was added. The mixture was heated at 80–90° for 2 hr. and the reaction product was cautiously oxidized at 0° by bubbling in oxygen while stirring, until no more oxygen was absorbed. The oxidized product was hydrolyzed with water and the gelatinous mass thus obtained was extracted many times by ether. The ethereal solution, dried over sodium sulfate, was distilled to eliminate the ether and then rectified to eliminate most of the isobutyl alcohol present (resulting from the oxidation of the $\rangle$Al-CH$_2$-CH(CH$_3$)$_2$ groups). The residue of the rectification was distilled and a fraction 99–100° (100 mm.), n^{20}_D 1.4170 (0.8713 g.) was separated which was practically pure 3-methyl-1-pentanol containing small quantities of 4-methyl-1-pentanol. This fraction solution has $[\alpha]^{25}_D$ +7.65° in petroleum ether. A solution of the same concentration of the starting 3-methyl-1-pentanol in petroleum ether has $[\alpha]^{25}_D$ +8.35°.

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PISA, ITALY

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Reduction of Polymers Using Complex Metal Hydrides

H. L. COHEN AND L. M. MINSK

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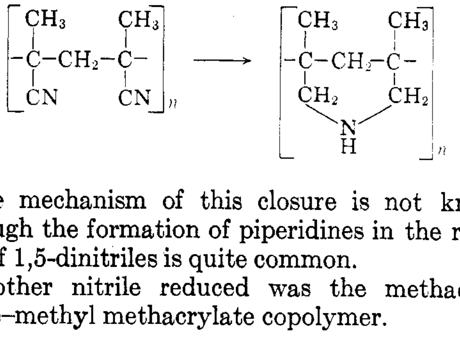
Polymeric nitriles, amides, imides, lactams, and oximes were reduced to the corresponding amines using lithium aluminum hydride. Polymeric hydrazides and hydrazones were reduced to hydrazines by the same procedure. Reduction of polymeric aldehydes and ketones gave alcohols.

Of the large number of publications that have appeared on the use of metal hydrides in reduction, only a few have been concerned with polymers. The reduction of poly(vinyl chloride) and poly(vinyl bromide) to polyethylene by lithium aluminum hydride in a hot (100°) tetrahydrofuran-decalin mixture was reported by Hahn and Muller.[1] Kern and Schulz[2] report the partial reduction of poly(acrolein oxime) by aqueous, alkaline sodium borohydride at 90°. The recent[3–5] publication of several additional papers concerned with the reduction by lithium aluminum hydride of specific polymers leads us to disclose similar, more general work which has been done at these Laboratories on the reduction of polymeric materials by complex metal hydrides. Polymers containing nitrile, amido, imido, oximino, lactam, hydrazide, hydrazone, and keto groups have been successfully reduced.

As with many other reactions of polymers, the proper choice of solvent is a major problem when reductions are carried out using complex metal hydrides. The requirements for the solvent in this case are quite stringent. Besides being a good solvent for both polymer and hydride, the medium must have a relatively high boiling point, as many reactions of polymers are exceedingly slow at ordinary temperatures. At these high temperatures, the solvent must be indefinitely stable to the hydride. Furthermore, because the addition complex formed between hydride and polymer is usually insoluble, the solvent must at least swell the complex so that reaction can go to completion.

N-Methylmorpholine met these requirements. It was also an excellent solvent for most of the reduced polymers, an advantage in that it enabled the use of a strong sodium hydroxide solution to hydrolyze the addition complex. The resulting strongly alkaline inorganic salts are insoluble in the amine, thereby simplifying isolation of the product. Tetrahydrofuran and the dimethyl ether of diethylene glycol (diglyme) were also useful on occasion.

Nitriles. The reduction of the styrene–methacrylonitrile copolymer was typical of the reduction procedures. Infrared analysis of this reduced polymer indicated the complete absence of nitrile groups. A Van Slyke nitrogen analysis indicated that about 70% of the nitrogen present was in the form of primary amino groups, while acetylation showed that the remaining 30% was in the form of secondary amino groups. As the nitrogen percentage was low, it may be assumed that ring closure had taken place, to some extent, with the loss of ammonia, giving a piperidine.



The mechanism of this closure is not known, although the formation of piperidines in the reduction of 1,5-dinitriles is quite common.

Another nitrile reduced was the methacrylonitrile–methyl methacrylate copolymer.

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[1] W. Hahn and W. Muller, *Makromol. Chem.*, 16, 71 (1955).

[2] W. Kern and R. C. Schulz, *Angew. Chem.*, 69, 153 (1957).

[3] B. G. Rånby, Abstracts of Papers, Miami Meeting of American Chemical Society, April, 1957, p. 10-S.

[4] J. Petit and B. Houel, *Compt. rend.*, 246, 1427 (1958). B. Houel, *Compt. rend.*, 246, 2488 (1958).

[5] J. A. Blanchette and J. D. Cotman, *J. Org. Chem.*, 23, 1117 (1958).

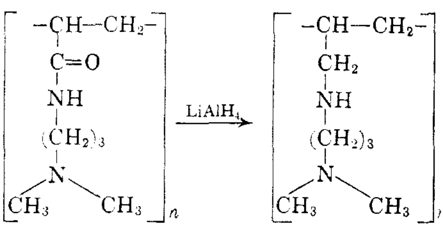
Neither poly(acrylonitrile) nor poly(methacrylonitrile) was soluble in *N*-methylmorpholine or any other useful solvent. The latter polymer was swelled by hot *N*-methylmorpholine, but attempted reduction was unsuccessful.

Attempted reduction of a styrene–fumaronitrile copolymer by using a mixture of the dimethyl ether of ethylene glycol (diglyme) and *N*-methylmorpholine as solvents was likewise unsuccessful.

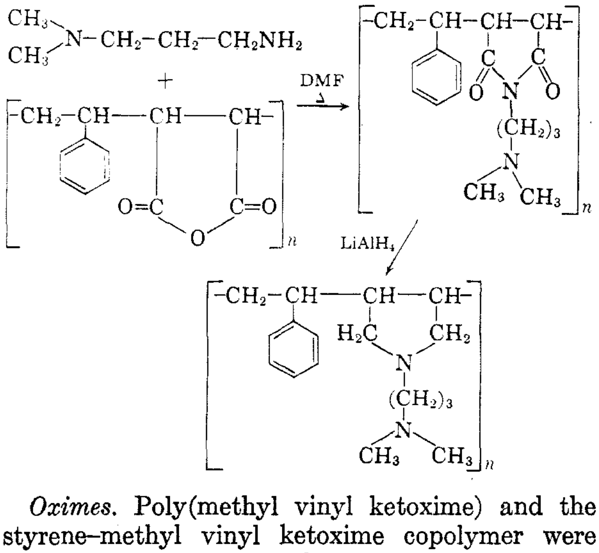
Attempts to reduce the methacrylonitrile-styrene copolymer with the sodium borohydride–aluminum chloride complex using diglyme as a solvent gave a small amount of partially reduced polymer. Most of the product was insoluble and probably crosslinked.

Diborane, likewise, gave a completely insoluble product.

Amides. Poly(*N*,*N*-dimethylacrylamide) was reduced in good yield to poly(*N*,*N*-dimethylallylamine) by lithium aluminum hydride in *N*-methylmorpholine. The resulting polymer was soluble in dilute acetic acid, methanol, and petroleum ether and was insoluble but swelled in acetone, dioxane, and dimethylformamide. Also reduced by this procedure was poly(γ - dimethylaminopropylacrylamide).



Imides. The imide produced in the reaction between γ-dimethylaminopropylamine and the styrene–maleic anhydride copolymer was reduced smoothly to the corresponding pyrrolidine polymer.

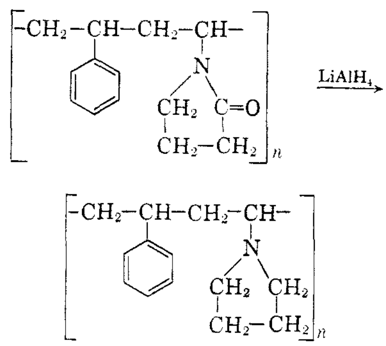


Oximes. Poly(methyl vinyl ketoxime) and the styrene–methyl vinyl ketoxime copolymer were reduced to the corresponding amines. The copolymer was reduced completely while the homopolymer contained a small amount of unreduced oxime. In both cases, a low nitrogen percentage in the product indicated piperidine formation.

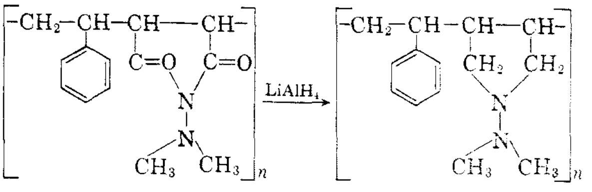
Attempted reduction of a styrene–methyl vinyl ketoxime copolymer with sodium borohydride in diglyme solution was completely unsuccessful. The starting material was recovered unchanged.

Lactams. Poly(vinylpyrrolidone) is dispersible in hot *N*-methylmorpholine although insoluble in the cold solvent. Reduction of the polymer gave a product which was initially soluble in *N*-methylmorpholine but which turned insoluble in the process of isolation and could not be purified.

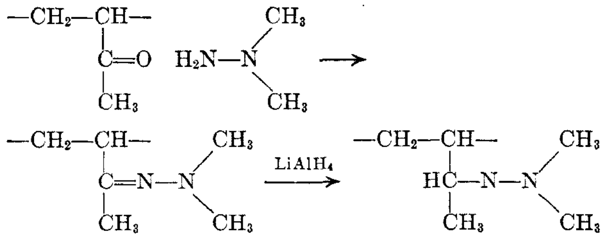
On the other hand, a styrene–vinylpyrrolidone copolymer was completely reduced by lithium aluminum hydride by the usual procedure.



Hydrazides. The reaction product between styrene–maleic anhydride copolymer and *N*,*N*-dimethylhydrazine was reduced to the corresponding substituted hydrazine by the usual procedure. It was readily soluble in dilute acetic acid while the starting material was not.



Hydrazones. The *N*,*N*-dimethylhydrazone of poly(methyl vinyl ketone) was also reduced by lithium aluminum hydride. However, the resulting polymer, initially soluble in water, became insoluble after standing for a short time. An aqueous solution gelled within 3 hr., while an aqueous acetic acid solution, though more stable than the free base, also gelled in several days.



The *N*,*N*-dimethylhydrazone of the styrene–methacrolein copolymer was completely reduced to the corresponding hydrazine with lithium aluminum

TABLE I

	Reduced Polymer or Copolymer	Method of Preparation	Analysis			*	Viscosity	**	Analysis			Percent Reduction
			C	H	N				C	H	N[a]	
I	Methacrylonitrile–styrene	Copoly	84.2	8.1	8.2	50	0.30[c]	A	84.8	9.8	6.7[a] 4.8[b]	100
II	Methacrylonitrile–methyl methacrylate	Copoly	65.2	7.9	8.8	50	0.42[c]	B	68.8	11.8	8.6	100
III	*N*,*N*-Dimethylacrylamide	Poly	61.2	9.7	13.8	100	0.41[c]	C	70.3	12.7	16.4[f]	100
IV	γ-Dimethylaminopropylacrylamide	Poly	60.8	10.2	17.6	100	0.11[d]	C	68.1	12.7	18.6	100
V	γ-Dimethylaminopropylmaleimide–styrene	Der	70.6	7.8	9.4	48		A	78.6	10.1	10.3	100
VI	Methyl vinyl ketoxime	Der	54.6	8.1	15.9	95		A	69.5	10.9	15.6	65
								E	54.7	8.0	15.7	0
VII	Methyl vinyl ketoxime–styrene	Der	77.5	8.3	7.2	50		A	84.0	9.0	7.1	100
VIII	Vinylpyrrolidone	Poly	64.3	8.5	12.0	94	0.34[e]	D	63.5	10.3	11.3	
IX	Vinylpyrrolidone–styrene	Copoly	88.5	8.1	2.1	14	0.6[c]	A	89.8	8.8	2.0	100
X	γ-Dimethylaminomaleimide–styrene	Der	68.2	6.9	9.7	42		D	77.1	9.1	10.5	100
XI	Methyl vinyl ketone *N*,*N*-dimethylhydrazone	Der	65.4	10.4	20.9	85		A	65.7	11.1	20.3	60
XII	Methacrolein–styrene *N*,*N*-dimethylhydrazone	Der	78.3	9.4	11.4	42		A	79.7	10.1	9.0	100
XIII	Methyl vinyl ketone	Poly	68.3	8.5		100	0.43[c]	A&B	64.0	10.8[g]		95
								E	64.1	9.6		50
XIV	Methacrolein–styrene	Copoly	82.5	8.4		50	0.1[c]	E	81.4	8.9		95
XV	Methyl vinyl ketone–styrene	Copoly	82.6	8.7		50	0.21[c]	A	81.4	9.4[h]		100
								E	82.5	8.7[i]		75

* Percent reducible compound. ** Method of reduction.

[a] Dumas unless otherwise noted. [b] Van Slyke. [c] In acetone. [d] In methanol. [e] In water. [f] Methyl *p*-toluenesulfonate. *Anal.* C, 57.8; H, 7.8; N, 5.2; S, 11.6. [g] Acetate. *Anal.* C,6 2.8; H, 8.6; Acetyl, 37.4. [h] Viscosity, 0.19 (propanol). [i] Viscosity 0.23 (propanol).

hydride. It was soluble and stable in dilute acetic acid solution.

Carbonyl Compounds. Simple organic carbonyl compounds are reduced completely to the corresponding hydroxyl compounds with both sodium borohydride and lithium aluminum hydride. Polymeric carbonyl compounds are only partially reduced (40–60%) by sodium borohydride in diglyme at 60–90°. On the other hand, the more powerful lithium aluminum hydride in *N*-methylmorpholine at 115° effected complete reduction.

Poly(methyl vinyl ketone) and the styrene–methacrolein and styrene–methyl vinyl ketone copolymers were reduced by the method described.

The product from the lithium aluminum hydride reduction of poly(methyl vinyl ketone) exhibited inverse solubility in water.

EXPERIMENTAL

Starting Materials. *N*-Methylmorpholine and diglyme were purified by refluxing over sodium, then fractionating through a helix-packed column.

Lithium aluminum hydride (Metal Hydrides, Inc.) and sodium borohydride were used as purchased.

The analytical data for the intermediate polymers are given in the table. Those marked "poly" and "copoly" were obtained by either bulk or solution polymerization. Of the derived polymers (marked "Der"), the preparation of the *N*,*N*-dimethylaminomaleimide–styrene copolymer (X) was similar to that of the *N*,*N*-dimethylaminopropylmaleimide–styrene copolymer (V) described here. Poly(methyl vinyl ketoxime) (VI) and the methyl vinyl ketoxime–styrene copolymer (VII) were made by the method of Marvel.[6] The hydrazones XI and XII were made by tumbling a solution of the intermediate carbonyl polymers in *N*,*N*-dimethylhydrazine overnight.

Reductions. To conserve printing space, only the reduction procedure for the styrene–methacrylonitrile copolymer with lithium aluminum hydride (Method A) and of poly(methyl vinyl ketone) with sodium borohydride (Method E) will be described in detail.

The properties of some of the other polymers necessitated changes in the basic procedures. The methyl methacrylate–methacrylonitrile copolymer, insoluble in *N*-methylmorpholine, was dissolved in tetrahydrofuran and then diluted with *N*-methylmorpholine. Poly(methyl vinyl ketoxime) and

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[6] C. S. Marvel and C. L. Levesque, *J. Am. Chem. Soc.*, **60**, 280 (1938).

poly(vinyl pyrrolidone) were insoluble in the cold, but dissolved and melted respectively in boiling *N*-methylmorpholine to give reducible mixtures.

In those cases where the reduced polymer, after hydrolysis, was insoluble in *N*-methylmorpholine and precipitated from the solution, it was isolated by extraction of the filtered solids with another organic solvent, usually methanol, followed by precipitation or evaporation (Method B). Those reduced polymers not precipitated because of solubility in the common organic solvents were purified by repeated solution and evaporation of a suitable solvent (Method C). Reduced polymers insoluble in the common organic solvents were dissolved in dilute acetic acid, dialyzed, and isolated by evaporation of the solvent or precipitation with sodium hydroxide solution (Method D).

Analytical values given in the table are the averages of at least two determinations, each of which agreed within 0.4 unit. Since the differences in theoretical hydrogen percentages for the pure, unreduced, and reduced polymers are sometimes quite small and since secondary reactions further complicated the situation, the percentage reduction given in the table is sometimes only a rough estimate.

Reduction of the Styrene–Methacrylonitrile Copolymer. A solution of 25 g. (0.145 mole) of this interpolymer in 250 ml. of *N*-methylmorpholine was added, with stirring, over a period of 2 hr. to a suspension of 9.5 g. (0.25 mole) of lithium aluminum hydride in 500 ml. of *N*-methylmorpholine under nitrogen kept at 100–110°. After addition was over, the mixture was stirred for an additional 4 hr. under reflux. After the mixture had cooled, 20 ml. of water, 12 ml. of 25% sodium hydroxide solution, then 20 ml. more water were added dropwise, giving a granular precipitate. After the mixture had been stirred for an additional 3 hr., the precipitate was filtered and discarded. The filtrate was then evaporated down to 100 ml. on a steam-bath under vacuum. On pouring the residual solution into water, the reduced polymer precipitated as a friable powder. It was washed several times with water, filtered, and vacuum-dried. Yield, 19 g. of a white powder, soluble in methanol, dimethylformamide, and dilute acetic acid. It swelled but did not dissolve in acetone.

Anal. Calcd. for completely reduced copolymer: C, 82.8; H, 9.7; N, 8.0. Found: C, 84.8, 84.7; H, 9.9, 9.7; N (Dumas), 6.7, 6.7; N (Van Slyke), 4.8, 4.7.

Acetylation of Styrene–Methallylamine Copolymer. A solution of 5 g. of the styrene–methallylamine copolymer in 100 ml. of pyridine was treated with 50 ml. of acetic anhydride. The mixture was heated for 1 hr. on a steam-bath, then precipitated in water. It was dissolved in acetone and reprecipitated in water.

Anal. Calcd. for complete acetylation of reduced copolymer: acetyl, 16.7. Found: acetyl, 16.4, 16.6.

Preparation of the γ-Dimethylaminopropylmaleimide–Styrene Copolymer. Preparation of the Copolymer. A solution of 20.2 g. (0.1 mole) of a styrene–maleic anhydride copolymer (Monsanto Lytron 810) in 200 ml. of dimethylformamide was added dropwise to a stirred, heated (100°) solution of 14 g. (0.14 mole) of γ-dimethylaminopropylamine in 200 ml. of dimethylformamide over a period of 1.5 hr. The temperature was then raised gradually until 100 ml. of solvent had distilled off. During this time, the distillate temperature rose to 152°. The solution was then cooled and poured into water, giving a friable precipitate. This was washed with water, then vacuum-dried, giving 23 g. of a white, voluminous powder which was soluble in acetone and dilute acetic acid.

Preparation of the N,N-Dimethylhydrazone of Poly(methyl Vinyl Ketone). A mixture of 10 g. of poly(methyl vinyl ketone), 100 ml. of *N*,*N*-dimethylhydrazine, and 2 drops of glacial acetic acid was tumbled at room temperature overnight. Complete solution resulted. The polymer was precipitated in petroleum ether, redissolved in acetone, and reprecipitated in petroleum ether, giving a soft, water-soluble solid which hardened somewhat on drying. Yield, 7 g.

Reduction of Poly(methyl Vinyl Ketone) with Sodium Borohydride. A solution of 7 g. (0.1 mole) of poly(methyl vinyl ketone) in 100 ml. of anhydrous diglyme was added dropwise to a stirred solution of 3.8 g. (0.1 mole) of sodium borohydride in 150 ml. of diglyme, kept at 55° over a period of 0.5 hr. Following addition, the mixture was kept at 65° for 3 hr., then poured into one l. of water. The product was filtered and vacuum-dried. It was dissolved in tetrahydrofuran and precipitated in ether, giving 4.5 g. of a white powder.

ROCHESTER 4, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

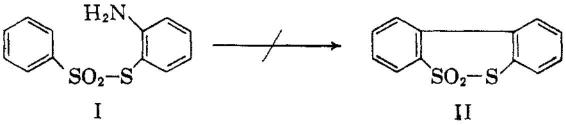
A Novel Displacement Reaction of the *N*-Nitroso Derivative of *N*-Acetyl-*o*-aminophenyl Benzenethiolsulfonate[1]

C. G. OVERBERGER, MICHAEL P. MAZZEO,[2] AND J. J. GODFREY

Received March 6, 1959

The preparation of *N*-acetyl-*o*-aminophenyl benzenethiolsulfonate is described. Decomposition of its *N*-nitroso derivative gave unexpectedly 1,2,3-benzothiadiazole and benzenesulfonic acid. A mechanism to account for this transformation is proposed.

The initial purpose of this work was to prepare unsymmetrically substituted biphenyl disulfinic acids in order to study the intramolecular reaction of the sulfinic acid groups with each other. One scheme proposed for this disulfinic acid synthesis involved preparation of unsymmetrically substituted biphenyl thiolsulfonates which could then be converted to the corresponding disulfinic acids.



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[1] (1) This is the 31st in a series of papers concerned with azo compounds; for the previous paper in this series see C. G. Overberger, George Kesslin and Pao-tung Huang, *J. Am. Chem. Soc.*, 81, 3779 (1959).

[2] (2) This paper comprises portions of dissertations submitted by Michael P. Mazzeo in partial fulfillment of the requirements for the degree of Master of Science and John J. Godfrey in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.