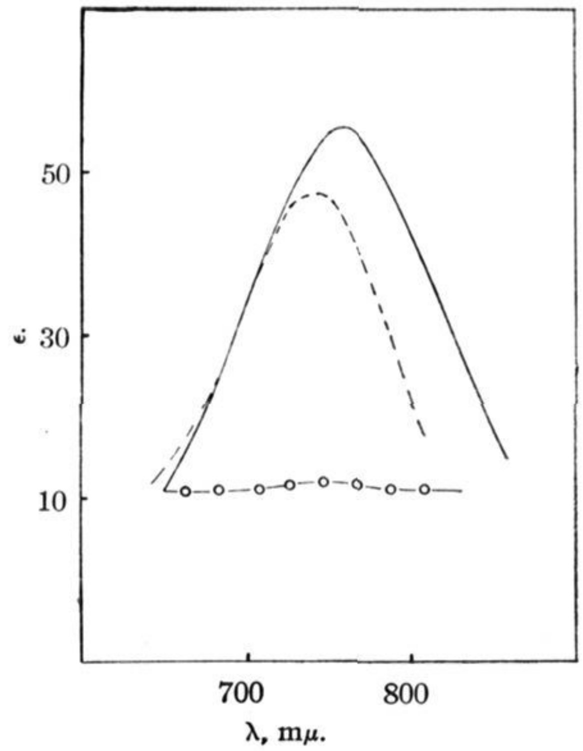

Fig. 1.——, Absorption *m*-nitrosonitrobenzene in ethyl alcohol. Photometer traces on arbitrary scale of polarized light in a crystal 25% *m*-nitrosonitrobenzene in *m*-dinitrobenzene: -------, vibrating parallel to needle axis; -O-O-, vibrating perpendicular to needle axis.

nearly parallel acicular crystals with black paint. All X-ray photographs were taken with copper radiation filtered through nickel.

Summary

m-Nitrosonitrobenzene monomer forms solid solutions in crystallographically known *m*-dinitrobenzene. The pleochroism of the solid solutions indicates that the polarization of the transition responsible for the green color of this monomer is approximately transverse to the C—N═O bonds. It is suggested that in general the insensitivity of the position of the long wave length characteristic absorption band of C-nitroso compounds to substituents elsewhere in the molecule is due to the direction of polarization.

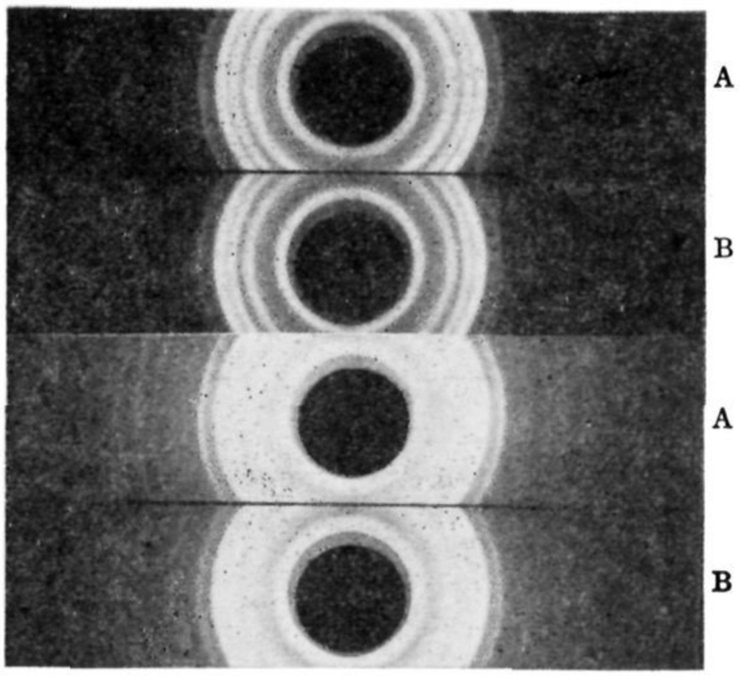

Fig. 2.—X-Ray powder photograph of A, *m*-dinitrobenzene; B, solid solution 66% *m*-nitroso–nitrobenzene, 34% *m*-dinitrobenzene (two prints of each photograph are needed to show both strong and weak lines).

ABERDEEN PROVING GROUND, MARYLAND

RECEIVED APRIL 16, 1948

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Anionic Chain Polymerization

BY RALPH G. BEAMAN[1]

The polymerization of vinyl compounds by a free-radical mechanism or by a cationic chain mechanism induced by acid catalysts is well-known. However, little attention has been paid to the theoretically possible base catalyzed polymerization which should proceed by an anionic chain mechanism.[2] The well-known polymerization of certain vinyl compounds by sodium and organoalkalies has been regarded as involving carbanion intermediates, although purely catalytic[3] and free-radical[4] mechanisms have been proposed.

That certain other basic reagents will cause polymerization has been noted in a few instances. For example, sodium ethoxide causes dimerization of ethyl crotonate,[5] sodiomalonic ester polymerizes styrene,[6] ethylmagnesium bromide as well as sodium and sodium ethoxide polymerize allyl cyanide,[7] and many bases effect polymerization of nitroölefins.[8] These reactions are either slow or give mainly dimers and trimers. In no case is there indication of very high molecular weight polymers.

Methacrylonitrile contains the highly electronegative cyano group which facilitates nucleophilic attack. In addition the compound contains no α-hydrogen atom which might give rise to chain termination by abstraction of a hydrogen

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[1] Allied Chemical and Dye Fellow, 1947–1948. Present address: E. I. du Pont de Nemours and Co., Buffalo, New York.

[2] For a discussion of the mechanisms of polymerizations see Price, "Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946.

[3] Morton and Letsinger, THIS JOURNAL, **69**, 172 (1947).

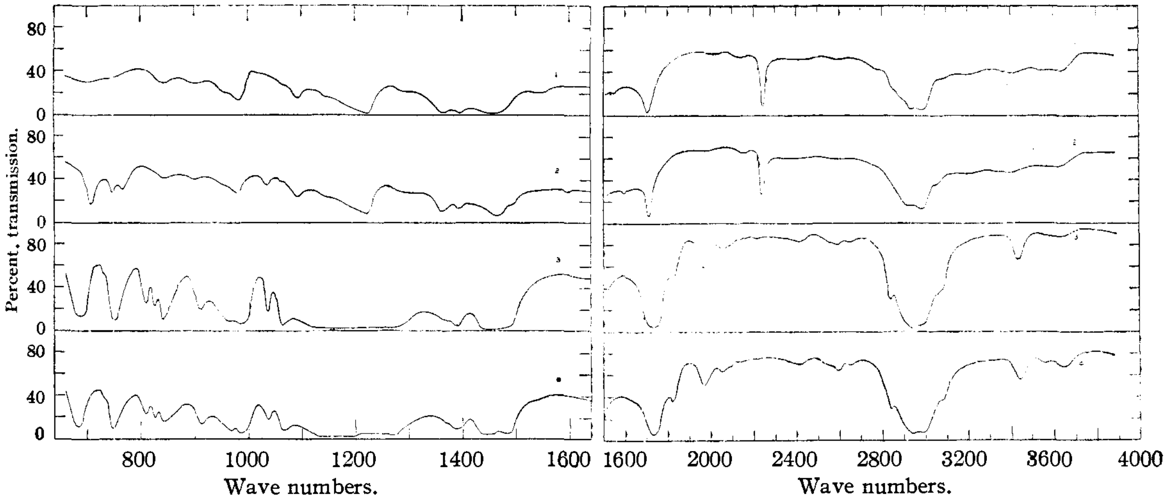
[4] Bolland, *J. Roy. Soc. London*, **178A**, 38 (1941).

[5] Pechmann, *Ber.*, **33**, [3], 3329 (1900).

[6] Hermann and Vorlander, *Chem. Zentr.*, **70**, I, 730 (1899).

[7] Bruylants and co-workers, *Bull. soc. chim. Belg.*, **32**, 317 (1923); *ibid.*, **35**, 239 (1926).

[8] See Blomquist, Tapp and Johnson, THIS JOURNAL, **67**, 1519 (1945).



Figs. 1a and 1b.—Infrared absorption spectra: 1, polymethacrylonitrile (sodium and liquid ammonia); 2, polymethacrylonitrile (triphenylmethylsodium); 3, polymethylmethacrylate (commerical "bead" sample); 4, polymethylmethacrylate (sodium and liquid ammonia).

atom from a polymer molecule by a growing chain and subsequent branching from the newly formed active center. Hence this monomer has been selected for study of the base catalyzed type of polymerization, and it has indeed been found that methacrylonitrile does polymerize with extreme rapidity even at temperatures as low as −75° when it is treated with a reagent such as RMgX, triphenylmethylsodium or sodium in liquid ammonia.

When butylmagnesium bromide or phenylmagnesium bromide in ether solution is allowed to react with methacrylonitrile a vigorous and immediate reaction occurs similar to that reported by Bruylants[7] for the reaction between allyl cyanide and ethylmagnesium bromide. The reaction proceeds in the same manner if carried out at room temperature or at −75° and if the monomer is added to the Grignard solution or *vice versa*. The polymer isolated is a light yellow solid with a molecular weight of about 8000 as estimated from viscosity measurements. Low molecular weight polymers of acrylonitrile are also obtained from reaction of that monomer with butylmagnesium bromide.

Triphenylmethylsodium causes polymerization of methacrylonitrile in much the same way as do the Grignard reagents. In this instance the molecular weight of the polymer is about 20,000.

When methacrylonitrile is added to a solution of sodium in liquid ammonia at −75°, it is immediately and quantitatively polymerized to a product of molecular weight over 100,000. Since this method is apparently a new one for carrying out polymerizations and because of the unusual nature of the reaction, the effect of this reagent on several other vinyl compounds has been investigated. Isobutylene and butadiene give no trace of polymer.[9] Styrene gives some low molecular weight polymer as expected from the work of Wooster and Ryan.[10] Vinyl acetate and ethyl acrylate yield very viscous oils. Methyl methacrylate yields a pure white solid which varies with different samples from a polymer of molecular weight 16,500 which became liquid at 165° to one of higher molecular weight more closely resembling the commercial bead polymethylmethacrylate.

The physical and chemical properties of the polymethacrylonitriles prepared by these anionic chain polymerizations are essentially identical and correspond to those reported by Kern and Fernow[11] for the polymer prepared by benzoyl peroxide catalysis. Infrared absorption spectra[12] of samples of polymethacrylonitrile prepared from the monomer by the action of sodium in liquid ammonia (curve 1, Fig. 1) and of triphenylmethylsodium (curve 2, Fig. 1) show that these two polymers are very much alike structurally. The polymer prepared from methacrylonitrile by the action of triphenylmethylsodium has extra bands at 708, 747, 768 and 1598 cm.$^{-1}$ which indicate the presence of phenyl groups. The spectra (not shown in the figure) of the polymers prepared by the action of butylmagnesium bromide and of phenylmagnesium bromide were nearly identical with curves 1 and 2 but showed additional bands at 3204 and 3360 cm.$^{-1}$ characteristic of the —NH group and at 1667 cm.$^{-1}$ characteristic of the CO group. The spectrum of the polymer prepared by the action of phenylmagnesium bromide also showed bands at 704 and 1600 cm.$^{-1}$ characteristic of the phenyl group. Presumably the amide groups present in the polymers prepared by the action of the Grignard reagents were produced by hydrolysis of nitrile groups during purification of

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(9) For reaction of isoprene with sodium in liquid ammonia see Midgley and Henne, THIS JOURNAL, **51**, 1293 (1929).

(10) Wooster and Ryan, THIS JOURNAL, **56**, 1133 (1934).

(11) Kern and Fernow, *J. prakt. Chem.*, **160**, 296 (1942); (Trans.) *Rubber Chem. Tech.*, **18**, 267 (1945).

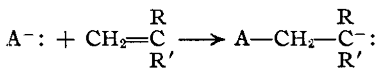
(12) The infrared absorption curves and their interpretation were kindly furnished by Mrs. J. L. Johnson.

the polymers. It is uncertain whether the phenyl groups are present as end groups or have become attached to the chain through reaction of phenylmagnesium bromide and triphenylmethylsodium with nitrile groups in the polymer. The polymethacrylonitrile polymers were deposited as solid films on rock salt plates from acetone solutions and the strong carbonyl absorption at 1715 cm.$^{-1}$ (curves 1 and 2) as well as some of the other bands in the lower frequency regions are due to solvent retained in the films.

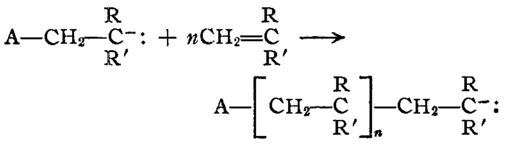
Infrared absorption spectra of a commercial bead polymethylmethacrylate (curve 3, Fig. 1) and of a polymethylmethacrylate prepared by the action of sodium in liquid ammonia on the monomer (curve 4, Fig. 1) show identical bands. These polymers were deposited on the rock salt plates from benzene solution and some bands due to retained benzene are to be seen in these curves.

The ionic nature of the Grignard reagent and of triphenylmethylsodium makes it seem highly unlikely that these reagents react by homolytic cleavage to yield free radicals especially in the presence of the highly polar methacrylonitrile. The immediate and quantitative polymerization brought about by sodium in liquid ammonia offers more direct evidence for an anionic mechanism. There is a striking similarity between this reaction and the polymerization of isobutylene[13] by boron fluoride which is known to proceed by an ionic mechanism. Further, if the reaction were free-radical in nature one would expect that butadiene and styrene would be polymerized readily. The failure to obtain any polymer with butadiene and only some low molecular weight polymers with styrene is understandable from the point of view of an anionic chain polymerization because of the relatively weak electronegative character of a vinyl or phenyl group. Further evidence that the reaction is not free-radical is that the presence of the sodium salt of hydroquinone neither retarded nor reduced the yield in the extremely rapid polymerization of methyl methacrylate.

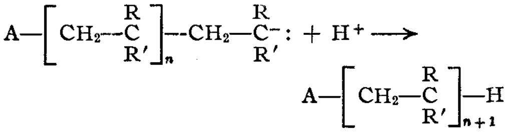
It is proposed that base-induced polymerization occurs as follows:



$$A^-: + CH_2{=}\overset{R}{\underset{R'}{C}} \longrightarrow A{-}CH_2{-}\overset{R}{\underset{R'}{C}}{}^-: \qquad (1)$$



$$A{-}CH_2{-}\overset{R}{\underset{R'}{C}}{}^-: + nCH_2{=}\overset{R}{\underset{R'}{C}} \longrightarrow A{-}\left[CH_2{-}\overset{R}{\underset{R'}{C}}\right]_n{-}CH_2{-}\overset{R}{\underset{R'}{C}}{}^-: \qquad (2)$$



$$A{-}\left[CH_2{-}\overset{R}{\underset{R'}{C}}\right]_n{-}CH_2{-}\overset{R}{\underset{R'}{C}}{}^-: + H^+ \longrightarrow A{-}\left[CH_2{-}\overset{R}{\underset{R'}{C}}\right]_{n+1}{-}H \qquad (3)$$

in which A^-: is the initiating negative fragment, R is an electron-withdrawing group, and R′ is H or some other substituent. The termination reaction (3) may occur in some other manner, such as elimination of A^-:.

Experimental

Polymerization of Methacrylonitrile by Grignard Reagents.—In a typical experiment the Grignard reagent was prepared in the usual manner from 45.7 g. (${}^1/_3$ mole) of *n*-butyl bromide and 8.1 g. (${}^1/_3$ mole) of magnesium turnings. An ether solution of 132 g. (*ca.* 2 moles) of methacrylonitrile was added slowly to the stirred solution held at 0°. Reaction proceeded vigorously with the formation of a green precipitate. The mixture was hydrolyzed by pouring into a cold solution of 23 g. of ammonium chloride. The green solid became orange upon exposure to air. The solid, which contained some magnesium particles, was collected on a Buchner funnel and washed with water and ether. The crude air-dried product weighed 32 g. The polymer was purified by solution in acetone and precipitation with petroleum ether and by solution in nitromethane and precipitation with ether.

Reaction in a nitrogen atmosphere and with reverse addition proceeded in the same manner. The most soluble fraction had $(\eta) = 0.03$ and the least soluble fraction $(\eta) = 0.13$. The use of one equivalent of methacrylonitrile, 22.4 g. (${}^1/_3$ mole), and at −75° with the same amount of Grignard reagent gave 17.5 g. of crude polymer of the same general properties. One-third equivalent of phenylmagnesium bromide yielded 62 g. of crude polymer ($(\eta) = 0.06$) from 67 g. of monomer.

Polymerization of Methacrylonitrile with Triphenylmethylsodium.—Triphenylmethylsodium was prepared by the method of "Organic Syntheses"[14] from 4.5 g. of triphenylmethyl chloride and an amalgam of 0.818 g. of sodium in 82 g. of mercury. This was allowed to react with 15 g. of methacrylonitrile in ether solution at −75°. A dark green precipitate was formed. Water was added to decompose any sodium alkyls and the solid was collected on a Buchner funnel and washed with water, petroleum ether and ether. The air-dried product weighed 11.9 g. $(\eta) = 0.22$.

Polymerization with Sodium in Liquid Ammonia.—Most of the reactions were carried out in a nitrogen atmosphere, although this precaution was probably unnecessary since no difficulty was encountered in a run with methyl methacrylate in air. Four-tenths of a gram of sodium was dissolved in 100 cc. of liquid ammonia contained in a 500-cc. flask immersed in a Dry Ice-bath and cooled to about −75°. From 15 to 20 g. of monomer was then introduced. The blue color was discharged at once, then 2 g. of ammonium chloride was added to decompose any sodium compounds, and the ammonia allowed to evaporate. The polymers produced were washed with water to extract inorganic salts. The yields were quantitative for methacrylonitrile [$(\eta) = 0.83$] acrylonitrile [$(\eta) = 0.20$] and methyl methacrylate [$(\eta) = 0.08$, 0.14 and 0.20 for different samples].

Relative viscosities were determined at 25.5° (${}^1/_6$ g. per 100 cc.). Polymethacrylonitriles gave identical results in cyclohexanone, nitromethane, and dimethylformamide. Viscosities of polymethyl methacrylate were determined in benzene.

Acknowledgment.—The writer is indebted to Dr. C. S. Marvel of the University of Illinois for suggestions and criticisms and to the Allied Chemical and Dye Corporation for a fellowship.

Summary

Polymerization of methacrylonitrile by means of butylmagnesium bromide, phenylmagnesium bromide, triphenylmethylsodium, and sodium in liquid ammonia has been effected.

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[13] See Thomas, Sparks and Frolich, This Journal, 62, 276 (1940).

[14] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

Polymerization by sodium dissolved in liquid ammonia, a new method for polymerization to give immediate and complete reaction at −75°, is described.

Evidence is presented to show that these polymerizations proceed by an anionic chain mechanism.

URBANA, ILLINOIS RECEIVED APRIL 1, 1948

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Effect of Ratio of Catalyst and Other Factors upon the Rate of Hydrogenation

BY HOMER ADKINS AND HARRY R. BILLICA[1]

The rate of a catalytic hydrogenation is particularly dependent upon the temperature, pressure of hydrogen and the amount and ratio of catalyst to hydrogen acceptor. The rate and even the possibility[2] of hydrogenation of α-amino and hydroxy esters over Raney nickel to the corresponding amino alcohols or glycols is so much influenced by these factors that a rather extensive study of the hydrogenation of ethyl piperidinoacetate and ethyl lactate to 2-piperidino-1-ethanol and 1,2-propanediol has been made. Some of the more significant results are recorded in Figs. 1–4 inclusive.

The rate of reaction of the esters was followed by recording the drop in pressure as the hydrogenations proceeded. The times recorded in the figures are for hydrogenations 75% complete, since these values could be more accurately observed than those for complete reaction. The relative effect of the variables is much the same irrespective of whether the comparison is based upon hydrogenations 50, 75 or 100% complete.

The effect of variations of temperature, pressure and amount of catalyst is quite similar for ethyl piperidinoacetate and ethyl lactate if the latter contains a little triethylamine. However, the slopes of the lines marked I in Figs. 1, 2 and 3 for pure ethyl lactate are quite different from the curves marked II, which are for the corresponding reaction mixtures containing triethylamine.

The rate of hydrogenation increased rather rapidly with temperature (Fig. 1) but the increase

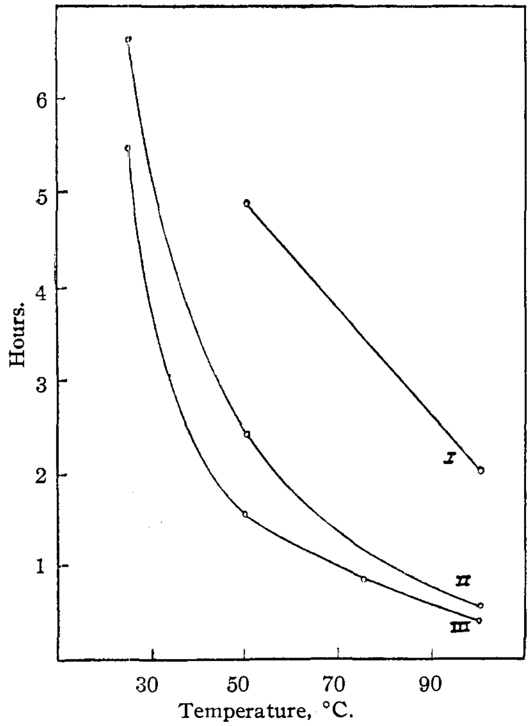

Fig. 1.—Effect of temperature in the hydrogenation of esters at 5000 p. s. i. with 15 g. of W-6 Raney nickel in 35 ml. of ethanol: I, 10 g. of ethyl lactate; II, 10 g. of ethyl lactate and 1.0 ml. of triethylamine: III, 10 g. of ethyl piperidinoacetate.

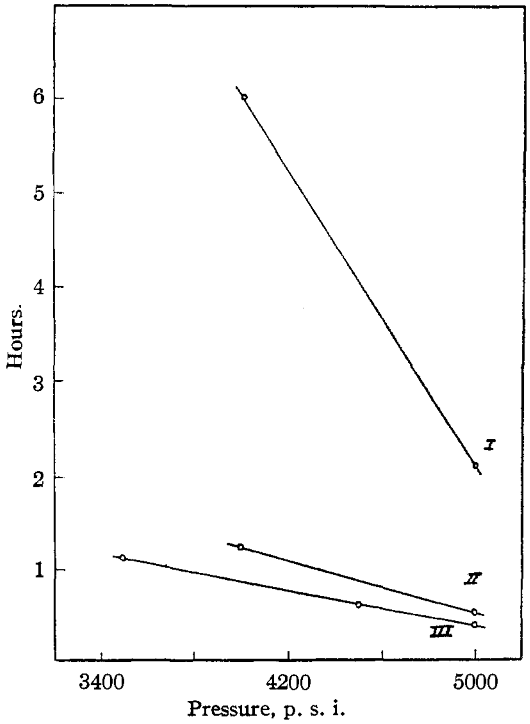

Fig. 2.—Effect of pressure of hydrogen on the hydrogenation of esters at 100° with 15 g. of W-6 Raney nickel in 35 ml. of ethanol: I, 10 g. of ethyl lactate; II, 10 g. of ethyl lactate and 1.0 ml. of triethylamine; III, 10 g. of ethyl piperidinoacetate.

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[1] Monsanto Chemical Co. Fellow in 1946 and 1947.

[2] Adkins and Billica, THIS JOURNAL, 70, 3121 (1948).