

the benzene ring of the halogen atom to be replaced and the complexity of the carbon chain of the alkoxide or aryloxy determined the procedure used in each synthesis. Variations in the

general procedure involved reaction temperature, exposure time and amount of water present.

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Polymerization. VI. The Alfin Catalysts^{1a}

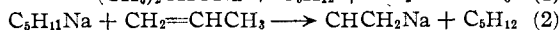
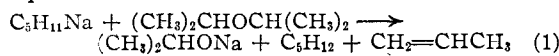
BY AVERY A. MORTON, EUGENE E. MAGAT^{1b} AND ROBERT L. LETSINGER^{1c}

The sodium salt of a methyl *n*-alkyl carbinol and the sodium salt of an olefin, for example propylene, form a complex that causes the catalytic polymerization of butadiene and isoprene. Agents of this type are called Alfin catalysts because an alcohol and an olefin are involved in their preparation. This paper (1) gives an account of the discovery of these catalysts, (2) lists the types of compounds that will form such agents, (3) describes the methods used for testing the catalysts (4) shows the unique features that mark the polymerization, induced by these agents, to be distinctly different from that caused by other polymerizing agents, (5) lists the general characteristics of Alfin polymerization, (6) shows some variations that are possible with different Alfin catalysts and (7) suggests a possible formula for the active catalyst complex.

Discovery of the Catalyst

The catalyst was discovered by accident in the course of our study² of the addition of organosodium compounds to dienes. The effect of diisopropyl ether was being tested in the same way as the effect of a tertiary amine on the addition of amylsodium to butadiene had previously been tested.² The reaction took, however, an entirely different course and high polymers resulted in spite of the fact that the diene was added drop by drop to a very large excess of the organoalkali metal reagent. A similar result was obtained with isoprene, although the polymer was stickier than that obtained from butadiene.

The explanation for this unusual effect on the two dienes lay in the formation of two products, sodium isopropoxide and allylsodium, derived from the ether and amylsodium, according to the equations



This conclusion was drawn after a series of experiments, shown in Table I. A rubber-like polymer was obtained only when sodium isopropoxide

(1a) The authors are indebted to the Research Corporation and to the Rubber Reserve for financial support of this investigation.

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(2) Morton, Brown and Magat, *THIS JOURNAL*, **69**, 161 (1947).

and allylsodium were both present and no polymer was obtained if either one was absent (experiments 7 and 8). Amylsodium or the ether could be absent without destroying the catalytic effect (experiments 4 or 1 and 2, respectively). Only a trace of reaction with the ether was needed in order to furnish enough of the two pertinent salts (experiments 3 and 5), although the amount could fall too low, as it did in experiment 6. The catalytic action was not induced by any energy or free radical liberated from the reaction of amylsodium with the ether because in experiments 2 and 4 the catalytic activity was present long after ether cleavage was concluded. The preparation of the catalyst from other reagents besides the ether confirmed this point (experiment 9). This series of studies was concluded by a successful test with a catalyst made by mixing a preparation of the alkoxide with an independent preparation of allylsodium obtained from the reaction of amylsodium with propylene. The unusual effect on dienes is clearly a consequence of the simultaneous presence of two particular alkali metal salts.

The Class of Compound

Allylsodium and sodium isopropoxide form one of a class, the components of which, as shown in Table II, are specific. Only alkoxides from methyl *n*-alkyl carbinols have so far proven effective. Only mono olefins that have at least one alkyl group attached to a carbon atom of the vinyl group or two alkyl groups attached, one to each of the carbon atoms, have so far been suitable.

The mercaptide $(\text{CH}_3)_2\text{CHSNa}$, and the amide $(\text{CH}_3)_2\text{CHNHNa}$, corresponding to the alkoxide, could not replace the isopropoxide in combination with 2-butene as the olefin.

The metalation product of diallyl in the presence of isopropoxide proved unsuitable, although one of the products of such a reaction was a propenyl substituted allylsodium,³ $\text{CH}_2=\text{CHCH}(\text{R})\text{Na}$ (where $\text{R}=\text{CH}_2\text{CH}=\text{CH}_2$). The addition product of amylsodium with butadiene likewise failed as a component of the catalyst, although the product² of such addition is a hexylallylsodium, either $\text{Na}(\text{R})\text{CHCH}=\text{CH}_2$ or $\text{RCH}=\text{CHCH}_2\text{Na}$ ($\text{R}=\text{C}_6\text{H}_{13}$) depending on whether the addition occurs 1,2- or 1,4. Both failures are important because

(3) Morton and Brown, *THIS JOURNAL*, **69**, 160 (1947), and unpublished research.

TABLE I
DETERMINATION OF THE CAUSE OF POLYMERIZATION ACTIVITY
Legend: R = isopropyl radical, tr = trace, P = rubber-like polymer.

Expt.	1	2	3	4	5	6	7	8	9	
Reagents										
Moles of										
$\left\{ \begin{array}{l} \text{C}_5\text{H}_{11}\text{Na} \\ \text{ROR} \\ \text{ROH} \\ \text{C}_3\text{H}_5 \end{array} \right.$	$\text{C}_5\text{H}_{11}\text{Na}$	0.19	0.19	0.19	0.19	0.095	0.028	0.19	0.19	0.19
	ROR	.066	.066	.19	.38	.19	.19			
	ROH							.066		.066
	C_3H_5								.6	.6 ^a
Time, min.	180	1200	5	1200	4	4	10	270	270	
Products ^b										
Moles of										
$\left\{ \begin{array}{l} \text{C}_5\text{H}_{11}\text{Na} \\ \text{C}_3\text{H}_5\text{Na} \\ \text{RONa} \\ \text{ROR} \end{array} \right.$	$\text{C}_5\text{H}_{11}\text{Na}$	0.11	0.11	0.19	0	0.095	0.028	0.124	0.076	0.05
	$\text{C}_3\text{H}_5\text{Na}$.014	.014	tr.	.036	tr.	tr.		.114	.074
	RONa	.066	.066	tr.	.154	tr.	tr.	.066		.066
	ROR			0.19	.226	0.19	0.19			
Action of products on butadiene ^c										
Polymer	P	P	P	P	P					P
Time, hr.	1	0.5	4.5	1.5	1.25	3	1.5	3.5	0.25	

^a The alcohol was added to amylsodium before the ether. ^b The reaction products are those that result after the reagents have been stirred together for the time indicated. The organosodium compounds are calculated from the carboxylic acids obtained by carbonation. ^c Butadiene, 0.25 mole, added to the products of the reaction.

TABLE II
SUITABILITY OF ALCOHOLS AND OLEFINS AS COMPONENTS OF ALFIN CATALYSTS

Miscellaneous	Olefins		Methyl <i>n</i> -alkyl carbinols	Alcohols	
	2-Alkenes	1-Alkenes		Other secondary alcohols	Primary and tertiary alcohols
Cyclohexene		Propylene	Propanol-2	Pentanol-3	<i>n</i> -Propanol
<i>i</i> -Butene	2-Butene	1-Butene	Butanol-2	Methylisopropylcarbinol	Allyl alcohol
Diallyl	2-Pentene	1-Pentene	Pentanol-2	Cyclohexanol	Isobutanol
		1-Hexene	Hexanol-2	<i>p</i> -Methyl cyclohexanol	<i>t</i> -Butanol
		1-Octene	Heptanol-2	Diphenyl carbinol	<i>t</i> -Pentanol
			Octanol-2		Pinacol
Inactive	No failures in catalysts			Rarely active ^a	Inactive

^a Only cyclohexanol can be used.

they show that the formation of a catalyst by metalation of or addition to a growing polydiene chain in the presence of isopropoxide is unlikely. The catalyst must be formed previously from a mono-olefin.

The metalation product of benzene in the presence of isopropoxide had a little catalytic effect, but no more than that reported⁴ already for the phenylsodium-sodium chloride complex. Sodium chloride is, of course, present in this instance also, since it is introduced by formation of the metalating agent, amylsodium, from reaction of sodium with amyl chloride.

A substitution of potassium for sodium in the catalyst proved unsatisfactory, although the test is not regarded as decisive. The allylpotassium was prepared by cleavage of diallyl ether with potassium metal in the presence of potassium isopropoxide, since the yield of the potassium reagent prepared by the method that parallels the usual formation of allylsodium is low. A preliminary test of this ether cleavage showed that the scission was comparatively easy and that the product after carbonation was the expected vinylacetic acid.

(4) Morton and Letsinger, *THIS JOURNAL*, **69**, 172 (1947).

Methods of Testing the Catalyst

Three general methods were used for testing catalytic action; first, by dropwise addition of the diene to a huge excess of the catalyst, second, by polymerization of the diene with a small amount of the reagent in the high-speed stirring apparatus, and, third, by polymerization in a bottle with quantities somewhat similar to those present in the second test. The first of these methods was always carried out in the high-speed stirring apparatus, and had the special value of being unusually well adapted for spotting a step-wise adduct type of chain growth, because intermediate salts could be recognized by carbonation and isolation of low molecular weight carboxylic acids as has been already described,² whereas, in the catalytic process, only high polymers were obtained.

The polybutadiene produced by the Alfin catalyst under the condition of this first test was a highly cross-linked elastomer, sometimes wholly insoluble in benzene, carbon tetrachloride or ether. It behaved as if vulcanized. The polyisoprene, on the other hand, was a soluble polymer. The highly cross-linked character of the polybutadiene may be caused by secondary reactions that arise from the presence of the huge excess of reagent

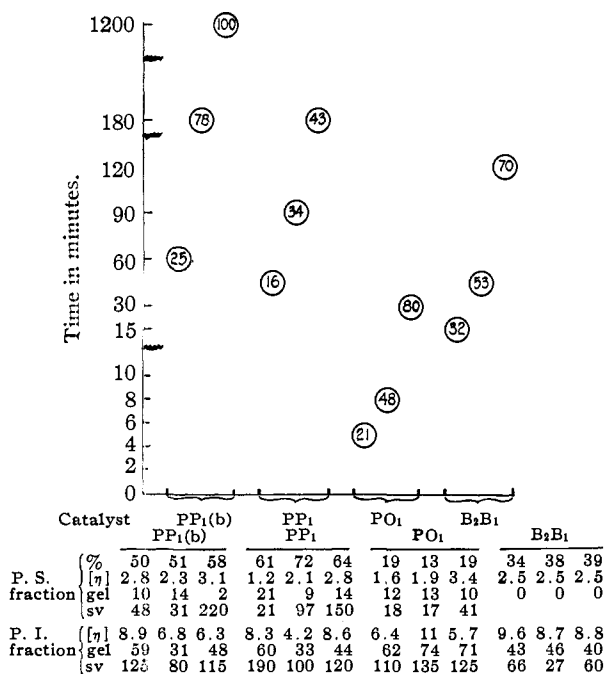


Fig. 1.—Formation of pentane-soluble and pentane-insoluble polybutadienes by Alfin catalysts: Numbers in circles represent percentage conversion. Catalyst symbols: P as the first letter signifies the alkoxide of propanol-2, B₂ indicates the alkoxide of butanol-2; P₁, O₁, and B₁ as second letters signify the sodium compounds derived by metalation of propylene, 1-octene, and 1-butene, respectively; (b) indicates that the polymerization was carried out in a bottle instead of a flask. P. S. and P. I. refer, respectively, to the pentane-soluble and pentane-insoluble fractions. $[\eta]$ refers to intrinsic viscosity. S. V. refers to swelling volume.

or by extraneous organoalkali metal reagent; and this opinion is in line with the results obtained when a smaller quantity of catalyst is used, as in the second method of testing.

In this second way, 66 mole equivalents of butadiene was added to one mole equivalent of the catalyst suspended in pentane. The mixture was stirred in the high-speed stirring apparatus until it thickened appreciably, so much so that a continuance would cause the mixture to swell as a rubbery mass and emerge from the flask. The polymerization was then stopped by a rapid addition of water, more pentane was added, and the contents stirred until well dispersed. The reaction products were then centrifuged in order to separate a pentane-soluble fraction, a pentane-insoluble polymer, and an aqueous alkaline layer.

The polymer obtained from the pentane-soluble portion differed markedly from the pentane-insoluble product in that it was either free from gel or had very low gel (the separation was not always perfect, especially if the proportion of pentane-insoluble rubber was high), and did not form appreciable gel when heated or steamed. The

pentane-insoluble part, on the other hand, contained a high proportion of gel and also formed more gel when heated or steamed. The swelling volumes of the gels after steaming were notably different, that from the pentane-insoluble fraction being almost nil. Specific examples are shown in Table III below. Ozonization⁵ of the two fractions obtained from a 2-butoxide/1-butenylsodium catalyst showed percentages of 1,2-addition, based on formaldehyde analyses of 4.5 to 6.0 and 19.0 to 24, respectively, for the pentane-soluble fraction (that amounted to 38% of the total polymer produced), and for the insoluble fraction.

TABLE III

INTRINSIC VISCOSITIES, GEL CONTENTS AND SWELLING VOLUMES OF PENTANE-SOLUBLE AND PENTANE-INSOLUBLE RUBBERS BEFORE AND AFTER BEING STEAMED

		Isopropoxide/1-pentenylsodium catalyst			
		$[\eta]^a$	% Gel	S. V. ^b	
Pentane-soluble	Before	3.3	8 to 10	94	
	After	2.5	13.5	29	
Pentane-insoluble	Before	6.75	50.5	136	
	After	1.2	90	3	
		2-Butoxide/1-hexenylsodium catalyst			
Pentane-soluble	Before	2.45	0	...	
	After	1.93	0	...	
Pentane-insoluble (55%)	Before	11.6	26	97	
	After	...	90	Slight	

^a $[\eta]$ signifies intrinsic viscosity. ^b S. V. signifies swelling volume.

The ratio of pentane-soluble polymer to pentane-insoluble polymer was surprisingly constant in several cases (see Fig. 1), although the conversions ranged from 16, 21, 25 or 32 to 43, 80, 70 or 100%, respectively. The pentane-soluble fraction is given major attention as a basis for rating the Alfin catalysts and the conditions under which they operate partly because this fraction is more likely to be free from secondary actions and partly because a pentane-soluble polymer would also be more desirable and more like a natural polymer.

The third test was a bottle polymerization, made with a large excess of diene over catalyst, much after the manner of the second test except that the reaction could be carried out to any desired end. This test was of real value only for polymers that formed little or no gel. Isoprene could be tested readily by this method. Butadiene tended to form excessive amounts of gel, much more than in the high-speed stirring apparatus. For example, an isopropoxide-allylsodium catalyst that produced 80% pentane-soluble polymer in the high-speed stirring apparatus gave only 20% pentane-soluble polymer in the bottle. Accordingly this test is largely restricted in this paper to some studies in the polymerization of

(5) The authors are greatly indebted to Miss Holden for the determination of the ozonization numbers.

isoprene, although in later papers it will be used extensively with butadiene.

A large amount of attention will be devoted to the polymerization of butadiene, in spite of the fact that isoprene gives a gel-free product. The purpose was partly to observe factors that had a bearing on gel formation as well as to work with the diene more commonly available. In so far as parallel tests with isoprene and butadiene have been made, conclusions based on the polyisoprene, all of which is pentane-soluble, follow closely those based on the pentane-soluble portion of the polybutadiene.

A little effort was also made to test the catalyst in dry form. The catalyst suspension was freed from all low-boiling hydrocarbons by successive applications of a vacuum from the water pump and oil pump. Olive-colored lumps of solid material were recovered that were stable in pentane or nitrogen but that caught fire after exposure to air. The 2-pentoxide/2-butenylsodium catalyst so prepared was not active but the corresponding 2-pentoxide/1-butenylsodium catalyst caused polymerization, according to the data shown in Table IV. The failure of the 2-butenyl product

TABLE IV

POLYMERIZATION OF BUTADIENE BY DRY ALFIN CATALYST

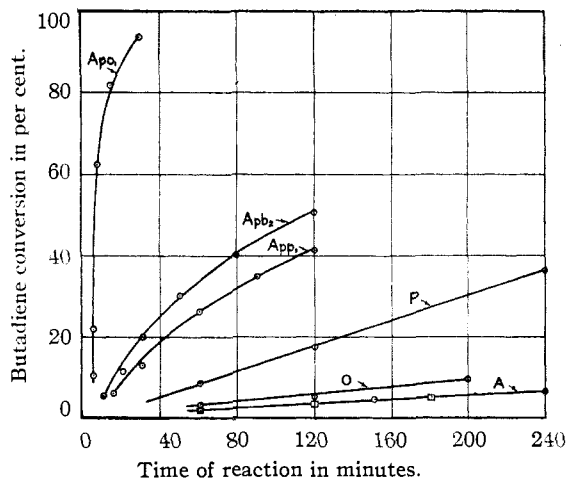
Method	Dry catalyst, g.	C ₄ H ₆ , ml.	Pentane, ml.	Time, hr.	Rubber, g.
Stirring	0.5	30	250	0.5	4
Bottle	.5	30	200	16	9
Bottle ^a	.5	30	200	16	9

^a 10 ml. of N(C₂H₅)₃ present during the polymerization.

was surprising, since the catalyst suspension made from 2-butene was usually better than that made from the 1-butene. Further attempts to develop a dry catalyst were postponed, partly because of the fire hazard, partly because the method had no immediate advantage in manipulation, and partly because of the risk of secondary effects such as deposition of high-boiling residues on the surface of the catalyst during the drying process.

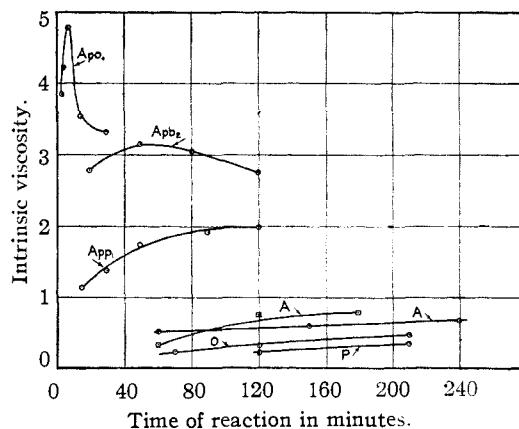
Unique Features of Alfin Polymerization

Alfin polymerization is distinct from the ordinary stepwise formation of adducts that characterizes the action of organoalkali metal reagents, such as amylsodium, on butadiene. The difference is shown clearly in Figs. 2 and 3. In the first figure, the percentage conversion caused by amylsodium (A), 1-pentenylsodium (P) and 1-octenylsodium (O), three reagents of the type that add to butadiene and cause the formation of a series of polymer adducts, is compared with three Alfin catalysts, marked as A with appropriate subscripts to designate the composition. Of the first trio of reagents, amylsodium caused the smallest amount of conversion and 1-octenylsodium and 1-pentenylsodium induced progressively faster reactions. The corresponding average intrinsic viscosities of the products, Fig. 3, were in the reverse order, that is, the polymer adduct from am-



App₁ { Sodium isopropoxide
1-octenylsodium
App₂ { Sodium isopropoxide
2-butenylsodium
App₃ { Sodium isopropoxide
1-pentenylsodium
P, 1-pentenylsodium
O, 1-octenylsodium
A□, Amylsodium with sodium isopropoxide
A○, Amylsodium

Fig. 2.—Comparative rates of polymerization of butadiene caused by three ordinary organosodium reagents and by three alfin catalysts.



App₁ { Sodium isopropoxide
1-octenylsodium
App₂ { Sodium isopropoxide
2-butenylsodium
App₃ { Sodium isopropoxide
1-pentenylsodium
P, 1-pentenylsodium
O, 1-octenylsodium
A□, Amylsodium with sodium isopropoxide
A○, Amylsodium

Fig. 3.—Comparison of the intrinsic viscosities of the polymers produced by organosodium reagents with those made under the influence of alfin catalysts.

ylsodium was highest; and this result is precisely that expected if the lower conversion is caused by a smaller number of starting nuclei. Not so, however, is the case of the three Alfin catalyzed reactions, carried out under conditions identical with those used for the first three. These three double salt complexes caused widely different rates of conversion and the agent that caused the fastest conversion also produced a product with the highest intrinsic viscosity.

A second distinguishing mark between the adduct type of chain growth and the catalytic one is

the influence of sodium isopropoxide on the action of the three ordinary organosodium reagents in question. The alkoxide had no influence on the velocity of the reaction caused by amylsodium and had a slight, almost negligible, influence on the intrinsic viscosity of the polymer adduct therefrom. Its influence on the two alkenylsodium reagents, was, however, outstandingly great in that the Alfin catalyst formed thereby caused marked acceleration of chain growth, in one case a hundredfold, and the greater the acceleration the higher the intrinsic viscosity of the polymer.

Further evidence that Alfin polymerization is distinct from the conventional idea⁶ of sodium polymerizations and, incidentally, from any ordinary free radical process, is seen in the polymerization of isoprene by a sodium isopropoxide/allylsodium catalyst. The velocity of polymerization of the diene with varying monomer-catalyst ratio (see Fig. 4) was as expected in that the more catalyst used the faster the conversion.

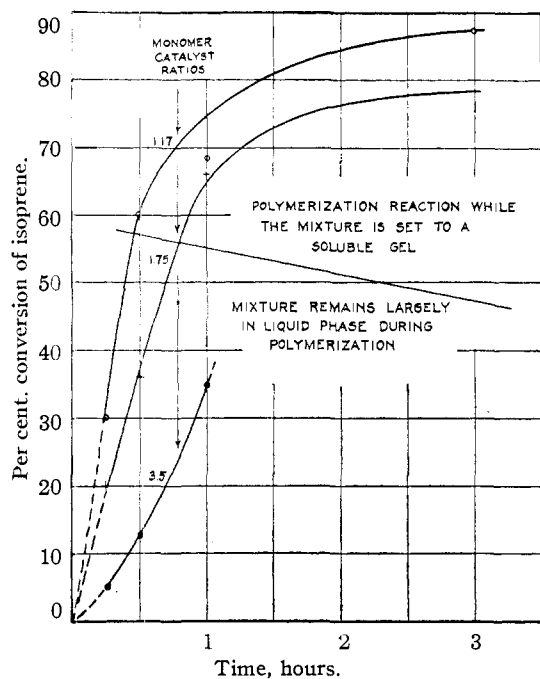


Fig. 4.—Per cent. conversion *vs.* time with varying monomer catalyst ratio: isopropoxide-allylsodium catalyst.

The activity of the catalyst in these three tests was substantially the same since the conversion per milliliter of catalyst suspension (Fig. 5) was essentially the same in the early phases of the three experiments, the deviation of the one with the smallest amount of catalyst being accounted for by the induction period present in that series. On the other hand, the intrinsic viscosities (Fig. 6) of the polymers produced in the three series are in the reverse order of that expected, because an

(6) Mark and Raff, "High Polymeric Reactions," Interscience Publishers, Inc., New York, N. Y., 1941, p. 272, *et seq.*

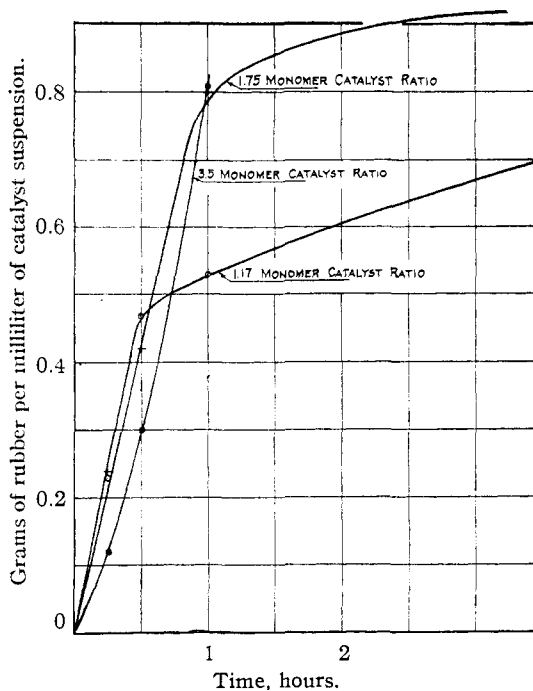


Fig. 5.—Conversion per unit of catalyst *vs.* time with varying monomer catalyst ratio: isopropoxide-allylsodium catalyst.

increase in reaction, occasioned by an increase in the number of starting nuclei, is accompanied, strangely enough, by an increase in the intrinsic viscosity.

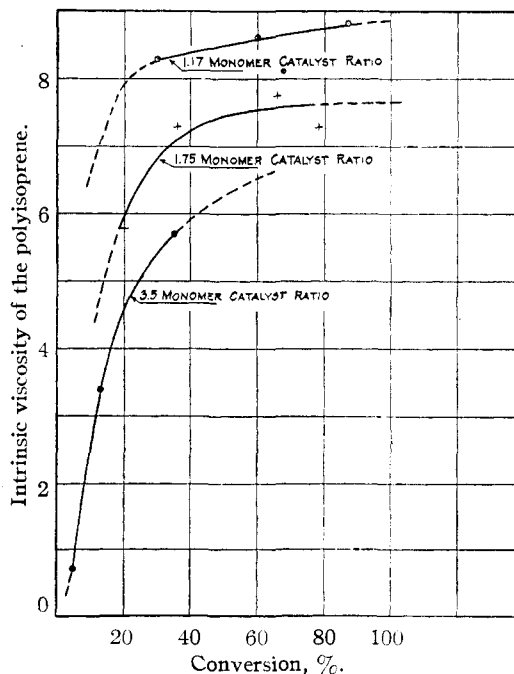


Fig. 6.—Intrinsic viscosity *vs.* per cent. conversion with varying monomer catalyst ratio: isopropoxide-allylsodium catalyst.

Another distinguishing mark is that the intrinsic viscosity approaches a limiting value. This fact is partly suggested by a graph (not herein shown) of intrinsic viscosities *vs.* monomer-catalyst ratio for corresponding conversions in the above-mentioned experiments, but is demonstrated effectively by a pair of experiments carried out with another sample of isoprene, in which the intrinsic viscosity of the two polymer products was the same, although the monomer-catalyst ratio varied about fifty-fold. In the first experiment, 7.5 ml. of this isoprene was added dropwise to a large excess of catalyst suspended in pentane in the high-speed stirring apparatus. The monomer-catalyst ratio in this instance, calculated on the basis of the total amount of isoprene added over the period, was 0.03 and the ratio was even lower than this value if the addition of the isoprene in drops is taken into account. In this instance, the reaction was stopped within six minutes because of the thickness of the mixture. The polymer contained no gel and had an intrinsic viscosity of 6.6. In the comparison experiment, a quantity from the same lot of isoprene was tested in an ordinary bottle polymerization with an amount of catalyst sufficient to give a monomer-catalyst ratio of 1.47; the conversion was 63% within one hour and the intrinsic viscosity of the polymer was 6.3. The tests of a limiting or constant intrinsic viscosity are, of course, best made with the polyisoprene, since the polybutadienes may contain small quantities of soluble gel that will be responsible for some variations in the constancy of the intrinsic viscosities of that polymer (*cf.* Fig. 3).

Although the intrinsic viscosity of the rubber was not related to the amount of catalyst present, it was affected greatly by the purity of the diene. The ordinary commercial grade of butadiene was not readily polymerized, and the polymers when formed had comparatively low molecular weights. For this reason we have reported no experiment with technical butadiene in this paper. Isoprene of different degrees of purity yielded polymers that differed in intrinsic viscosity, although the percentage conversion might be only slightly affected. This fluctuation was observed in samples of isoprene that had been refined in this Laboratory in the course of the above described work.

General Characteristics of Alfin Polymerization

An induction period was present in many cases. This fact is already apparent from Figs. 2, 4 and 5. The effect is well marked in the polymerization with the sodium isopropoxide/1-octenylsodium catalyst (Fig. 2).

The polymerization reaction is approximately one of first order. This fact is indicated by the graph of the logarithm of the butadiene concentration against the time of reaction (Fig. 7) for polymerizations induced by the three catalysts shown in Fig. 2. The considerable variation at

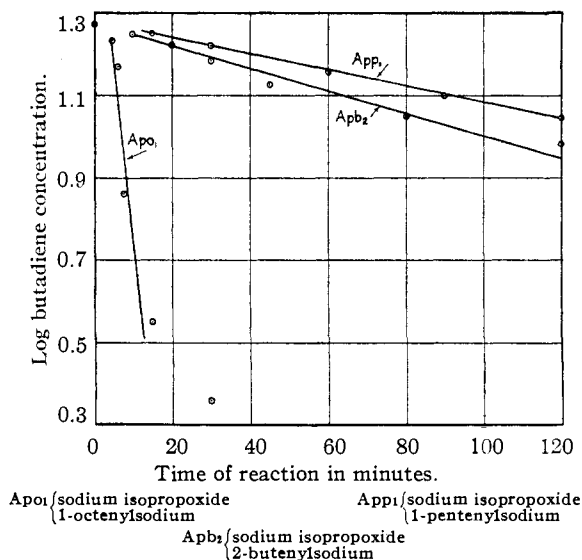


Fig. 7.—Log of the butadiene concentration as a function of the time of reaction for various alfin polymerizations.

the end of the line that represents the action of the propoxide-2/1-octenylsodium catalyst may reasonably be attributed to reactions caused by other agents, such as octenylsodium itself, associated with the catalyst. As will be shown later in this section, the amount of alkoxide (approximately one alkoxide to one octenylsodium) present in this instance was not adequate to ensure optimum activity.

With respect to the influence of temperature, the conversion caused by three different catalysts was a maximum at 20° as compared with 0 and 50° and the intrinsic viscosities of the corresponding pentane-soluble polymers was either a maximum at 20° or was as high as that observed at the other two temperatures (see Fig. 8). The percentage of pentane-soluble polymer increased as the temperature was raised (read left to right for each catalyst in the figure). The results at 50° are those expected if the complex partly dissociates to free alkoxide and the organosodium compound so that the character of the reaction changes from one that is primarily catalytic to one that is at best only partly so. The slower rate at 0° is that expected from the usual temperature coefficient of a reaction.

Figure 9 shows the influence of inert solvents, arranged in order of increasing boiling points, on the polymerization. Five different catalysts were tried. Almost without exception the percentage of polymer soluble in pentane increased with increase in boiling point, the intrinsic viscosity usually increased, and the gel, except in one case, decreased to zero. In the case of the isopropoxide/1-octenylsodium catalyst (PO₁) the change from pentane to hexane to benzene was truly astonishing.

The conversion values for the first four catalysts, arranged in order of increasing alkenyl chain

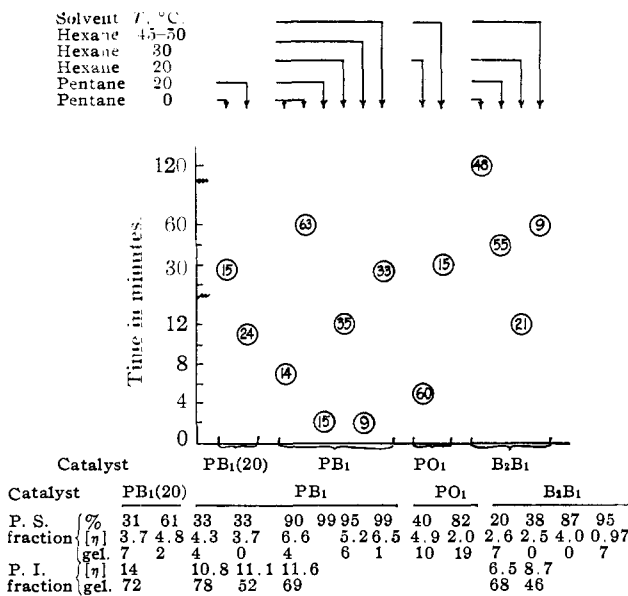


Fig. 8.—Effect of temperature upon alfin polymerization: Numbers in circles represent percentage composition. Catalyst symbols: P as the first letter signifies the alkoxide of propanol-2, B₂ signifies the alkoxide of butanol-2; B₁ and O₁ as second letters signify the sodium compound derived by metalation of 1-butene and 1-octene, respectively; (20) signifies that 20% of the total sodium is present as the alkoxide in contrast to the 50% present in the other catalysts. P. S. and P. I. refer to the pentane soluble and pentane-insoluble fractions, respectively.

length in Fig. 9, reveal also a definite minimum when the alkyl chain of the olefin component has carbon atoms.

The effect of varying amounts of sodium isopropoxide with 1-octenylsodium is shown in Fig.

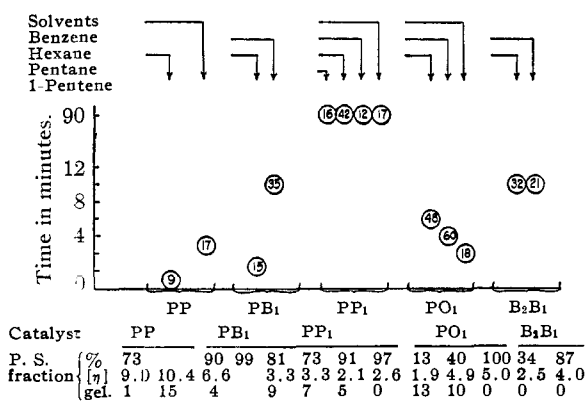


Fig. 9.—Effect of solvents on the polymerization of butadiene by alfin catalysts: numbers in circles show percentage conversion. Catalyst symbols: P as the first letter signifies the alkoxide of propanol-2, B₂ signifies the alkoxide of butanol-2; P, B₁, P₁, and O₁ as second letters signify the sodium compound derived by metalation of propylene, 1-butene, 1-pentene and 1-octene, respectively. P. S. fraction refers to the pentane-soluble fraction, [η] indicates the intrinsic viscosity.

10. As the proportion of alkoxide increases the process changes from one that is of the adduct compound type to one that is catalytic. The velocity of the catalytic process continues to increase as more alkoxide is used in spite of the fact that the quantity of octenylsodium correspondingly decreases. The maximum value, especially with respect to the amount of octenylsodium present, occurs when 75% of the total sodium present is combined as the isopropoxide salt; and at this proportion the percentage of polymer soluble in pentane is highest, the intrinsic viscosity is the highest and the amount of gel is the lowest of any of the other products produced catalytically.

This high proportion of alkoxide is not always necessary to attain optimum effects. Figure 11 shows that in three other cases the maximum or optimum effect was nearer 50 mole per cent. of isopropoxide; and this value would be that expected if the catalyst consists of one mole of alkoxide with one mole of alkenylsodium compound.

The observations with respect to gel-formation are appropriately summarized in this section. The total amount of gel is obviously less as the proportion of pentane-soluble polymer increases and as the gel content of that fraction decreases. Factors that improve the dissolving power of the medium reduce the gel. For example, the vigorous agitation of the high-speed stirring apparatus kept the gel lower than the mild agitation in the bottle (see section on methods of testing), the change from pentane to hexane to benzene usually caused an increase in the pentane-soluble fraction and a decrease in gel (see Fig. 9), and the reduction in temperature (see Fig.

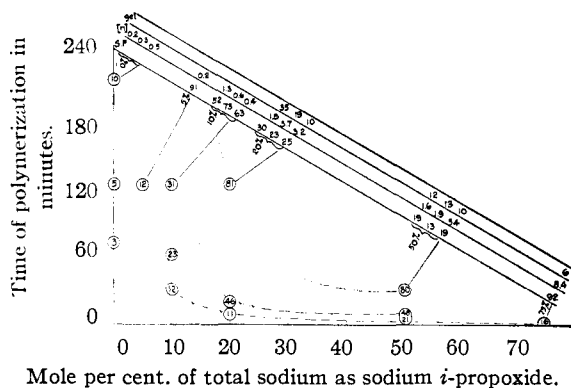


Fig. 10.—Effect of varying the percentage of sodium *i*-propoxide with 1-octenylsodium in polymerization of butadiene. [η] = Intrinsic viscosity. S. P. is percentage soluble in pentane. Values in circles, O, represent percentage conversion. Dotted lines connect positions of approximate equal conversion. Numbers grouped by brackets show values for a particular mole percentage of sodium alkoxide, the values for the highest conversion being farthest to the right with other values in progressive order.

8) lowered the proportion of pentane-soluble polymer and increased the gel. Some Alfin catalysts also favor gel formation as will be shown in the next section. The general subject of gel formation in Alfin catalysis and its relation to impurities or composition of the catalyst, will be discussed fully in subsequent papers in this series.

The Variations in Catalytic Effect

The isopropoxide/allylsodium catalyst is the best, judged by the high proportion of pentane-soluble product, the low gel content, the high intrinsic viscosity and the rapidity of action. The isopropoxide/1-butenylsodium is second best. Of all catalysts the 2-pentoxide/allylsodium seems the worst in that it causes a high percentage of pentane-insoluble product, although its rapidity of action is high. These conclusions are made after consideration of the data in Tables V and VI. The first table shows not only the extreme variation caused by the change from 2-pentoxide to isopropoxide in the catalytic activity induced by the complex with allylsodium, but shows also the relative influence of these catalysts and a few others on the polymerization of styrene. As far as this group of agents is concerned, the catalysts that gave a high percentage of pentane-insoluble polybutadiene usually caused the most rapid polymerization of styrene. The other table lists approximately the velocity of polymerization for a wide variety of catalysts and shows that the intrinsic viscosities vary over a wide range. In general, the faster acting catalysts have the higher intrinsic viscosities. The values for pentane-solu-

TABLE V
APPROXIMATE RATES^a OF FORMATION OF POLYBUTADIENE AND POLYSTYRENE BY VARIOUS CATALYSTS

Catalyst ^b	Approximate butadiene conversion, %	Pentane-soluble, %	Approximate rates of formation of		
			Pentane-soluble polybutadiene	Pentane-insoluble polybutadiene	Poly-styrene
P ₂ P	11	7	0.8	10.	5.2
PO ₁	2	19	1.1	0.9	5.5
PP ^c	10	40	4.	6.	1.9
PB ₁	6	90	5.4	0.6	2.0
PP ^d	8	73	5.8	2.2	2.4
PP ^e	12	95	11.4	0.6	1.5

^a These approximate rates were determined from a graph of the conversion *versus* time in minutes. The early portions of each curve are sufficiently straight lines to permit a rough comparison in terms of percentage yield per minute. ^b The abbreviations in this column are the same as recorded for Fig. 8. ^c This PP catalyst was prepared by a single addition of propylene to amylnsodium and sodium isopropoxide at low temperature and then stirring for three hours as the system warmed. Such catalysts have usually lacked the good qualities of those prepared by multiple additions of propylene. ^d This catalyst was prepared by stirring propylene with amylnsodium in the presence of sodium isopropoxide for three hours. ^e This PP catalyst was made by bottling the organosodium product after the amylnsodium-sodium isopropoxide mixture had been repeatedly treated with propene at low temperature, and each time allowed to warm to room temperature.

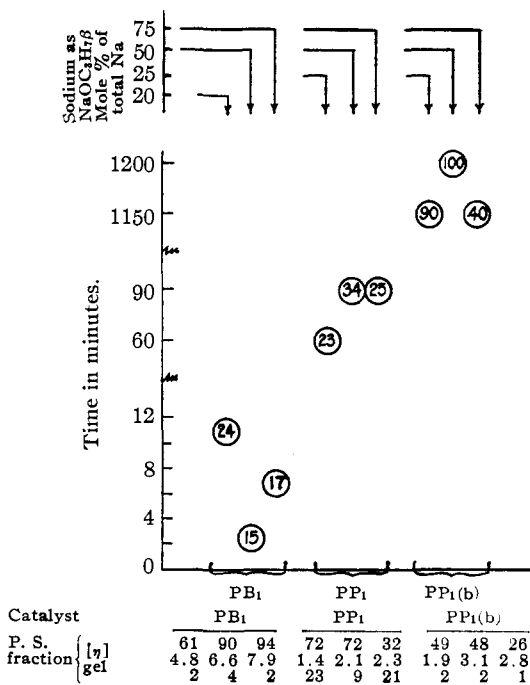


Fig. 11.—Effect of varying percentages of sodium alkoxides on alfin catalysts: numbers in circles indicate percentage conversion. PB₁ = sodium isopropoxide/1-butenylsodium. PP₁ = sodium isopropoxide/1-pentenyl sodium. PP₁(b) signifies that polymerizations were carried out in bottle rather than in the high-speed stirring apparatus. P. S. refers to the pentane-soluble fraction.

bility change considerably but this factor seems subject to other controls than that by the catalyst.

These data, together with those presented earlier in this paper, show further the uniqueness of Alfin polymerization, in that polymer size is dependent on the composition of the catalyst. Particularly is this evident in some instances where different alkoxides, used with the same alkenylsodium compound, have been responsible for the changes, although the alkoxides by themselves are comparatively inert and have no influence on either chain initiation or termination. The impurities associated with the alkenylsodium compound are constant in these cases, and the presence of a soluble impurity, such as the alkene from which the alkenylsodium compound is derived, is without apparent influence during polymerization because (a) the polymerization induced by the sodium isopropoxide/1-octenylsodium catalyst in the presence of 1-pentene and that induced by the sodium isopropoxide/1-pentenylsodium in the presence of 1-octene gave essentially the same results as when none of the added olefin was present and (b) the polymerization in pentene as a solvent gave nearly the same result as the polymerization in pentane as a solvent (see Fig. 9).

If initiation and termination of polymerization are dependent on the Alfin catalyst used, the

TABLE VI

COMPARISON OF ALFIN CATALYSTS WITH RESPECT TO RATE OF POLYMERIZATION IN PENTANE AND THE INTRINSIC VISCOSITY AND PER CENT. PENTANE SOLUBILITY OF THE POLYMERS

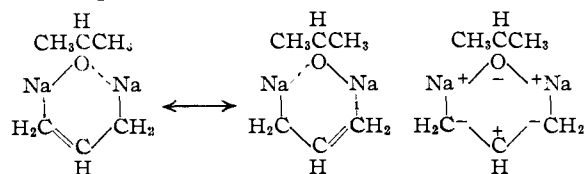
Components of catalyst Alcohol	Olefin	Time necessary for the solution to become viscous after the buta- diene is added	In- trinsic vis- cosity	% Pen- tane solu- bility ^a
Propanol-2	Propylene	1 minute or	9.0	73
Propanol-2	1-Butene	less	6.6	90
Propanol-2	1-Octene	1 to 4 min- utes	3.4	20
Propanol-2	2-Butene		5.6	
Octanol-2	2-Pentene		4.0	98
Propanol-2	1-Hexene	4 to 7 min- utes	4.0	
Butanol-2	1-Hexene		2.5	45
Pentanol-2	1-Hexene		3.8	87
Pentanol-2	2-Pentene	7 to 10 min- utes	3.0	87
Butanol-2	1-Butene		2.5	40
Propanol-2	2-Pentene		2.6	89
Butanol-2	2-Pentene		2.6	70
Hexanol-2	2-Pentene		2.7	53
Heptanol-2	2-Pentene	10 minutes or more	2.6	81
Propanol	1-Pentene		3.0	75
Butanol-2	1-Pentene		2.6	
Pentanol-2	1-Pentene		3.5	
Pentanol-2	1-Butene		1.5	61
Cyclohexanol	2-Pentene		2.5	50

^a These values are subject to wide variations. Polybutadienes have been made that are over 90% pentane-soluble.

reasonable viewpoint might be taken that the intermediate phase of chain growth is also influenced by the catalyst. If so, the catalyst would be similar to the large class of metallic catalysts, for example nickel, that activate each molecule that participates in the reaction, but dissimilar to those agents that induce diene polymerization by a free radical process. A discussion of the possible manner by which this effect could be achieved must await specific experiments related to the mechanism of polymerization by these reagents.

Structure of the Catalyst

A structure that accounts for the known facts is that of a double coordination complex, shown below, as two structures that contribute to resonance or as a polar structure.



Structures that contribute to resonance Polar formula

This proposal, regarded as a good working hypothesis, is plausible and adaptable to all facts so far at hand. It has the double salt complex characteristic of the phenylsodium-sodium chloride complex or the amylpotassium-potassium chloride complex already found⁴ to have moderate

polymerizing activity but is uniquely different from these others with respect to the possibility of double coordination, and this fact would account nicely for the uniform success attained with all components of the Alfin series. Facts that show the conformity of this ring structure with resonance are presented in the next paper of this series.

Experiments

The Influence of Di-isopropyl Ether (by E. M.).— Unless otherwise listed in Table I, the amylsodium was prepared in 200 ml. of pentane by the manner described⁷ in a previous paper so that about 0.19 mole of amylsodium was obtained. This amount is based on a 75% yield when 0.25 mole of amyl chloride and 0.5 g. atom of sodium react at -10° with subsequent temperature increase to 25° after addition of amyl chloride is completed. Di-isopropyl ether was freed from peroxides by treatment with ferrous sulfate and the dried (over sodium) product was distilled before use. The quantities used and the time allotted for reaction with amylsodium are recorded in Table I. All experiments with the ether were at room temperature. The stirring apparatus was operated in the range of 8000 to 11000 r. p. m. when the reactions were no longer than three hours. For periods beyond that time, that is, for overnight stirring, the speed was reduced to 1500 r. p. m.

The products of the reaction between amylsodium and the ether, as listed in Table I, were determined by forcing the mixture on solid carbon dioxide and then separating the caproic acid, vinylacetic acid and butylmalonic acids, the first two by fractionation of the petroleum ether and the ethyl ether extracts of the acidified aqueous layer, and the last as a residue in traces only after fractionation of the ether extract. The quantity of alkoxide produced by the reaction was assumed to be quantitative with respect to loss of amylsodium. The amount of allylsodium, derived as an aftermath of cleavage, and recovered as vinylacetic acid, was about a fifth or a fourth that of the alkoxide.

For each polymerization a preliminary experiment was always made to determine the sodium compounds present and a second identical one then carried out to test the effect of these compounds on the diene. A solution of 22 ml. (0.25 mole) of butadiene in 33 ml. of pentane was added dropwise at room temperature to the suspension of organosodium reagent prepared as described above and stirred in the high-speed stirring apparatus. When rubber was formed the full quantity of diene could not be added. At the end of the stated period of polymerization the mixture was forced onto solid carbon dioxide or, if the contents were very viscous, the carbon dioxide was added to the mixture in the flask. Water was then added and the contents stirred together as thoroughly as possible. The lump of rubber was removed, the pentane layer separated and evaporated, if desired, and the aqueous layer acidified in order to find any intermediate low molecular weight polymer adducts that would indicate a stepwise series of polymers. In all experiments in which rubber was produced no adducts were isolated.

In experiment 7 the isopropyl alcohol was added to amylsodium. The reaction was complete within ten minutes. The products of the diene reaction were approximately the same as those observed with butadiene, amylsodium and triethylamine.²

In experiment 8 the suspension of amylsodium was cooled to -50° before addition of 50 ml. of propylene (Phillips Petroleum Company pure grade). The mixture was allowed to warm over a two-hour period and the escaping propylene was collected in a trap. The reaction mixture was again cooled to -50° and treated with the trapped propylene as before with subsequent warming. About one-eighth of the contents were removed for the customary

(7) Morton, Patterson, Donovan and Little, *THIS JOURNAL*, **68**, 93 (1946).

analysis (shown in Table I) of the carboxylic acids. The remainder was tested as usual with butadiene. The mixture was stirred for three and one half hours during which the color changed from blue to green. The product was carbonated and the emulsion acidified. The aqueous layer was extracted with ethyl ether, the subsequent evaporation of which yielded 2.5 g. of vinylacetic acid. The organic layer was filtered in order to separate about 1 g. of a sticky solid, quite unlike the usual rubbery material obtained with the product of the amylosodium-di-isopropyl ether reaction, and more like that found by addition of diene to amylosodium. Evaporation of the pentane and treatment of the residue with potassium hydroxide yielded no clear solution of potassium salts, but a thick curd. No caproic acid was found.

In experiment 9, the isopropyl alcohol (3.75 g. or 0.06 mole) was added to amylosodium and ten minutes later the mixture was cooled to -50° and 50 ml. (0.6 mole) of propylene was added over a period of fifteen minutes. The mixture was then allowed to warm to 25° during forty-five minutes and was stirred for an hour at that temperature. The mixture was then somewhat viscous. An additional small amount of isopropyl alcohol (0.5 ml.) in 10 ml. of pentane was added and the mixture thoroughly stirred. Addition of the butadiene was commenced. Within three minutes 10 ml. had been added and the mixture was extremely thick. After fifteen minutes (9 ml. added), solid dioxide followed by water was added. The mixture was then acidified and the rubbery mass taken from the flask and subjected to steam distillation to remove pentane and other extraneous material. The rubber was the same type of polymer produced in the experiments with the product from the reaction of amylosodium with di-isopropyl ether.

In another experiment not recorded in the table the sodium isopropoxide was prepared in a separate container and added to the allylsodium prepared from amylosodium and propylene. The activity of this mixture was the same as that described in the foregoing paragraph.

Reaction with Isoprene (by E. M.).—The same molar proportions of isoprene were used to replace the butadiene in a test with the product of the amylosodium and diisopropyl ether reaction. The polymer was the same general type except softer.

Allylpotassium (by R. L.).—A pentane solution of diallyl ether (12.3 g. or 0.125 mole in 40 ml.) was added over a fifteen-minute interval to 10 g. (0.25 g. atom) of potassium sand suspended in 200 ml. of decane with high-speed stirring. The temperature was 10° at the start of action and rose rapidly after twenty minutes, so much so that the bath temperature had to be maintained at -20° in order to keep the temperature inside the reaction flask at 30° . The rapid evolution of heat soon ceased and the reaction mixture was stirred for a total time of three hours after which the blue suspension was forced onto carbon dioxide. The acids recovered after acidification were distilled. From $40-82^{\circ}$ at 28 mm., 1.3 g. of a liquid that had a refractive index of 1.4253 (n_D^{20}) was obtained; and at $82-83^{\circ}$ and 28 mm., 4.89 g. that had an index of 1.4240 was collected. The observed neutralization equivalent was 88. No residue was present. Pure vinylacetic acid* has a refractive index of 1.4252 (n_D^{20}) and a neutralization equivalent of 86. One gram of acid was heated with 10 ml. of 25% potassium hydroxide for twenty minutes. The free acid recovered therefrom melted at $70-71.5^{\circ}$. Crotonic acid is reported⁹ as melting at 72° .

The cleavage reaction was repeated with the same quantity of ether and with 12.5 g. (0.031 mole) of potassium sand to which 3.8 g. (0.63 mole) of isopropyl alcohol had been added previously. The blue color formed as before but later faded to white. Carbonation and subsequent recovery of the acids yielded 1.4 g. that boiled at $42-60^{\circ}$ (20 mm.) and 6.1 g. that boiled at $73-75^{\circ}$ (16 mm.). The corresponding refractive indices were 1.4132 and 1.4220.

(8) Linstead, Noble and Bornman, *J. Chem. Soc.*, 560 (1933).

(9) Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1941.

The last reaction was repeated and 0.25 ml. of butadiene was added prior to carbonation. The action on the diene was allowed to progress for two hours before carbonation. A thick viscous oil only was obtained.

Components of Catalyst (by E. M.).—The procedure for testing a mixture of alkoxide and a metalated olefin was substantially the same as that described for the mixture of sodium isopropoxide and allylsodium, except that a low temperature was not required for the metalation of the higher boiling olefins. In all cases the olefins were the best grade obtainable from Phillips Petroleum Co. Isopropyl alcohol was obtained from Carbide and Carbon Co. and was fractionated before use. The other alcohols were obtained from Eastman Kodak Co. and were redistilled before use. The mole proportions of reagents were as described before. The diene was added dropwise in order to catch any low molecular weight products that might happen to form. Under these conditions and with propylene as the olefin component, isopropanol, 2-butanol and cyclohexanol were successfully used as components in the catalyst for the formation of rubber but *n*-propanol and *t*-butanol were not. When isopropyl alcohol was used as the alcohol component, rubber was obtained when the olefin components were 1-butene, 1-pentene, 1-hexene, 1-octene, 2-butene and 2-pentene. No rubber was obtained when the olefin was isobutene, cyclohexene and diallyl. Benzene (thiophene-free) gave a product much like that described⁴ before. Other combinations that proved effective as catalysts were derived from 2-butene and butanol-2, from 2-pentene and pentanol-2, and 1-pentene and pentanol-2. Ineffective combinations were obtained from isobutylene and isobutyl alcohol and from the reaction of amylosodium with di-isobutyl ether, a combination that should lead to 2-methylallylsodium and sodium isobutyl oxide. Similarly a combination derived from butene-2 and isopropylmercaptan and from butene-2 and isopropylamine was ineffective. These last two pairs gave a sticky pasty product very similar to that obtained when the complex of amylosodium with triethylamine reacts with butadiene, and quite unlike the rubbery products obtained with the complexes that contain the alkoxide.

Separation of Pentane-soluble and Pentane-insoluble Rubber (by E. M.).—The 2-butoxide/1-hexenylsodium (B_2H_4) catalyst for this experiment was made by addition of 30.6 ml. of *n*-amyl chloride to 11 g. of sodium sand in 175 ml. of 1-hexene and 85 ml. of pentane at -10° over a period of fifty minutes. The mixture was allowed to warm to room temperature during thirty minutes before addition of 7.4 ml. of 2-butanol, after which it was stirred for four hours at 30° . The polymerization was then carried out by addition of 240 ml. of butadiene to 110 ml. of the above green colored catalyst suspension in 1000 ml. of pentane. The mixture was stirred in the high-speed stirring apparatus at room temperature for an hour, 200 ml. of water was then added to stop the reaction, and 1.2 g. of phenyl- β -naphthylamine in 20 ml. of alcohol added to act as an antioxidant. The well-stirred mixture separated into a pentane phase that contained finely dispersed particles of rubber and a lower aqueous alkaline phase. The upper layer was poured into 250-ml. centrifuge bottles and allowed to stand overnight. The rubber settled to about half the height of the liquid. Some of these bottles were then centrifuged in order to separate the rubber as much as possible into pentane-soluble and pentane-insoluble portions. The pentane-soluble portion was evaporated overnight under a water-pump vacuum. The drying was then completed in a vacuum oven at room temperature. The settled or pentane-insoluble rubber was dried at room temperature in a vacuum oven overnight. Portions of each rubber were also steam distilled for one and a half hours. Other bottles were treated without separation into soluble and insoluble fractions. The coagulation with alcohol was made by addition of 100 ml. of ethyl alcohol. The product was filtered and then dried in a vacuum oven at 40° for one hour. Intrinsic viscosity and gel determinations were made in benzene according to the method of Baker.¹⁰ The results of all these tests are shown in Table III.

(10) Baker, Mullen and Walker, private communication.

The isopropoxide/1-pentenylsodium (PP_1) catalyst was prepared in a similar manner from 70 g. of sodium, 180 ml. of *n*-amyl chloride, 500 ml. of 1-pentene, 1000 ml. of pentane and 38 ml. of isopropyl alcohol. The polymerization was carried out as before with 120 ml. of the light blue catalyst suspension, 240 ml. of butadiene and 1500 ml. of petroleum ether. At the end of one and one-half hours 300 ml. of water was added to the viscous mixture, followed by the solution of phenyl- β -naphthylamine. The pentane layer was poured into five bottles which were handled as indicated in Table III.

Comparative Rate of Formation of Pentane-soluble and Pentane-insoluble Rubber (by R. L.).—The catalysts for these experiments were made under conditions similar to those described in the foregoing section from 0.5 g. atom of sodium, 0.25 mole of amyl chloride, excess of the olefin, and 0.1 mole of the alcohol. Each catalyst was then forced into a bottle by pressure of nitrogen and aliquot portions withdrawn as desired. The polymerization was carried out by addition of 30 ml. of butadiene to 20 ml. of the catalyst suspension in 25 ml. of petroleum ether or hexane in the high-speed stirring apparatus. The reactions were allowed to progress at the temperature and for the times indicated in Fig. 1, after which water was added followed by phenyl- β -naphthylamine as a stabilizer. The pentane or hexane layer was centrifuged and the rubbers recovered from the pentane-soluble portion by evaporation of the pentane under a water pump as described before. Both rubbers were dried in a vacuum at 30° before determination of values recorded in the table.

The Dry Catalyst (E. M.).—The isopropoxide/1-butenylsodium (PB_1) catalyst for this experiment was made from amylsodium (derived from 71 g. of sodium and 183.6 ml. of *n*-amyl chloride in 1500 ml. of pentane) by addition of a solution of 28.8 ml. of isopropyl alcohol in 31 ml. of pentane at 20° followed by addition of 300 ml. of 1-butene at -15°. The mixture was then allowed to warm and was stirred for four hours. About one-fourth of this olive colored mixture was siphoned into a one-liter Erlenmeyer flask and the pentane evaporated, first by use of a water pump and then an oil pump. The solid, almost dry, catalyst was obtained in olive colored lumps. The color changed to orange-brown as air came slowly in contact with the solid. If removed from the flask and the protection of a nitrogen atmosphere, the particles caught fire. Three lumps of the dry catalyst (approx. 0.5 g.) was added to 30 ml. of butadiene in 30 ml. of pentane in a high-speed stirring apparatus. After one-half hour the reaction was stopped by addition of water. Approximately 4 g. of polymer was recovered. An identical preparation of an isopropoxide/2-butenylsodium (PB_2) catalyst yielded a solid that caused no polymerization of butadiene although the liquid suspension of this catalyst was active.

Comparative Rates of Polymerization of Butadiene Caused by Ordinary Organosodium Reagents and by Alfin Catalyst (by R. L.).—Amylsodium was prepared at -10° in the high speed stirring apparatus from 11.5 g. (0.5 g. atom) of sodium and 26.6 g. (0.25 mole) amyl chloride in pentane. 1-Pentenylsodium and 1-octenylsodium were made by addition with stirring of 0.4 mole of each olefin to this amylsodium. At the end of three hours, the mixture was forced into a bottle by pressure of nitrogen and allowed to stand for at least three days before use.

The corresponding isopropoxide/1-butenylsodium (PB_1) and isopropoxide/1-pentenylsodium (PP_1) catalyst suspensions were made by addition of 0.1 mole of isopropyl alcohol to 0.19 mole of amylsodium. The mixture was well stirred for one-half hour and then treated with 0.4 mole of the olefin. After three more hours of stirring, the mixture was forced into a bottle through a siphon by application of a pressure of nitrogen. The isopropoxide/1-octenylsodium (PO_1) catalyst was made somewhat similarly except that 1-octene was used as the solvent in place of pentane during the preparation of amylsodium. All catalyst suspensions were allowed to stand at least three days before use. Carbonation of portions of each catalyst suspension and isolation of the corresponding carboxylic

acids showed that metalation of the olefins had been complete.

The polymerizations were carried out in the flask with high speed stirring at room temperature. The bottles that contained the organosodium reagents were first shaken in order to insure a uniform suspension of the solids. Ten milliliters of the alkenylsodium reagents or an equivalent amount, 20 ml. of the catalyst suspension was forced from the bottle into a buret by gentle pressure of nitrogen and the reagent was then added to 250 ml. of pentane in the reaction flask. Butadiene (30 ml. in cold pentane 30 ml.) was added rapidly to the well-stirred mixture. The reactions were allowed to progress for the period of time indicated in Fig. 2, after which water was added to stop the reaction. Hydrochloric acid and phenyl- β -naphthylamine (4% by weight of the polymer) was added. The polymers were freed from the pentane by steam distillation, were squeezed as dry as possible and then dried in vacuum oven at 40°. No separation was made in this instance into pentane-soluble and pentane-insoluble parts. All results are recorded in Figs. 2 and 3.

Polymerization of Isoprene and the Monomer-catalyst Ratio (E. M.).—The isopropoxide-allylsodium (PP) catalyst for this series of experiments was made by passing propylene through 42.5 cc. of isopropyl alcohol and into the suspension of amylsodium that had been made from 70 g. of sodium and 180 ml. of pentane. In this manner 250 ml. of propylene was passed into the reaction mixture. The propylene that passed through was caught in a trap and then recirculated. These operations were repeated for a total of four and one-half hours, after which the mixture was forced into a bottle from which aliquot parts could be removed as desired.

The polymerization experiments were carried out in tonic bottles with 30 ml. of isoprene and 8.5, 17, and 25.5 ml. of catalyst suspension, respectively, for the time shown in Figs. 4 and 5. The monomer catalyst ratios shown in the figure are the relative volumes of monomer to volume of suspension that contained the catalyst. Enough pentane was present in each bottle to make the total volume 270 ml. The bottles were capped and shaken on a machine at room temperature. After the period of time indicated the bottles were opened and the reaction stopped by addition of an antioxidant, phenyl- β -naphthylamine, acetic acid, ether and water. The rubber gel obtained in each reaction was stirred with enough petroleum ether to dissolve the polymer. The petroleum layer was then washed well with water to remove all salts and was then treated in the usual way to recover the rubber.

The isoprene (Newport grade) used for this and subsequent series of experiments was first stirred in the high speed stirring apparatus with solid sodium hydroxide. The mixture was then allowed to stand overnight and the upper layer decanted from the viscous brown residue that had settled. This isoprene was then distilled from sodium bisulfite at the pressure of a water pump vacuum and the distillate collected in a Dry Ice trap. The distillate was then shaken with aqueous sodium hydroxide and the isoprene (4L) stored overnight over calcium chloride and a little ferrous sulfate. This isoprene was then distilled from a little ferrous sulfate through a 60-plate fractionating column. Three fractions were collected in which the refractive index changed from 1.4209 to 1.4210. This material, 1150 ml. was stirred for three minutes with 20 ml. of a pentane suspension of amylsodium at 25° in order to remove traces of material easily metalated. The mixture was then carbonated by pouring on Dry Ice. The product contained a little pentane from the amylsodium suspension, but otherwise was free from extraneous compounds that would react with the organosodium catalyst. The material was kept in an ice-box and a quantity was distilled just before use for each series of experiment.

The Monomer-Catalyst Ratio and the Intrinsic Viscosity (E. M.).—A solution of isoprene in an equal volume of pentane was added dropwise at 25° to 250 ml. of the catalyst suspension described in the previous experiment. The mixture was stirred vigorously in the high speed

stirring apparatus during addition. Within six minutes addition of 15 ml. had been completed. The thick mixture was then forced onto solid carbon dioxide and water was added. The polymer was isolated and dried in the usual manner. The yield was 3.3 g. or 64% from 5.1 g. of isoprene. The intrinsic viscosity of this polymer was 6.6.

The effect of 17 ml. of the same catalyst was tested with 25 ml. of the same quality isoprene (distilled from the lot described in the previous section) in a bottle polymerization in pentane sufficient to make a volume of 250 ml. The conversion was 63% within one hour and the intrinsic viscosity of the polymer was 6.3.

Effect of Temperature in Alfin Polymerization (R. L.).—The 50 and 20% alkoxide sodium isopropoxide/1-butenylsodium (PB₁) catalysts for these experiments (Fig. 8) were made by addition of 7.65 or 3.05 ml. of isopropyl alcohol, respectively, to amylsodium that had been made from 30.6 ml. of amyl chloride, 11.5 g. of sodium in 270 ml. of pentane. Phillips pure grade 1-butene (60 ml.) was then added at 0° and the mixture allowed to warm slowly to room temperature.

The polymerizations were carried out in each case with 20 ml. of the above catalyst suspension, well shaken before removal of sample, 30 ml. of butadiene and 250 ml. of the hydrocarbon solvent in the high-speed stirring apparatus. Other pertinent conditions are recorded in Fig. 8. The antioxidant used was phenyl-β-naphthylamine.

The sodium 2-butoxide/1-butenylsodium (B₂B₁) catalyst was made similarly from 0.5 g. atom of sodium, 0.25 mole of amyl chloride, 0.1 mole of 2-butanol and 60 ml. of 1-butene. The sodium isopropoxide/1-octenylsodium (PO₁) catalyst was made similarly, except for the use of 200 ml. of freshly distilled 1-octene in place of 1-butene.

Effect of Solvents and Alkoxide Content (by R. L.).—The catalysts were prepared by addition of appropriate amounts of alcohol and olefin to amylsodium which had been previously prepared in 80% yield from 0.5 g. atom of sodium and 0.25 mole of amyl chloride. Sixty ml. of 1-butene or its equivalent of other olefins was used. Larger quantities were made in proportion.

The polymerizations were carried out by addition of 30 ml. of butadiene to 20 ml. of the catalyst suspension, stirred in 250 ml. of the solvent in the high-speed stirring apparatus. Other significant data are recorded in Figs. 9, 10 and 11.

Comparative Formation of Polybutadiene and Polystyrene by Alfin Catalysts (by R. L.).—The catalysts were

prepared by the method already described. Any variations are described in Table V. The polymerizations were carried out in the high-speed stirring apparatus at 20°. In each experiment 20 ml. of catalyst suspension in 250 ml. of pentane was used with 30 ml. of butadiene or 15 ml. of styrene. The styrene (Eastman Kodak Co. grade) was previously shaken with sodium hydroxide to remove inhibitor, then dried over magnesium sulfate, filtered and distilled at 4 mm. in order to get a middle fraction. After polymerization, the polystyrene was lifted from the pentane and water, squeezed as dry as possible and dried in a vacuum oven at 50°.

Comparative Yields, Intrinsic Viscosities, Pentane Solubilities of Polymers Produced by Alfin Catalysts (by E. M.).—The catalysts were prepared as described in the previous sections. The polymerizations were carried out in the high-speed stirring apparatus with 20 ml. of catalyst suspension, 30 ml. of butadiene and 240 ml. of solvent. Data are recorded in Table VI.

Summary

Di-isopropyl ether reacts with amylsodium to give sodium isopropoxide and allylsodium which form a complex that causes the catalytic polymerization of butadiene and isoprene, rather than the formation of a series of adducts.

Similar agents can be made from sodium alkoxides of methylalkyl carbinols and from metalated olefins. The reagents are called alfin catalysts because a secondary alcohol and an olefin enter into their preparation.

These catalysts are unique because the intrinsic viscosities of the polymers produced therewith are dependent on the components of the catalyst but independent of the monomer-catalyst ratio.

The testing of the catalyst and the general character of the polymerization reactions are described.

A cyclic formula is suggested for the catalyst complex.

CAMBRIDGE, MASS.

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CONTRIBUTION FROM THE INSTITUTE FOR CHEMICAL TECHNOLOGY, COLLEGE OF ENGINEERING, KYOTO IMPERIAL UNIVERSITY, JAPAN]

Friedel-Crafts Reactions with Organic Dihalides¹

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The Friedel-Crafts reaction of 1,3-dichlorobutane and benzene might be expected to yield 1-methylindane, since the latter substance is produced by the action of aluminum chloride upon δ-chlorobutylbenzene^{1a}; since the Friedel-Crafts reaction of 1,4-dichlorobutane and benzene² as well as that of δ-chlorobutylbenzene³ both yield tetralin; and, further, since 1,3,3-trimethyl-6-hydroxyindane and 1,1,2-trimethyl-5-hydroxyindane are obtained from the reactions of phenol with diace-

tone alcohol and pinacol, respectively, in the presence of zinc chloride as the condensing agent.⁴

Our experiments show, however, that treatment of 1,3-dichlorobutane with benzene and aluminum chloride does not yield 1-methylindane, but rather a mixture of substances among which we have been able to identify 2,3-diphenylbutane and *s*-butylbenzene. The identity of the 2,3-diphenylbutane was established by a mixed melting point determination of material obtained from the reaction by fractional distillation with an authentic sample of the substance.

In addition to the solid 2,3-diphenylbutane obtained by fractionation of the crude product of

(1) This paper represents a combination of two manuscripts originally entitled "The Organic Reactions with Aluminum Chloride. XIX and XX."

(1a) v. Braun and Neumann, *Ber.*, **50**, 50 (1917).

(2) Yura and Oda, *J. Soc. Chem. Ind., Japan*, **46**, 531 (1943).

(3) v. Braun and Deutsch, *Ber.*, **45**, 1267 (1912).

(4) Niederl, *TEIS JOURNAL*, **58**, 657 (1936).