

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

Polymerization. XIII. A Comparison of the Action of Organosodium Reagents and of the Alfin Catalyst on Styrene¹

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RECEIVED AUGUST 20, 1951

Amylsodium, of a series of organosodium reagents including allylsodium, caused the largest amount of polymerization of styrene. When, however, allylsodium was combined with sodium isopropoxide and sodium chloride to give the Alfin catalyst, the polymerization was as much as six to ten times faster than that produced by amylsodium. The intrinsic viscosities of the Alfin polystyrenes are higher than for the corresponding polymers made with amylsodium and other similar reagents in spite of the faster polymerization. In general the comparison of sodium reagent and Alfin reagent shows differences similar to those noted for butadiene, although to a lesser degree.

Reagents of the type of amylsodium differ markedly from the Alfin catalyst^{2,3,4,5} in their effect on butadiene. Per given mole quantity the former causes a slow polymerization in a 1,2-manner chiefly (about 70%) to polymers with intrinsic viscosities of 1 or less. Intermediate stages in polymer growth can be demonstrated by carbonation and isolation of the corresponding carboxylic acids. The same quantity of Alfin catalyst causes polymerization with extreme rapidity in a 1,4-manner—70% and more^{6,7}—to polymers with intrinsic viscosities of 12 or more which can be obtained—with care—completely free from gel. X-Ray diffraction measurements show a regular pattern. No intermediate stages can be detected. The two types of polymers are more unlike than those produced by sodium and by emulsion polymerization of butadiene. These remarkable effects and others produced by the Alfin catalyst are brought about solely by the association of sodium isopropoxide and sodium chloride⁸ with the organosodium reagent, allylsodium. The purpose of the present work on styrene was to see if some of the differences between the two types of activities by sodium reagents were exhibited in the polymerization of styrene and the conclusion will be drawn that they do exist, although to a less degree than with butadiene.

For the action of amylsodium and like compounds, a series of reagents with varying reactivity was used. In the order of decreasing effect in inducing polymerization of styrene these reagents were amylsodium, benzylsodium, allylsodium, diphenylmethylsodium, β -methylstyrylsodium, triphenylmethylsodium and fluorenylsodium. The positions of key members of this series is the same as has been shown⁹ in displacement reactions or is generally accepted^{10,11} for good reasons. The positions of allylsodium and β -methylstyrylsodium have not

been observed in any series previous to this study but would be below amylsodium because of their formation from that reagent and the corresponding hydrocarbon in an irreversible reaction. Their positions in the above scale are approximately where expected from considerations of their structure.¹¹ The effect of these reagents on styrene was in the order 7, 4, 3, 1, 0.2, 0 and 0.

A test was made with vinylsodium¹² which, with phenylsodium,¹³ enjoys the unique distinction of not adding appreciably, if at all, to 1,1-diphenylethylene, a compound unusually well adapted for addition reactions to the double bond. Vinylsodium induced a reasonably rapid polymerization of styrene (phenylsodium does also), although to a far less extent than does amylsodium (0.5 compared to 7).

In all these cases the amount of polymerization was less than caused by amylsodium, which is outstandingly the most active of all in ordinary metalation reactions, since it can be used for the preparation of the others. Of particular interest is the fact that allylsodium in the series had less than half the polymerizing activity of amylsodium.

When sodium isopropoxide and sodium chloride were present with allylsodium to give an Alfin catalyst, the yield of polymer sharply increased. The amount was dependent on the proportion of sodium isopropoxide but in the best case the catalyst was six to ten times more active than amylsodium. This increase in velocity was accompanied, surprisingly enough, by an increase also in the viscosities which were never lower than 1.2 and were as high as 3.6. Those made by polymerization with amylsodium were as low as 0.22 and never higher than 1.04. These higher viscosities for the Alfin polymer were not caused by increased viscosity of the solvent, as in a peaking¹⁴ effect, because the polymer was largely insoluble in the pentane used as the medium for the reaction. The chief factor affecting the viscosity from the Alfin reagent was the proportion of isopropoxide in the catalyst, the two with the highest ratio having the highest viscosities. The determining factor with the other sodium reagents was the monomer catalyst ratio and the amount of polymerization.

The uniqueness of Alfin catalysis on styrene was largely destroyed when β -methylstyrene or tri-

(1) This work was carried out under the sponsorship of the Office of Synthetic Rubber, Reconstruction Finance Corporation, Washington, D. C.

(2) A. A. Morton, E. E. Magat and R. L. Letsinger, *THIS JOURNAL*, **69**, 950 (1947).

(3) A. A. Morton, *Ind. Eng. Chem.*, **42**, 1488 (1950).

(4) J. D. D'Ianni, F. J. Naples and J. E. Field, *ibid.*, **42**, 95 (1950).

(5) W. K. Taft and H. Goldsmith, *ibid.*, **42**, 2542 (1950).

(6) A. W. Meyer, private communication (1950).

(7) Unpublished experiments with J. R. Critser and Irina Nelidow.

(8) A. A. Morton and F. H. Bolton, Boston Meeting of the American Chemical Society (1951); *Ind. Eng. Chem.*, in press.

(9) J. B. Conant and G. W. Wheland, *THIS JOURNAL*, **54**, 1212 (1932); W. K. McEwen, *ibid.*, **58**, 1124 (1936).

(10) H. Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 448.

(11) A. A. Morton, *Chem. Revs.*, **35**, 1 (1944).

(12) A. A. Morton and F. D. Marsh, *THIS JOURNAL*, **72**, 3785 (1950).

(13) A. A. Morton and H. C. Wohlers, *ibid.*, **69**, 167 (1947).

(14) E. M. Frith and R. F. Tuckell, "Linear Polymers," Longmans Green and Co., London, 1951, p. 90.

phenylmethane was added to the reagent. These two hydrocarbons, increasing in the order named, reacted with the catalyst and were converted to the corresponding organosodium reagent. Thereby polymerization of the Alfin type was reduced or destroyed, even though the other components for the catalyst had been present in a combination which had possessed catalytic activity.

These results contrast the Alfin reagent in polymerization with ordinary sodium reagents. The difference is not as great as in the case of butadiene where this Alfin reagent was approximately 60 times more active than the corresponding amount of amylsodium. This narrowing of the range of reactivity produces the interesting effect that amylsodium causes styrene to polymerize about 16 times faster than butadiene, whereas the Alfin reagent causes butadiene to polymerize about four times faster than styrene. Also the Alfin polymerization of butadiene was not decreased by a small amount of β -methylstyrene. On the contrary, it was actually increased.¹⁵

A previous paper¹⁶ has shown that in ordinary reactions allylsodium in the Alfin catalyst is less reactive than allylsodium without the alkoxide, and for reasons already stated, allylsodium must be less reactive than amylsodium. Hence the greater activity of the Alfin catalyst in polymerization might not seem to be ascribed reasonably to an increase in the rate of an initiation reaction in the ordinary sense of metalation by substitution or addition. The same argument applies to the case of Alfin polymerization of butadiene and a similar situation was mentioned¹⁷ before in the polymerization of butadiene by phenylsodium.

Experiments

General Methods.—All preparations of sodium reagents and all polymerizations were carried out according to the methods which have already been described and will not be given in detail here.¹⁸ The styrene, Eastman Kodak Company, was washed with two portions of 10% sodium hydroxide, dried over magnesium sulfate and distilled freshly before use; n_D^{20} 1.5438–1.5442, recorded¹⁹ 1.5441.

Polymerization of Styrene by Amylsodium and the Monomer/Reagent Ratio.—Two preparations of polystyrene were made by the dropwise addition method, one where 23.4 g. (0.225 mole) of styrene in 100 ml. of pentane was added over a 30-minute period to amylsodium prepared from 1.02 gram atoms of sodium and the other where 0.26 mole of styrene was added at once to amylsodium made from only 0.02 gram atom of sodium. In each case the temperature was 20–25° and the mixture was stirred for about 30 minutes after addition was completed. The polymerizations were then stopped with isopropyl alcohol and the mixtures were treated with water to remove alkali. The insoluble material which separated from the first experiment was removed by decantation and washed twice with 100-ml. portions of pentane and then with water. It was next dissolved in 300 ml. of benzene and washed three times with 300 ml. of water each. Most of the benzene was removed by vacuum and the polymer was rinsed with 100 ml. of *n*-pentane. When dried, 9.8 g. (41%) of white polymer was obtained. At a

concentration of 4.00 g. per 100 ml. of benzene this material had a viscosity of 0.054, and when the data were extrapolated²⁰ to zero concentration, the viscosity was 0.057. The pentane-soluble part from this first experiment and the pentane washings were combined, were dried over magnesium sulfate and the solvent was removed under vacuum. The residue consisted of 13.8 g. (59%) of a light orange transparent glass-like material which was not volatile at 180° (3.5 mm.).

The insoluble material from the comparison or second experiment was separated by filtration, was washed with 100 ml. of pentane, was suspended in 200 ml. of pentane and therein stirred three times with water in the high-speed stirring apparatus. When filtered and dried the polymer weighed 14.0 g. (52% yield). At a concentration of 0.54 g. per 100 ml. of benzene the viscosity was 0.21 and at infinite dilution was 0.22.

Comparison of Polymerization of Styrene by Different Sodium Reagents.—Two preparations of amylsodium in each of which 3 g. atoms of metal had been used were combined, diluted to 6 liters and allowed to stand for about a month. Aliquots of 558 ml. of this material were stirred for about five hours each with 0.31 mole of the required hydrocarbon, amylsodium itself being treated the same way in order to make the comparison as thorough as possible. Each mixture was then diluted to 800 ml. with dried (over amylsodium) *n*-pentane and allowed to stand in tightly-stoppered bottles for at least two weeks before use. Carbonation of 372 ml. of the triphenylmethylsodium reagent thus prepared gave 19.0 g. of a solid which had a neutralization equivalent of 240, a little low for triphenylacetic acid (neut. equiv. 288), because of some amylsodium not yet reacted with the triphenylmethane. The total concentration of organosodium compound in that reagent was 0.212 meq./ml. A similar analysis of the benzylsodium reagent gave 9.9 g. of acid and the neutralization equivalents showed a total of 0.207 meq./ml. of organosodium reagent, of which probably 11% represented unchanged amylsodium. The average concentration (0.210 meq./ml.), as determined from these analyses, was assumed to be the concentration for amylsodium, benzylsodium, β -methylstyrylsodium, diphenylmethylsodium, triphenylmethylsodium and fluorenylsodium. The allylsodium was made by metalation of propylene in the manner usually employed in this work and the total concentration of organosodium reagent present in

TABLE I
POLYMERIZATION OF STYRENE BY ORGANOSODIUM REAGENTS

Sodium reagent	Amount ^a	Polymer Yield, %	Yield, ^a %	Vis. ^b
Amyl	5.25	70.4	13.4	0.30
	2.1	19.5	9.3	.26
Benzyl	5.25	35.0	6.7	.27
	5.25	26.0	5.0	.22
	2.1	1.7	0.8	.41
Allyl	5.55	26.5	4.8	.75
	5.55	39.1 ^c	3.5 ^d	1.04
Diphenylmethyl	5.25	10.0	1.9	.48
	2.1	3.4	1.6	.63
Vinyl ^e	4.1	4.5	1.1	1.0
	4.1 ^f	13.4 ^c	1.6 ^d	0.68
β -Methylstyryl	5.25	1.6	0.3	
	2.1	0.5	.2	
Triphenylmethyl	5.25	.07	.01	
	2.1	.04	.02 ^g	
Fluorenyl	5.25	0.4	.08 ^g	
	5.25	.4 ^c	.08 ^g	

(15) A. A. Morton and E. Grovenstein, Jr., *THIS JOURNAL*, **74**, 5437 (1952).

(16) A. A. Morton and M. E. T. Holden, *ibid.*, **69**, 1675 (1947).

(17) A. A. Morton and R. L. Letsinger, *ibid.*, **69**, 172 (1947).

(18) A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little, Jr., and R. L. Letsinger, *ibid.*, **72**, 3785 (1950).

(19) Selected Values of Properties of Hydrocarbons, National Bureau of Standards, Washington, D. C., 1947.

^a Amounts expressed in milliequivalents. ^b Intrinsic. ^c The polymerization time was 60 minutes instead of 30. ^d This value is corrected for the longer polymerization time of this experiment. ^e Sodium isopropoxide was present with the vinylsodium. ^f The volume of pentane in this experiment was 225 ml. ^g The yield is estimated and is not in excess of that recorded.

(20) H. C. Tingey as cited by W. V. Smith, *THIS JOURNAL*, **68**, 2059 (1946).

TABLE II
 POLYMERIZATION OF STYRENE BY ALFIN CATALYSTS

Cat. No.	Reagent		RNa used milliequivalents	Polymerization		Polymer		$[\eta]$
	Sodium isopro. moles	Allyl-sodium mole		Conv., %	Conversion per milliequivalent	Vis. at g./100 ml.		
1	0.30 ^a	0.30	6.50	107	16	1.4	0.15	1.4
			3.25	98	30	1.2	.26	1.2
			1.30	60	46	1.3	.14	1.4
2	.60	.60	4.1	58	14	1.7	.11	1.8
			5.5	65	12	1.6	.12	1.6
3 ^b	.60	.60	2.2	17	8	1.7	.22	1.8
			2.3	87	38	2.6	.15	2.8
4	.96	.24	1.4	38	28	3.1	.08	3.2
			.9	28	30	2.9	.11	3.1
			1.4	103	76	2.4	.15	2.5
5	1.14	.07	.7	61	90	3.4	.10	3.6

^a In this reagent, 0.60 mole of sodium *t*-pentoxide was also present. ^b This catalyst was the same as No. 2 except that it was in the high-speed stirring apparatus resaturated with propylene on four different days in order to remove any trace of unused amylsodium.

that reagent was 0.222 meq./ml. of which about 8% was amylsodium which had not yet reacted with propylene. The small quantity of amylsodium present in each of these reagents would not affect the general conclusion of lessened polymerizing activity as amylsodium was converted to a less reactive salt. Furthermore in these insoluble reagents this unreacted amylsodium would be on the interior of the solid particles and less available for affecting polymerization.

Vinylsodium was obtained through the kindness of Frank D. Marsh and had been made¹² in a similar way (except that sodium isopropoxide was present) by metalation of ethylene. The concentration of this sodium reagent was 0.164 meq./ml. of which less than 1% was amylsodium. The smaller amount of amylsodium present in this case probably resulted from the presence of sodium isopropoxide which facilitates metalation reactions of this type.

The activity of each reagent was tested by bottle polymerization of 30 ml. of styrene in 210 ± 5 ml. of *n*-pentane for 30 minutes, according to the general method already described¹⁸ for butadiene. The data in Table I are arranged in descending order of reactivity except for the last two reagents which are in the inverted order but each had virtually zero activity.

For comparison the polymerization activity of 5.25 milliequivalents of amylsodium on 30 ml. of butadiene under comparable conditions was found to be 3.8% and the conversion per milliequivalent was 0.72, that is to say, only one-sixteenth, approximately the conversion observed on styrene. Also 1.11 milliequivalents of allylsodium caused a 0.7% conversion of butadiene or a 0.6% conversion per milliequivalent of reagent.

Action of the Alfin Catalyst on the Styrenes.—Alfin catalysts which contained allylsodium, sodium isopropoxide and sodium chloride were made according to the method previously described.¹⁸ These catalysts contained different

quantities of isopropoxide. The amounts listed in column 2 of Table II are the moles of isopropyl alcohol added to the preparation in the 3-liter flask, where 3 g. atoms of sodium and 1.5 moles of amyl chloride were used. The amount of allylsodium is the quantity estimated on the basis of the usual yield of 80%. Other variations in the preparations are listed in footnotes to the table. The activity of these catalysts was tested on styrene in the same manner as with the organosodium reagents listed in Table I. For comparison 1.10 equivalents of catalyst No. 3 caused 45 to 58% polymerization of butadiene under comparable conditions.

Effect of the β -Methylstyrene and Triphenylmethane on the Polymerization of Styrene by an Alfin Catalyst.—With 4.1 milliequivalents of an Alfin catalyst, which had a ratio of approximately one mole of allylsodium to one mole of sodium isopropoxide, the conversion of styrene to polystyrene was 58% when tested by bottle polymerization for 30 minutes. The intrinsic viscosity was 1.77. In a parallel experiment with an aliquot of this catalyst which had allowed one equivalent of β -methylstyrene per allylsodium to age for 57 days, the conversion was 13% and the viscosity was 0.65. When two equivalents of the methylstyrene had been allowed to age for 39 days with the catalyst, the conversion fell to about 13% also.

A similar series of tests were carried out on the effect of triphenylmethane which is attacked more easily than β -methylstyrene. A half equivalent of the triphenylmethane cut the polymerization from 65% in 30 minutes in the control to 2% in 60 minutes and caused the intrinsic viscosity to fall from 1.62 to 0.26. When 1 equivalent of triphenylmethane was added just prior to use in polymerization, the yield fell to 47%. Four equivalents of triphenylmethane were then tried in a similar way. The yield fell to 33% and the polymer had a viscosity of 1.08.

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