sodium sulfate and the amino ketone hydrochloride was precipitated by the addition of ethereal hydrogen chloride, yield 59%.

It was observed that the amino ketones were sensitive compounds and in several experiments the yields were very poor. The diethylamino compound, for example, suffered decomposition with the formation of appreciable amounts of 4,4′-dichlorobenzil. Each successive crystallization of the hydrochloride of this amino ketone from the methanol–butanone mixture involved the formation of significant amounts of 4,4′-dichlorobenzil which was difficultly soluble in the solvent and crystallized out during the manipulation.

In one preliminary experiment V was obtained in only 26% yield upon heating a solution of 0.2 mole of III and 0.424 mole of diethylamine in benzene on the water-bath without the precaution of excluding air.

(3) Preparation of the 1,2-Di-(4-chlorophenyl)-N-substituted-ethanolamines by Reduction of Amino Ketones.—The amino ketones prepared as above were reduced to the corresponding alcohols (IV and VI) in the usual way by means of an excess of 1.5 *N* aluminum isopropoxide. The butylamino and octylamino alcohols were purified as the free bases, while all the other amino alcohols were purified as the hydrochlorides.

(4) The Preparation from 4,4′-Dichlorostilbene Oxide.—A mixture of X and a large excess of the amine was heated at (a) 130° and (b) 150°, respectively, taken up in (c) benzene or (d) ether, washed with water to remove excess amine, dried over sodium sulfate, and treated with ethereal hydrogen chloride to precipitate the salt. (e) The condensation using 28% concd. aqueous ammonium hydroxide in dioxane as solvent (sealed tube) was at 100°.

Summary

An improved preparation of 4,4′-dichloro-benzoin and 1,2-di-(4-chlorophenyl)-ethanol, and the syntheses of 4,4′-dichlorodesyl chloride, *trans*-4,4′-dichlorostilbene and 4,4′-dichlorostilbene oxide, are described.

From these compounds a series of secondary and tertiary-amino desoxybenzoins and the corresponding amino and substituted-amino alcohols, have been prepared.

Resistance to aluminum isopropoxide reduction of the ethylethanolamino ketone as contrasted with the facile reduction of the monoethanolamino analog, indicates a cyclic hemiacetal structure for the former.

CHARLOTTESVILLE, VIRGINIA

RECEIVED SEPTEMBER 7, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Polymerization. IX. Metalation during Alfin Polymerization of Butadiene and the Formation of Gel[1]

BY AVERY A. MORTON, RICHARD P. WELCHER,[2] FRANCES COLLINS, SIEGFRIED E. PENNER AND ROBERT D. COOMBS

The previous paper[3] showed that metalation of rubber caused gel to form in proportion to the metalating activity, and the paper[4] before that showed that an Alfin[5] catalyst was a poorer metalating agent than the allylsodium component of the catalyst. It seemed likely, therefore, that the amount of gel formed during Alfin polymerization would have a direct connection with the lack of correct proportioning of alkoxide with alkenylsodium, or, in the absence of a specific combination, would have a connection with the quantity of catalyst in excess of that needed for polymerization. In either event the relation would be expressed by the rule that minimum gel would accompany maximum polymerizing activity. The idea of a specific combination has been confirmed with two moderately active catalysts and that of quantity with an extremely active catalyst that is less sensitive to proportioning.

The first catalyst (PB_1)[5] was made from sodium isopropoxide and 1-butenylsodium. Two series of reagents, A and B, were used. A was made by combining the two components after each had stood for some time. Figure 1 shows clearly that in four separate trials during a period of over two months the peak of activity (with reagent no. 4) was also the one with minimum gel. B was made by mixing immediately after preparing the two components separately. Figure 2 shows again the relationship but only after the catalyst had aged for some time (test no. 3). The aging process (in B) unquestionably would have been accelerated if the mixing had been done in the high-speed stirring apparatus. Figure 3 confirms this action of the B series with a mixture of butadiene and isoprene, the latter being added to slow down the action, erase part of the gel formation (isoprene[5] forms little or no gel when polymerized) and bring out the action more distinctly. The particular proportions for maximum activity with A and B have no significance since particle size of the two components was probably not the same. The method of combination was not ideal, but was chosen because it permitted proportioning from stock preparations of the two components. The total amount of each present, therefore, has less significance than the composition of the available surface.

The second catalyst was made from sodium phenylmethyl carboxide and allylsodium and a

---

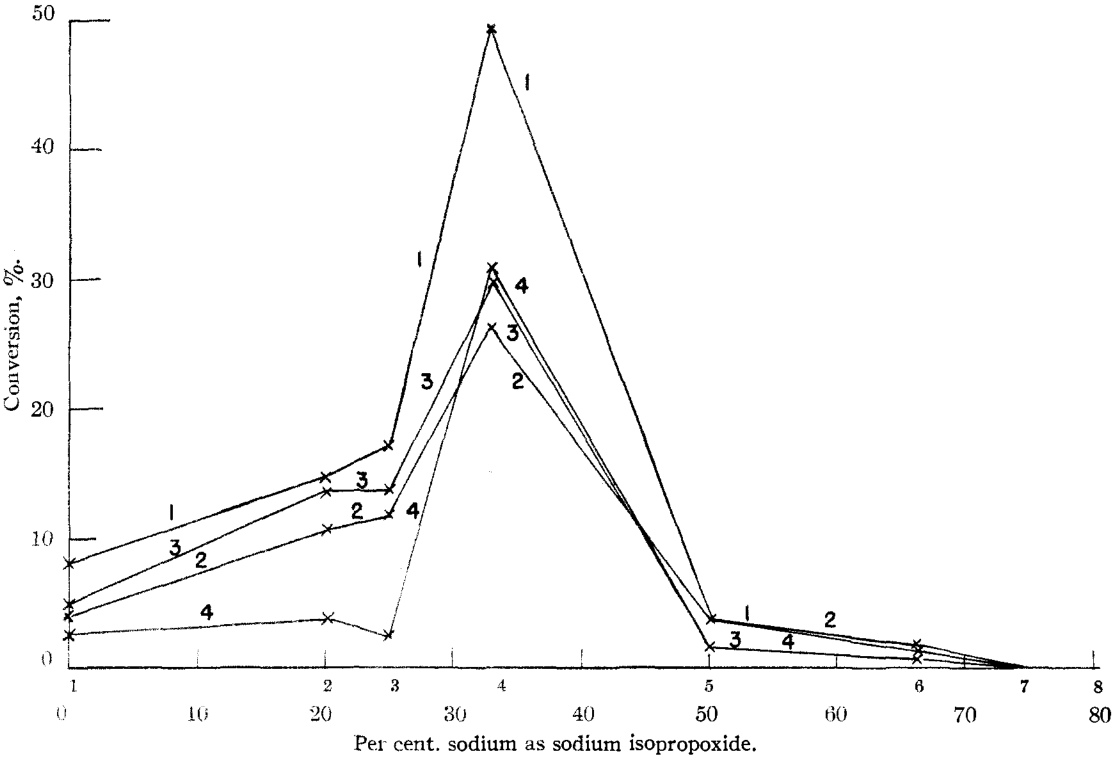
[1] This work was part of the program of research carried out in recent years under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation.

[2] Present address: The American Cyanamid Company, Stamford, Connecticut.

[3] Morton and Ramsden, THIS JOURNAL, **70**, 3132 (1948).

[4] Morton and Holden, *ibid.*, **69**, 1675 (1947).

[5] Morton Magat and Letsinger, *ibid.*, **69**, 950 (1947).



Reagent no.	1				2				3				4			
Test no.	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Cat. age, days	4	7	18	70	6	9	20	72	5	8	19	71	11	14	25	77
[η]	0.15	0.20	..	..	6.2	5.8	4.4	..	7.7	5.9	4.7	..	5.0	6.8	5.4	..
Gel, %	8	11	..	..	50	59	51	..	65	44	61	..	10	7	7	..

Reagent no.	5				6				7				8			
Test no.	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Cat. age, days	6	9	20	72	5	8	19	71	6	9	20	72	4	7	18	70
[η]	2.0	0.8	..	..	2.0	2.1	2.5	..	1.0	0.1	..	..	..	..	..	..
Gel, %	55	59	..	..	79	26	54	..	58	15	..	..	..	..	..	..

Fig. 1.—Polymerization of butadiene by PB_1 catalyst, series A.

different method was used to adjust the proportions. In the first preparation, C, phenylmethylcarbinol was allowed to react with part of the amylsodium, after which propylene was added to the remainder, so that allylsodium was prepared in the presence of the alkoxide and combination occurred before either component had much chance to agglomerate. This method is the one usually employed for making Alfin catalysts but is less suitable for proportioning the components because of variations in the yields of amylsodium. The product, C, gave good conversion with very low gel (see Table I). D was a similar preparation, the initial behavior of which was clearly similar to those of A and B that had high proportions of alkoxide. Accordingly two small portions of allylsodium, each equal to approximately one-twentieth of the allylsodium originally present, were added, each time with vigorous stirring, and allowed to age for a short or moderate time. A point of maximum activity and zero gel was thus reached (see Table I).

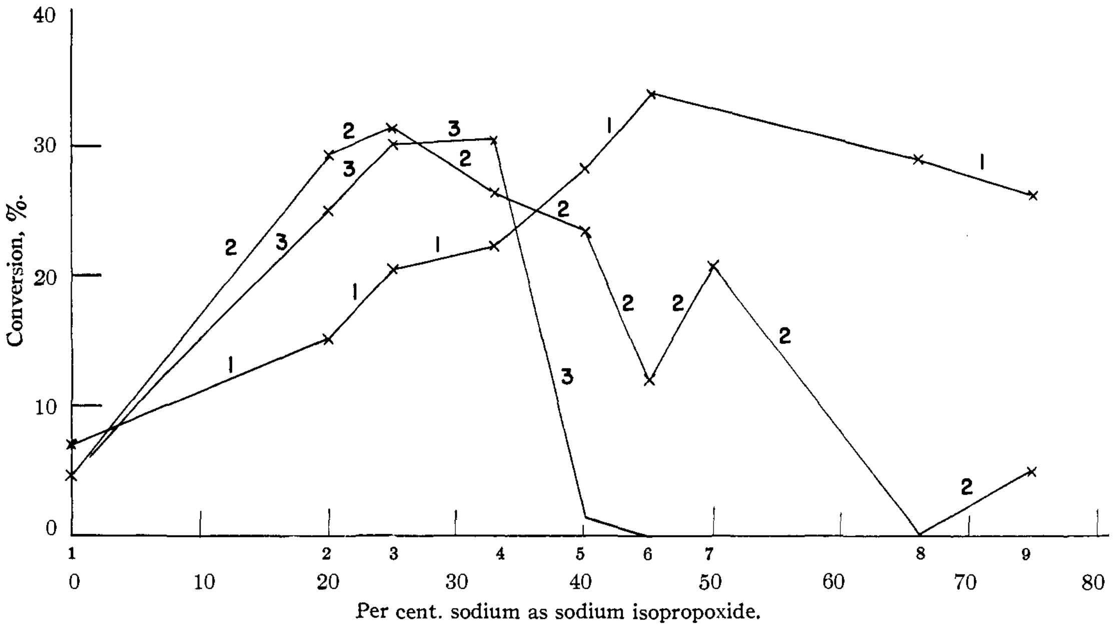
The third catalyst (PP) was from sodium isopropoxide and allylsodium. This pair had extraordinarily high activity, did not lose activity in the presence of excess alkoxide (as do the other two) and gave a product of very high intrinsic viscosity which unquestionably increased the tendency to form gel. The usual percentage of gel from such a catalyst is around 60 to 90. Just once out of well over two hundred preparations of catalyst was one obtained that produced, by bottle polymerization, a rubber with gel as low as 23%. When, however, the quantity of catalyst was reduced to one-fourth, the percentage of gel fell. Values below 20%, some as low as 2%, became

Table I

Effect of Addition of Allylsodium to Inactive Catalyst Made from Sodium Phenyl Methyl Carboxide and Allylsodium

Catalyst	Additions or other changes	Conversion, %	Intrin. vis.	Gel, %
C		35	6	0 to 10
D	As prepared	16	1	34
D_{1-3}	D with RNa[a] added and aged 3 days	19	3.8	18
D_{1-18}	D_1 15 days later	28	6.0	14
D_2	D_1 with RNa added	29	5.8	13
D_{2-8}	D_2 8 days later	33	5.8	0
D_3	D_{2-8} satd. with C_3H_6	32	6.6	0

[a] R = allyl.



Reagent no.	1			2			3			4			5			6			7			8			9		
Test no.	1	2	3[a]	1	2[a]	3[b]	1	2	3[c]	1	2	3[a]	1	2	3	1	2[a]	3	1	2	3	1[a]	2	3	1	2	3
Cat. age, days	3	23	37	3	23	37	3	23	37	3	23	37	3	23	37	3	23	37	3	23	37	3	23	37	3	23	37
|n|	0.14	0.17	0.31	2.7	4.1	7.2	6.9	8	10.6	8.0	9.6	10.7	9.6	10.6	2.5	9.7	7.4	..	..	9.8	..	9.3	..	..	6.5	3.9	..
Gel., %	27	0	16	32	0	27	14	7	37	12	12	21	35	16	...	32	41	..	..	33	..	23	..	..	...	...	..

[a] 31 min. polymerization time. [b] 32 min., [c] 33 min. All other times, 30 min.

Fig. 2.—Polymerization of butadiene by PB_1 catalyst, series B.

common. Conversions, on the other hand, remained high, some as high as 70%. The efficiency was obviously higher and the percentage of gel was lower.

The authors are indebted to Christiana Clapp and Jeanne Kilduff for valuable technical assistance and determination of the constants of the polymers.

Experiments

General Methods.—The operations of preparing amylsodium, metalating the olefins, and polymerizing the dienes have now become routine. The description below will suffice for this paper and others to come, the small variations introduced by each operator having been found to have little effect that exceeds the variation necessarily imposed on any reaction where the reagents are in different phases.

The amylsodium necessary for metalation of the olefins was prepared by drop-wise addition at −10° of 63 ml. (0.5 + mole) of amyl chloride on 23 g. of sodium sand in 500 ml. of pentane under an atmosphere of nitrogen in the high-speed stirring apparatus[6] in the usual manner as described in a previous publication.[5] This size preparation is referred to hereafter as the standard. Larger preparations were made with proportionately larger amounts. They are referred to as two or three times the standard, depending on the amount.

Allylsodium was prepared by bubbling propylene (Phillips Petroleum Company, pure grade) into the amylsodium suspension at 10° to room temperature and with high-speed stirring for about five hours. 1-Butynylsodium was made by addition of 1-butene at −10° to amylsodium. The temperature was then allowed to rise gradually over a one and a half to three and a half hour period to around 20°. Two additions of 60 ml. of 1-butene each per standard batch (total 120 ml.) were thus made in the preparation of Series A reagents; and a single addition of 120 ml. per twice the standard batch was made in preparing the Series B reagents. All reaction mixtures were allowed to stand overnight to complete the metalation.

If metalation of the olefin was to be carried out in the presence of an alkoxide, the alcohol was added to the reaction mixture at 0° just before addition of the olefin. The time needed for metalation of the olefin in the presence of alkoxide was only about half that in the absence of alkoxide. The common practice, however, was to allow all such reaction mixtures to stand overnight.

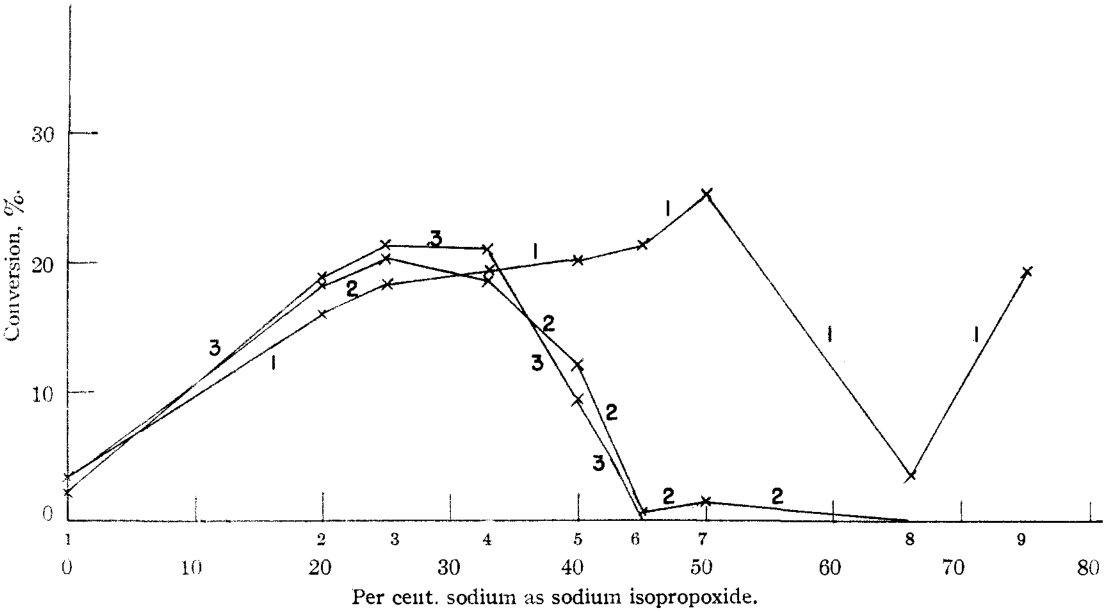
The alkoxide for the stock solutions was prepared by addition of alcohol to amylsodium. This method probably ensured the same state of subdivision that was present in the alkenylsodium suspension, although this precaution might have been unnecessary.

All preparations were transferred from the reaction flask to glass bottles through a siphon tube under pressure of nitrogen. The glass bottle, used for storage, was a common narrow-mouth 500-ml. container, roughly calibrated, which had previously been rinsed with dry pentane and flushed with dry nitrogen. After the contents were transferred to the bottle together with the pentane rinsings from the reaction flask, more pentane was added to bring the volume to a desired amount, the bottle was stoppered with a well rolled cork stopper, and the top covered with a glyptal resin spread. The contents were well shaken, and the mixture set aside until needed. These suspensions settled very little. Some have kept for months without clarifying at the top more than one-quarter inch out of a total height of about 4 in. No appreciable sediment collected in the bottom. The stock preparations were handled in the same way except for proportionately larger bottles.

Before removal of an aliquot portion for compounding or for a polymerization, the bottle was shaken vigorously by

---

(6) Morton and Redman, *Ind. Eng. Chem.*, **40**, 1190 (1948).



Reagent no.	1			2			3			4			5			6			7			8			9		
Test no.	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Cat. age, days	10	32	39	10	32	39	10	32	39	10	32	39	10	32	39	10	32	39	10	32	39	10	32	39	10	32	39
[η]	0.2	0.3	0.3	2.2	6.2	7.1	4.0	5.7	6.5	4.1	7.7	8.1	4.8	6.9	6.8	5.1	1.2	..	5.6	4.1	..	3.5	..	..	5.9	..	..
Gel, %	1	6	15	10	22	22	2	2	5	1	16	9	0	29	6	1	...	..	0	...	..	0	..	..	1	..	..

Fig. 3.—Polymerization of mixture of 25 parts isoprene and 75 parts butadiene by PB_1 catalyst, Series B.

hand. The suspension was then transferred through a siphon tube under nitrogen pressure into the new container or into a transfer tube, if for a polymerization. These transfer tubes, if for 20 ml. or more of suspension, were graduated tubes of about 12 mm. diameter, with a stopcock large enough to permit rapid draining, a size as large as 8 mm. i. d. being preferred. Later, as 5 ml. were used in the tests, the exclusion of traces of moisture became necessary. The tube and siphon was therefore replaced by a two-holed stopper carrying a nitrogen inlet tube and a small pipet, the lower end of which was not constricted. Rapid drainage was thus insured. The suspension was forced into this pipet by nitrogen pressure, the suspension allowed to drain back, and then forced up again to the graduated mark, after which the aliquot part was transferred quickly to the reaction vessel.

The butadiene (Phillips research grade) was condensed in a 28 × 4 cm. test-tube cooled to −72° from which it was poured through a dry cotton plug in a funnel into a graduated dropping funnel. The dry cotton removed a little cloudiness in the liquid butadiene. The diene, which was by that time at a temperature just below its boiling point, was admitted rapidly to the bottle.

Later, as 5 ml. of catalyst was used, and the need for more careful exclusion of water became apparent, the end of the line that led the butadiene into the large test-tube was fitted with a one in. sintered glass disc, the butadiene was collected over anhydrous magnesium sulfate, and was then transferred to the dispensing pipet by pressure of dry gas that forced the butadiene through the sintered glass filter. The dispensing pipet was an ordinary graduated dropping funnel fitted with a three-way stopcock at the bottom and a nitrogen inlet at the top. This stopcock permitted removal of excess butadiene in order to adjust the volume without passing the cold liquid through the delivery tube with consequent condensation of moisture on that member. After delivery of butadiene from the pipet to the reaction bottle, a stream of dry nitrogen was passed through the pipet and delivery tube so that no moisture condensed on the inside of the tube.

Isoprene (Phillips research grade) was freshly distilled and poured from the container as desired.

The polymerization vessel was a 12-oz. soft drink bottle. The order of admission of all components used was 180 ml. of pentane, especially dried with amylsodium (see under PP catalyst) when 5 ml. of catalyst was used, dry nitrogen, catalyst, and butadiene. The bottle was promptly capped, and shaken vigorously by hand for about thirty seconds in order to disperse the catalyst in the medium. The bottle was then transferred to an air-pump shaking machine[7] for moderate agitation. When the desired period (30 min. unless otherwise stated) for polymerizing was over, the bottle was removed, and, in case the mixture had warmed a little, cooled under the water tap for a minute—included in the time of polymerization—then opened with the bottle inverted and so placed that the contents would be blown out by the pressure of unused butadiene into a 2-liter beaker. This blowing-out process was slow and gradual if the polymerization was 70 to 80% complete, and was violent if around 20%. For polymerizations 90% or better the contents were pulled out of the bottle with forceps.

The heat evolved in these reactions was scarcely noticeable to the hand unless the polymerization was 50% or more complete. Above that amount the bottle became warm but not hot. The relatively large volume of solvent used, and the heat of vaporization of pentane inside the bottle apparently kept the temperature within bounds. If a preliminary test showed that a reaction went too fast the quantity of catalyst was reduced. A close regulation of temperature was not deemed essential at this stage of the work where the nature of the several catalysts, their

---

[7] Morton, *Ind. Eng. Chem., Anal. Ed.*, **6**, 469 (1934).

characteristics and polymerizing activities were being surveyed. An increase in temperature from increased conversion would magnify the greater polymerizing activity shown by a particular catalyst, but in the range studied did not increase the proportion of gel that was formed, and possibly caused only a slight decrease in gel. This point will be clearly seen in the experiments reported for the sodium methylphenyl carboxide and allylsodium pair in which 20, 40 and 60 ml. of catalyst suspension, caused 35, 75 and 82% conversion to products that had 5, 2 and 0% gel, respectively, all with about the same intrinsic viscosity. Such small differences in gel are not regarded at this time as having any real significance.

The 2-liter beaker contained about 500 ml. of petroleum ether, 10 ml. of methanol to destroy the catalyst and 1 to 10 ml. of a reagent ether solution of N-phenyl-β-naphthylamine (PBN), the amount being so varied that the quantity of antioxidant would be 2% of the expected polymer. This mixture was usually allowed to stand overnight in order to soften the rubber gel a little, or the rubber gel was removed, cut into chunks, put into a meat chopper with solid carbon dioxide and cut into small bits in order to hasten the process. The rubber was then stirred mechanically in petroleum ether for five minutes with about 200 ml. of distilled water, more pentane being added in order to get the rubber into solution or homogeneous dispersion. The lower aqueous layer was removed by a siphon and the washing with stirring repeated with another 200 ml. of distilled water. This operation had to be repeated about three or four times before the wash water was neutral to litmus and free from chloride ion. The final pentane solution was milky with scarcely any solid particles if the polymer was free from gel but contained small particles of suspended matter if the gel were high.

An aliquot portion sufficient to contain two grams of rubber in the pentane solute was removed for analysis of intrinsic viscosity and gel. The solvent was removed first at room temperature by a water pump and then overnight by an oil pump, at a temperature not exceeding 40°. The remainder was evaporated on the steam-bath and then in the vacuum oven at room temperature in order to determine the percentage conversion.

Intrinsic viscosities and gels were determined by the method employed[8] by Rubber Reserve Co. on 0.2 g. of the polymer. This method was not developed for polymers that had such high intrinsic viscosities as did some of the products from Alfin polymerization. Use of 0.1 g. of material frequently gave more consistent results.

PB_1 Catalyst (by R. P. W.).—For Series A the stock suspension of butenylsodium was made by combining three standard preparations as described before. The stock suspension of sodium isopropoxide was also made by combining three lots each obtained by addition of 26 g. of isopropyl alcohol to a standard preparation of amylsodium. For Series B the stock reagents were prepared in single batches, each twice the size of the standard one. Enough pentane was added to each suspension to make the mixture reasonably fluid. The final volumes of the Series A stock solutions were 3600 and 2400 ml. respectively for 1-butenylsodium and sodium isopropoxides and for the corresponding pair of Series B reagents were 2400 and 1600 ml. The estimated amount of 1-butenylsodium per ml. in each preparation was 0.00033 mole and the known amount of sodium isopropoxide was 0.0005 mole.

A better knowledge of the concentration of the components in each stock preparation was unnecessary and probably without significance. The stock reagents differ in their state of aggregation, and the combination to form the catalyst makes a third insoluble product besides the various aggregates in which occlusion of one or another component occurs. Analysis of organosodium reagents is difficult even in the case of soluble compounds—Conant[9] and McEwen[10] claim only 10–15% accuracy in their studies of ether-soluble reagents—and for the case of even more reactive reagents in an insoluble medium, it is much more difficult. For these tests the object was to prepare enough reagents to cover a wide range, and to compound and test them under as uniform conditions as possible and to make enough tests of each reagent over long enough periods of time to insure that a relatively constant state of reactivity has been attained.

As a first approximation, this compounding was done on the assumption that an 80% yield of amylsodium had been obtained and that the conversion to butenylsodium had been quantitative; and the mole percentages of sodium isopropoxide from this reckoning were used as the abscissas in Fig. 1. Had the estimate been correct and had there been no occlusion, all reagents to the left of no. 5 inclusive would have had the same amount of catalyst but would have had increasing amounts of butenylsodium except, of course, reagent no. 1 which contained no isopropoxide. Correspondingly, all reagents to the right of number 5 inclusive would have had a constant amount of catalyst but would have contained increasingly large amounts of isopropoxide. Of the eight reagents prepared, the graph shows that number four actually had the maximum rate of conversion and hence contained the largest number of available catalyst units. Accordingly, reagents 3 and 2 should have contained the same amount of catalyst as no. 4 because each contained the same amount of sodium isopropoxide and more than enough 1-butenylsodium to combine with this alkoxide; and reagents 5 to 8 inclusive should each contain the same amount of catalyst, although less than reagent 4. This method covers a broad range and is largely independent of an exact knowledge of the composition of the stock preparations.

The compounding of the reagents was carried out as shown in Table II.

TABLE II

COMPOUNDING OF REAGENTS FROM STOCK SOLUTIONS

Reagent no.	Series A Volume in ml. of P[a]	 B_1[b]	 PB_1[c]	Series B Volume in ml. of P[a]	 B_1[b]	 PB_1[c]
1	...	540	600	0	360	400
2	120	720	1200	80	480	800
3	120	540	1200	80	360	800
4	120	360	600	80	240	400
5	120	180	600	80	180	400
6	240	180	600	80	150	400
7	360	180	600	80	120	400
8	480	180	1200	160	120	400
9	120	180	600	240	120	400

[a] P refers to the isopropoxide suspension used. [b] B_1 refers to the 1-butenylsodium suspension used. [c] PB_1 shows the volume of the mixture after pentane has been added as a diluent.

The stock preparations for the Series A reagents stood for several days before the compounding. The mixtures were first shaken together in the bottle by hand but developed no catalytic activity even after two days. Each was then stirred vigorously in the high-speed stirring apparatus. The aging of the reagent, as given in the Table, dates from the time they were stirred together. For the Series B reagents the mixing was done by hand shaking the day after preparation of the stock solutions. They were then catalytically active but did not attain a stable state until some time later.

The quantity of catalyst used in the polymerizations was 20 ml. for the 600 or 400 ml. of PB_1 suspension or twice that amount in the case of the 1200 or 800 ml. lots.

Sodium Methylphenyl Carboxide and Allylsodium (by F. C.).—Methylphenylcarbinol was prepared by catalytic reduction[11] of acetophenone over Raney nickel at 110° and 1800 lb., which frequently proved unsatisfactory, or by the reactions of benzaldehyde with methylmagnesium iodide

---

[8] Baker, Mullen and Walker, private communication.

[9] Conant and Wheland, THIS JOURNAL, **54**, 1212 (1932).

[10] McEwen, *ibid.*, **58**, 1124 (1936).

[11] Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., p. 30.

according to a typical procedure.[12] The first product boiled at 92° (12 mm.) and had a refractive index, $n^{20}D$ 1.5280, the second one had a refractive index of 1.5282. The recorded[13] value is 1.5275.

The catalyst, C, was prepared by passage of propylene into a standard preparation of amylsodium to which 0.2 mole of methylphenylcarbinol had been added. Twenty ml. of this catalyst caused 35% conversion of 30 ml. of butadiene during one hour to a polymer that had an intrinsic viscosity of 5.8 and a gel of 5%; 40 ml. caused 75% conversion and the viscosity and gel were 5.2 and 2%, respectively; 60 ml. caused 82% conversion and the polymer had 4.9 viscosity and zero gel. The approximate constancy of intrinsic viscosity as the catalyst is doubled and tripled accords with the general behavior of Alfin catalyst. When applied to 20 ml. of isoprene, the conversion values for 20, 40 and 60 ml. of catalyst suspension were 8, 19 and 35% respectively, the corresponding intrinsic viscosities were 1.8, 2.8 and 2.3, and the respective gels were 0.6 and 19%.

In the making of catalyst D, this preparation was repeated with three times the proportions of reactants. The catalytic activity of D as tested by 20, 40 and 60 ml. of catalyst with butadiene was 16, 37 and 43% respectively, the corresponding intrinsic viscosities 1.0, 0.6 and 0.8 and the respective gels were 34, 15 and 33%.

Addition of 30 ml. of standard preparation of allylsodium suspension to 1675 ml. of the above catalyst suspension followed by thirty minutes of high-speed stirring to give D, altered the catalytic activity so that the conversions caused by 20, 40 and 60 ml. of catalyst, after three days of aging, D_{1-3}, were 28, 58 and 89%, respectively. The corresponding intrinsic viscosities were 6.0, 5.3 and 4.3 and the respective gels were 14, 19 and 22%. After this suspension had aged for fifteen days, D_{1-18}, the corresponding three sets of values were 32, 62, 79%, 6.7, 6.6, 5.3 and 4, 6, 7%. Another quantity of 30 ml. of allylsodium was added to give D_2. The remaining tests used only 20 ml. of catalyst suspensions. These results with others are listed in Table I.

Tests with PP Catalyst (by R. P. W., S. E. P., and R. D. C.).—Four separate preparations of PP catalyst were made by passage of propylene through standard batches of amylsodium in the presence of different quantities of isopropoxide (see Table III).

Each lot of catalyst was analyzed for its content of organosodium compound by addition of 8 g. of fluorene to 100 ml. of catalyst suspension, followed by high-speed stirring for three hours, standing overnight, carbonation on solid carbon dioxide, recovering the 9-carboxylic acid, and weighing.

The activity of these four catalysts was tested with only 5 ml. of the catalyst suspension. The results recorded in Table II show that the percentages of gels were uniformly low and the activity of the catalyst on the excess alkoxide side decreased no more within one month's time than it did on the excess allylsodium side.

The use of such a small quantity of catalyst as 5 ml. required extra precautions to eliminate moisture or other material that would destroy the catalyst. The pentane was therefore treated with amylsodium in the proportion of 100 ml. per gallon. The mixture was shaken by hand for about a minute and allowed to stand overnight by which time the solid, largely free from its color, had settled to the bottom and left the pentane layer water-white. This pentane was used as a rinse for the polymerization vessel (12 oz. soft drink bottle) as well as for the medium of the reaction. The moisture or air on the wall[14] of these glass bottles would destroy most of the color of 2 ml. of catalyst suspension added to 200 ml. of the above dried pentane within a few minutes of gentle agitation. When 2 ml. more of the catalyst suspension was added, the color of the solid was more permanent, although it, too, was decolorized by overnight standing in the sealed bottle. By rapid handling of all reagents the effect of moisture on the glass walls was minimized. Satisfactory polymerizations were carried out with as little as 3 ml. of catalyst suspension. Below 1.5 ml. of catalyst the amount of polymer formed was as low as 1 mg. even in an indefinitely long period of time.

TABLE III

PREPARATION OF PP CATALYSTS AND POLYMERIZATIONS CAUSED THEREWITH

Reagent no.		1[a]	2[a]	3[b]	4[b]
Total vol. of cat. suspension, ml.		850	850	875	850
Sodium isopropoxide,[c] moles		.20	.16	.12	.10
Allylsodium,[d] moles		.12	.13	.16	.19
Catalyst, total[e] moles		.12	.13	.12	.10
Catalyst used in polymerization, moles × 10⁶		750	765	685	585
Poly. of butadiene[f]					
Test No. 1	Conversion, %	71	61	51	28
	Intrinsic viscosity	8.6	17.0	15.7	11.7
	Gel, %	4.4	11	11	16
Test No. 2[g]	Conversion, %	66	57	49	25
	Intrinsic viscosity	12.8	15.1	13.9	13.0
	Gel, %	7	9	4	[low]

[a] The color of these suspensions was gray-green to blue-green and the fluidity was high. [b] The color of these two catalysts was slate-blue and the fluidity was low. When used as the polymerization agent they show a tendency to form clumps of insoluble polymer at the beginning of the reaction. [c] The moles of isopropoxide was calculated from the amount of isopropyl alcohol added. [d] Calculated from the weight of fluorene-9-carboxylic acid isolated. [e] Calculated from the quantity of that one of the two components present in lesser amount. [f] Polymerization test one day after preparation of the catalyst. [g] Polymerization test one month after preparation of the catalyst.

The results with the above PP catalysts are typical of many now being obtained. Many polybutadienes that contain no gel have been obtained, although occasionally one as high as 70% is still formed.

Summary

In Alfin polymerization of butadiene a minimum of gel appears to accompany a maximum of conversion. Incorrect proportioning of the catalyst component or a large excess of catalyst beyond that needed for high efficiency may cause the formation of gel during polymerization.

RECEIVED SEPTEMBER 22, 1947

---

(12) Dreger, *Organic Syn.*, Coll. Vol. I, p. 307.

(13) Dechamps, *Bull. soc. chim. Belg.*, **33**, 270 (1924).

(14) Bent and Lesnick, THIS JOURNAL, **57**, 1246 (1935).