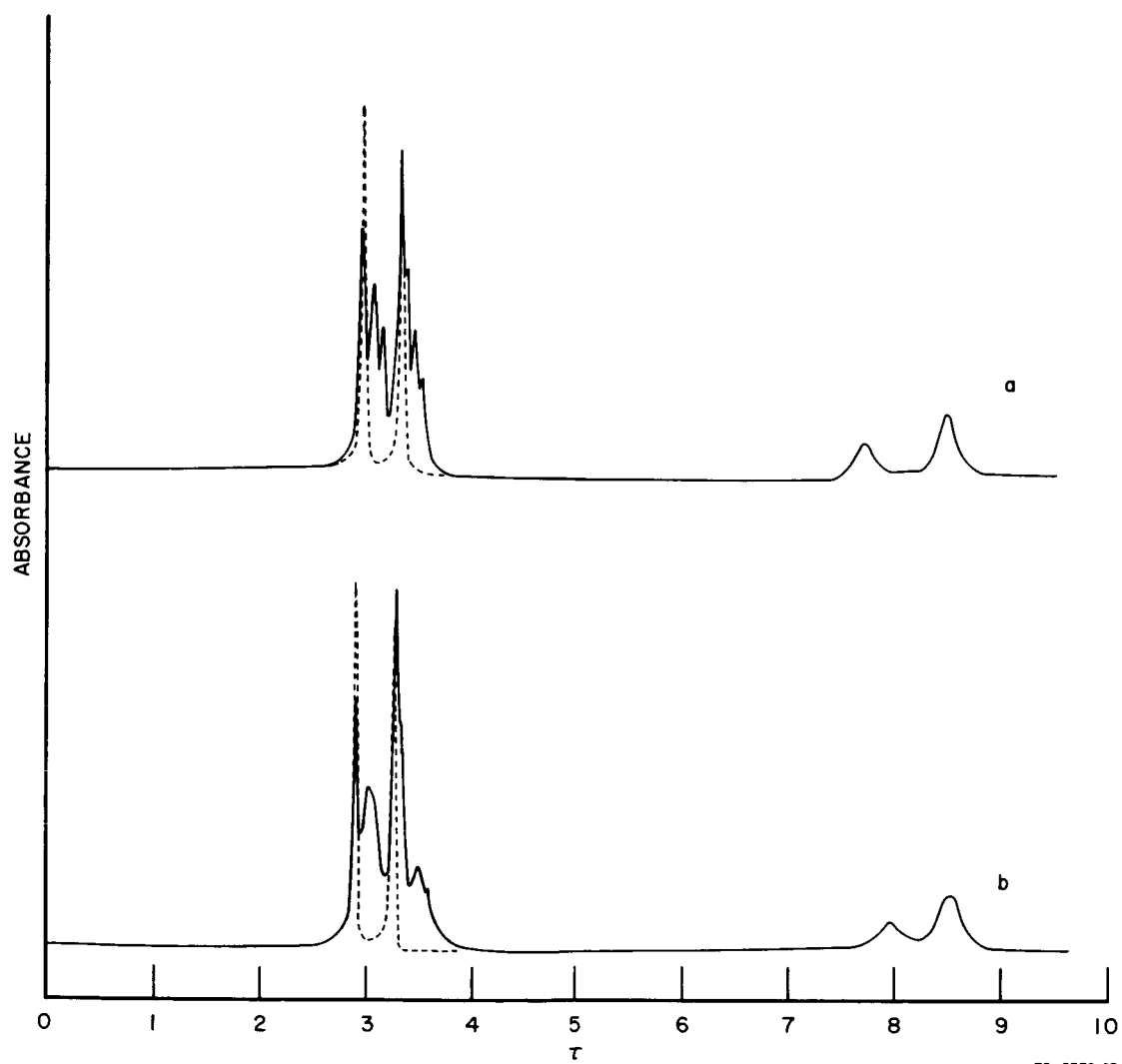


FIG. 7 NMR SPECTRA OF (a) ISOTACTIC,
 (b) ATACTIC, AND (c) STERICALLY
 INTERMEDIATE POLY-2-VINYLNAPHTHALENE



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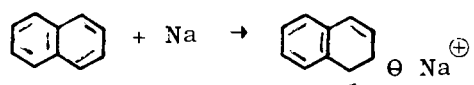
FIG. 8 NMR SPECTRA OF (a) ISOTACTIC AND (b) ATACTIC POLY-4-VINYLBIPHENYL SUPERIMPOSED ON THE SPECTRUM OF NAPHTHALENE- d_8

Phase II

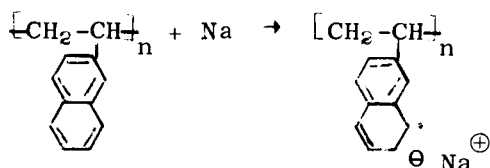
I INTRODUCTION

Phase II of the present contract was concerned with reactions of vinylaromatic polymers with alkali metal atoms, the degradation of radical anions thus formed, and the utilization of these anions in block copolymerization reactions.

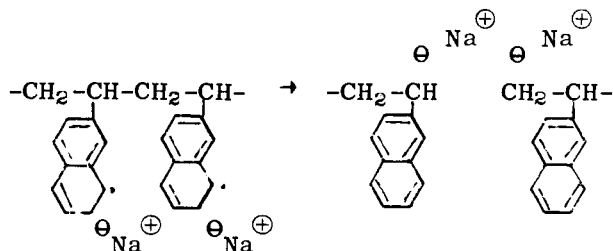
Reactions between alkali metal atoms and aromatic nuclei take place by an electron transfer from the alkali metal to the aromatic nucleus. For example,



The same reaction will take place when the aromatic nucleus is attached to a polymer chain as, for example, in poly-2-vinylnaphthalene:



The polymeric radical anions formed undergo cleavage reactions, yielding as products polymeric living anions. The cleavage reaction is thought to involve adjacent vinylaromatic radical anions. Thus,



These living anions can then be utilized to prepare block copolymers. One novel feature of this procedure is that block copolymers containing an isotactic segment can thus be produced.

II SUMMARY

Poly-2-vinylnaphthalene dianions prepared both by sodium initiation and by α -methylstyrene dimer initiation were used to initiate the polymerization of isoprene. Even though a vigorous isoprene polymerization occurred, no color change took place and only a small portion of the vinylaromatic dianion copolymerized. These observations were interpreted in terms of a slow initiation and a fast propagation reaction. Polymeric dianions prepared by a sodium degradation of polyvinylaromatics were found to behave similarly.

The reaction of poly-2-vinylnaphthalene with α -methylstyrene dimer dianion or cumyl potassium in tetrahydrofuran was found to involve an electron transfer from the anion into the naphthalene nucleus. The resulting radical anions then undergo degradation reactions.

III RESULTS AND DISCUSSION

Initial work on this phase consisted of preparing bifunctional living anions of poly-2-vinylnaphthalene (P2VN) in tetrahydrofuran by means of sodium initiation and then using these blocks to initiate the polymerization of isoprene. It was consistently found that although in tetrahydrofuran the P2VN anion is green and the isoprene anion is yellow, no color change occurred even when a large excess of isoprene was used. Furthermore, initial fractionation data indicated that the reaction products were mixtures of 2VN and isoprene homopolymers.

These results were first interpreted to mean that, in addition to P2VN anions, an appreciable concentration of 2VN radical anions are formed and that isoprene polymerization is initiated by these radical anions. In order to explain the lack of copolymerization it was necessary to postulate that the basicity of 2VN is too weak to initiate isoprene polymerization.

In order to verify this hypothesis, P2VN dianions were formed by initiation with α -methylstyrene dimers. Since no sodium was used, no 2VN radical anions could form. When isoprene was added to the P2VN dianions formed the polymerization again occurred without a color change. Thus, the initial hypothesis that P2VN anions will not polymerize isoprene was incorrect. However, work carried out during the last month of this contract has shown that α -methylstyrene dimers easily transfer an electron into the naphthalene nucleus, so that these experiments are not as rigorous as initially thought.

In order to guard against the possibility that the isoprene polymerization was due to unreacted α -methylstyrene dimer which remains in solution, a UV cell was attached to the reactor. No absorption characteristic of the dimer (340 m μ) was noted, and only the strong 410 m μ absorption characteristic of 2VN was observed.

Efforts were next concentrated on evolving a method for quantitatively fractionating the reaction products. Work with gel permeation chromatography did not yield conclusive results, since this method depends primarily on molecular weight distribution and is not very sensitive to molecular species. It was found that Soxhlet extraction with n-heptane will quantitatively leave behind polyvinylaromatics and dissolve out block copolymers and isoprene homopolymers. Unfortunately, however, low molecular weight polyvinylaromatics are partially soluble in n-heptane, so that this extraction cannot be used indiscriminately, and a control must be run on a terminated polyvinylaromatic portion before isoprene is added.

No general method has yet been found that will separate block copolymer and isoprene homopolymer. However, the fact that after treatment with isoprene some P2VN becomes soluble in n-heptane represents strong evidence that block copolymerization did indeed take place.

Results of these fractionation experiments are shown in Table I. Although the data are too incomplete to justify a rigorous interpretation, it would appear that the copolymerization behavior of 2VN and

Table I

n-HEPTANE EXTRACTION DATA ON BLOCK COPOLYMERIZATION
EXPERIMENTS

Exp. No.	Vinyl-Aromatic	Initiator	n-Heptane Soluble (%)	Vinylaromatic Co-polymerized (%)	Mole Ratio Isoprene/Vinylaromatic
8080-78-1	2VN	Na	0.2	---	---
8080-78-2	2VN	Na	76.2	25.5	5
8080-86-1	4VB	Na	64.3	---	---
8080-86-2	4VB	Na	92.0	~ 0	10
8080-98-1	2VN	α MeStDi	68.5	---	---
8080-98-2	2VN	α MeStDi	91.2	6.5	4
8080-108-1	2VN	α MeStDi	14.9	---	---
8080-108-2	2VN	α MeStDi	100	100	49

2VN, 2-Vinylnaphthalene.

4VB, 4-Vinylbiphenyl.

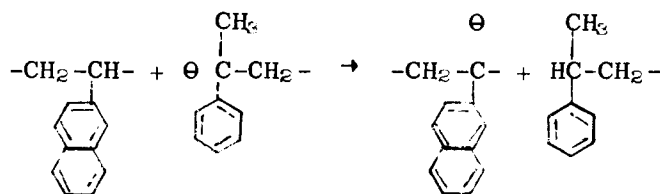
isoprene in tetrahydrofuran can best be rationalized by assuming a slow initiation and a fast propagation reaction. Under these circumstances, little of the initiator dianion would be consumed, and there would be no color change. Similar kinetics were reported by Waack and Doran¹ in the polymerization of styrene with various organo-lithium compounds. It is not clear, however, why no significant color change was noted in experiment 8080-108, which indicates that virtually all of the dianion copolymerized with isoprene. It is obvious that more work is needed before any significant conclusions can be drawn.

Experiments were performed in which P2VN in tetrahydrofuran was placed on sodium and allowed to degrade, and isoprene was then added to the living anion. These experiments were qualitatively identical with those in which isoprene was added to P2VN dianions formed by sodium or α -methylstyrene dimer dianion initiation in that, again, no color

change was noted even when a large excess of isoprene was used. No n-heptane extractions were carried out, but GPC measurements showed that the reaction products were clearly heterogeneous.

During the course of these studies it was noted that when α -methylstyrene dimer dianions in tetrahydrofuran are added to a P2VN solution in tetrahydrofuran, the UV spectrum of α -methylstyrene dimer dianions gradually disappears and the UV spectrum of 2VN anions gradually appears. The reaction is complete in approximately 3 days.

Initial interpretations of these results, in analogy with a similar situation described by Bahsteter et al.² were that the α -methylstyrene anions remove the more acidic hydrogens from the polymer backbone. Thus:



Such a reaction would be of considerable interest, since it would allow racemization of isotactic polymers and controlled grafting reactions. It was found, however, that the isotactic P2VN formed by this procedure could not be racemized. Similar results were obtained with cumyl potassium in tetrahydrofuran. Since a similar failure to racemize isotactic polystyrene was also noted by Kern,⁵ the metalation reaction was studied further.

In order to verify that anions are actually formed on the polymer backbone, a number of runs were terminated with deuterium oxide and the isolated polymer was examined by IR and NMR. Only trace amounts of deuterium were found.

During the work-up procedures in these experiments, extensive degradation of the polymers took place. This degradation, coupled with the fact that no deuterium could be found in the polymer backbone, strongly suggests that P2VN radical anions were formed. Thus, α -methylstyrene dianion or cumyl potassium transfers an electron into the

naphthalene nucleus. Supporting evidence has now also been obtained by ESR spectroscopy.

IV EXPERIMENTAL

Initial reactions were carried out under a purified argon atmosphere. It was found, however, that these experimental conditions were not rigorous enough, and so the bulk of the work was carried out under high vacuum using all glass systems with breakseals. All experiments described in this report are the high vacuum experiments.

A. Vacuum System and Reactors

The vacuum system (shown in Fig. 1) consisted of a manifold of 30 mm OD tubing 28 inches long. It could be routinely evacuated to 10^{-5} torr by means of a Duo-Seal mechanical fore-pump and a mercury diffusion pump. Bulb A (1000 ml) was used for storage of purified tetrahydrofuran which was kept over sodium-potassium alloy and later over sodium naphthalene.

Glass reactors used in polymerization and degradation experiments are shown in Figs. 2 and 3.

B. Procedure

1. Sodium Initiated Polymerization

The apparatus shown in Fig. 2 was used. Purified vinylaromatic monomer was placed into bulb A, and tube C, equipped with a glass break-seal containing purified isoprene, was sealed onto the reactor. Tube D, containing sodium pellets, was next sealed onto bulb B, and the whole assembly was placed on the vacuum system and thoroughly evacuated. The sodium metal in tube D was then gently heated, and a sodium mirror formed in bulb B. Tube D was next sealed off. A measured amount of tetrahydrofuran was distilled into the reactor via a graduated cylinder and degassed, and the whole reactor was sealed off at E. After the solvent was melted, the solution was mixed and a small amount was poured

from bulb A into bulb B and allowed to react with the sodium mirror. The intensely colored solution was then poured back into bulb A. One or two small portions were usually used to titrate all impurities before the monomer in bulb A was polymerized. Bulb A was then sealed off at F. After 2-3 hours reaction time, a small amount of living polymer solution was poured into bulb G, which was then sealed off at H. Isoprene was added to bulb A by breaking the break-seal with an glass-enclosed iron slug, and the polymer was isolated after ca 13 hours reaction time by pouring into methanol.

2. α -Methylstyrene Dimer Initiated Polymerization

The apparatus shown in Fig. 3 was used. Purified vinylaromatic monomer was placed in bulb A; tubes B and C, equipped with break-seals and containing isoprene and α -methylstyrene dimer, respectively, were sealed onto the reactor, which was then placed on the vacuum system and thoroughly evacuated. A measured amount of tetrahydrofuran was distilled into the reactor and degassed, and the reactor was sealed off at D. After melting the solvent and mixing the monomer, tube C was broken. An instantaneous color change took place. After 2-3 hours reaction time a small amount of living polymer solution was poured into bulb E which was then sealed off at F. Isoprene was next added by breaking tube B, and the polymer was isolated after ca 12 hours reaction time by pouring into methanol.

3. Degradation Experiments

The apparatus shown in Fig. 2 was used. The procedure was essentially identical to that used in the sodium initiated polymerization experiment, except that polymer was placed into bulb A and the whole solution was poured into bulb B and allowed to react with the sodium mirror overnight. The colored solution was then poured back into bulb A, sealed off at F, and allowed to stand for 3-4 days before isoprene was added.

4. Purification of Isoprene

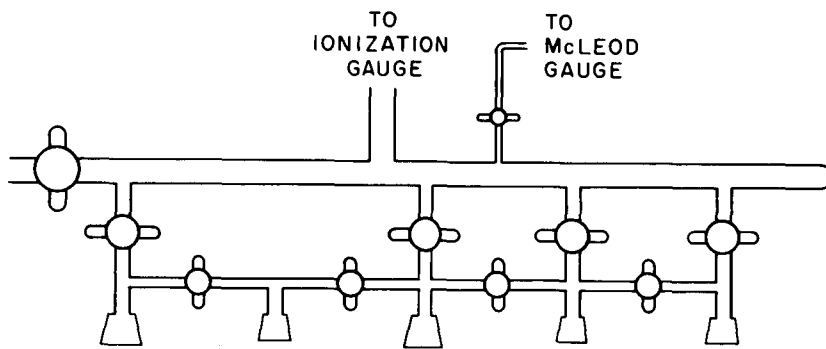
Isoprene (Phillips Petroleum, Research Grade) was placed over CaH_2 on the vacuum system, degassed, and allowed to sit for 24 hours. It was then distilled into a bulb containing a sodium mirror, allowed to react 2-3 hours, and then distributed into six tubes equipped with breakseals. These were stored in a freezer until used.

5. Preparation of α -Methylstyrene Dimer

Purified α -methylstyrene was placed over CaH_2 on the vacuum system, degassed, and allowed to sit for 3-4 days. Tetrahydrofuran and monomer were then distilled into a bulb containing an excess of sodium mirror and allowed to react overnight, and the red solution was distributed into six tubes equipped with breakseals. They were stored in a freezer until used.

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FIG. 1 SCHEMATIC DIAGRAM OF VACUUM SYSTEM

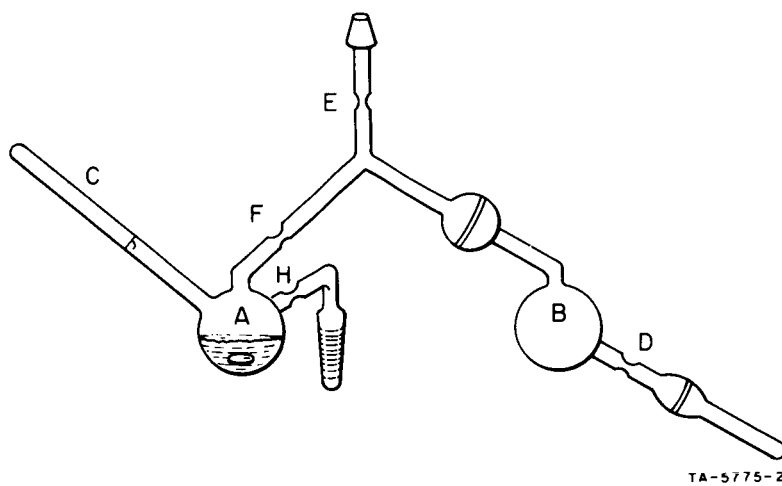
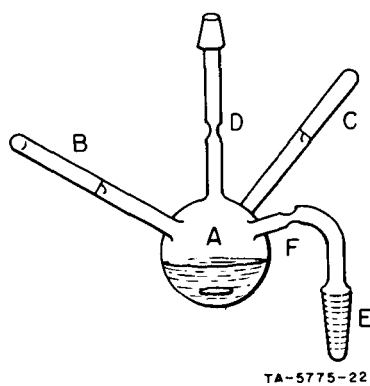


FIG. 2 REACTOR FOR POLYMERIZATION AND DEGRADATION STUDIES



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FIG. 3 REACTOR FOR
POLYMERIZATION
STUDIES