189. *Alkoxides as Initiators of Anionic Polymerisation of Vinyl Monomers. Part I. Polymerisation of Acrylonitrile by Use of Sodium Alkoxides.**

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Acrylonitrile was polymerised by various sodium alkoxide catalysts at low temperature in a non-polar medium. Factors and conditions of polymerisation were studied. The relative reactivity of the catalysts followed the acidity of the parent alcohol.

The most common basic catalysts for the anionic polymerisation of vinyl monomers reported include organometallic compounds such as Grignard reagents,[1] alkali-metal alkyls,[2] alkali metals,[3] and amides of alkali metals in liquid ammonia.[1,4] Only few instances are given of the use of alkali-metal alkoxides. Ethyl crotonate [5] and allyl cyanide [6] are polymerised by sodium ethoxide and the polymerisation of acrylonitrile by sodium methoxide has been mentioned.[7]

The anionic polymerisation of vinyl monomers having electronegative groups attached to the double bond depends on the basic strength of the catalyst. Sodium alkoxides being strongly ionic were found to be very effective for the polymerisation of acrylonitrile initiated by alkoxide anions. These alkoxides have different basic strengths depending on the acidity of the hydroxyl-hydrogen atom of the alcohol. The more acidic alcohols give less basic alkoxides and therefore weaker catalysts.

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* For a preliminary account of some of this work, see *Proc. Chem. Soc.*, 1958, 255.

[1] Beaman, *J. Amer. Chem. Soc.*, 1948, **70**, 3115.

[2] Hsieh and Tobolsky, *J. Polymer Sci.*, 1957, **25**, 245; Morita and Tobolsky, *J. Amer. Chem. Soc.*, 1957, **79**, 5853; Zilkha, Albeck, and Frankel, *J. Chem. Educ.*, 1958, **35**, 345.

[3] Ziegler, *Angew. Chem.*, 1938, **49**, 499.

[4] Higginson and Wooding, *J.*, 1952, 760.

[5] Pechmann, *Ber.*, 1900, **33**, 3329.

[6] Bruylants, *Bull. Soc. chim. Belg.*, 1923, **32**, 317.

[7] Bullitt, U.S.P. 2,608,554—5; *Chem. Abs.*, 1953, **47**, 1430; Schildknecht, " Polymer Processes," Interscience, New York, 1956, p. 225.

The relative acidity of the hydroxyl-hydrogen atom in alcohols depends on the chain length of the alcohol and on the position of a side chain with reference to the hydroxyl group.[8] The determining factor in the acid strength of an alcohol depends on its being primary, secondary, or tertiary owing to the inductive (+ *I*) effect of the alkyl groups, and chain length is of secondary importance. The relative acidity of various alcohols was determined by Norris and Cortese [9] from the velocity of the reaction with *p*-nitrobenzoyl chloride to be methanol > ethanol > hexan-1-ol > pentan-1-ol > butan-1-ol > propan-1-ol > benzyl alcohol > propan-2-ol > *tert.*-butyl alcohol.

From the definition of autoprotolysis constants ($K_{\text{auto}} = K_a \,.\, K_b$), decrease in the acidity of the alcohol increases K_b. Thus the less acidic alcohols yield stronger catalysts.

Acrylonitrile was polymerised at low temperature (—15°) in a non-polar medium (light petroleum). The solubility of acrylonitrile in this medium was low at this temperature and two liquid phases were formed.

The dependence of yield of polymer on the amount of catalyst was studied under otherwise constant conditions with methanolic sodium methoxide (5·3N), the catalyst being added to the polymerisation mixture. Up to a certain limit, increase in amount of catalyst increased the yield (Table 1, *A*). Similar results were obtained with ethanolic sodium ethoxide (2·5N) (Table 1, *C*). Differences in yield were found if the catalyst was added in one portion (Table 1, *A*) or at intervals (Table 1, *B*). The latter gave smaller yields, especially with small amounts of catalyst owing to the small effective amount present at the start. A threshold concentration of catalyst was needed to start polymerisation. With large amounts of catalyst, the polymerisation started in a short time and was more energetic, yielding coloured polymer.

This dependence was also investigated with use of constant quantities of alcohol (Table 2). The yield increased continuously with increase in amount of catalyst (Table 2, *A*) indicating that the lowering in yield at large amounts of catalyst (Table 1) was due to the greater amount of alcohol present in the catalyst. Use of more alcohol gave respectively lower yields (cf. Table 2, *A* and *B*).

TABLE 1. *Dependence of polymerisation yield on amount of catalyst.*

([Alcohol] not kept constant.)

A. *Experimental conditions*: Methanolic solution of sodium methoxide (5·3N) was added in one portion dropwise from a pipette to cooled acrylonitrile (40 ml.)–light petroleum (b. p. 40—60°; 75 ml.). Polymerisation temperature —15°, time 120 min.

Catalyst (ml.)	1	2	3	5	6	10	15
Polymer (g.)	0	8	13·5	16	21·5	23	15·5

B. *Experimental conditions*: As in *A* except that the catalyst was added in 4 portions at intervals of 30 min.

Catalyst (ml.)	2	4	5	6	8	10	15
Polymer (g.)	0	11·5	13·5	15·5	20·5	22·5	17·5

C. *Experimental conditions*: As in *A*; ethanolic sodium ethoxide (2·5N) used as catalyst.

Catalyst (ml.)	3	5	8	10	15	20
Polymer (g.)	3·5	13	17·5	20·5	19	15·5
Induction period (min.)	16	4	4	4	3	2

Under otherwise constant conditions, there was a continuous increase in yield with time. However most of the polymerisation was over after 90 min.; longer polymerisation time led to very small increase in yield. Thus increase in the polymerisation time from 2 to 4·5 hr. gave a 6% increase in yield while that from 30 min. to 60 min. caused about 150% increase in yield (Table 3).

The order of addition of reactants was important. Comparing the experimental conditions of Table 1 and Table 3, we see that there are great changes in yield. Addition

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[8] McEwen, *J. Amer. Chem. Soc.*, 1936, **58**, 1124; Norris and Ashdown, *ibid.*, 1925, **47**, 837.

[9] Norris and Cortese, *J. Amer. Chem. Soc.*, 1927, **49**, 2640.

TABLE 2. *Dependence of polymerisation yield on amount of catalyst.*

([Alcohol] kept constant.)

A. Experimental conditions: Methanolic sodium methoxide (5·86N) was diluted with methanol to 10 ml. and added in one portion to the polymerisation mixture prepared as in Table 1. Polymerisation temp. −15°, time 90 min.

Catalyst (5·86N) (ml.)	1	2	3	4	5	7
Concn. of catalyst after diln. (N)	0·586	1·17	1·76	2·34	2·93	4·1
Induction period (min.)	—	25	8	2	2	0
Yield (g.)	0	10·5	18	18	18·5	21·5 *

* Polymerisation was very energetic and a coloured polymer (brown-red) was obtained. Greater amounts of catalyst gave still more energetic reactions.

B. Experimental conditions: As in *A*, the catalyst being diluted with methanol to 15 ml.

Catalyst (5·86N) (ml.)	2	3	5	7
Concn. of catalyst after diln. (N)	0·78	1·17	1·95	2·73
Induction period (min.)	64	36	20	1·5
Yield (g.)	9	13	14	12

TABLE 3. *Dependence of yield on polymerisation time.*

Experimental conditions: Methanolic sodium methoxide (5 ml., 5·3N) was added from a pipette in one portion to light petroleum (b. p. 40—60°; 75 ml.) cooled to −15°, and immediately followed by acrylonitrile (40 ml.). Polymerisation temp. −15°.

Time (hr.) *	0·5	1	1·5	2	2·5	3·5	4·5
Polymer (g.)	7	17·5	23	24·5	24·5	25	26

* Induction period in all experiments was about 5 min.

of the monomer to the catalyst gave greater yield than the reverse order [cf. Table 3 with Table 1 (with 5 ml. of catalyst) where 24·5 g. and 16 g. polymer were obtained, respectively].

The dependence of yield on the quantity of monomer was investigated under constant conditions (Table 4); it increased with monomer up to a limit and then decreased. It is noteworthy that use of small amounts of monomer, thus having a proportionally high concentration of catalyst, gave relatively low yields. Large quantities of monomer led to long induction periods (Table 4).

TABLE 4. *Dependence of polymerisation yield on quantity of monomer.*

Experimental conditions: Methanolic sodium methoxide (5 ml., 5·35N) was added from a pipette to cooled light petroleum (b. p. 40—60°; 75 ml.) and stirred for 5 min.; acrylonitrile was then added. Polymerisation temp. −15°, time 90 min.

Monomer (ml.)	10	20	30	40	50	60 *
Yield (g.)	5·2	11·5	18·5	26·5	24	27·5
Yield (%)	65	72	78	82	60	57

* Induction period 50 min.

Dilution of the monomer was necessary for controllable polymerisation. Addition of catalyst to undiluted monomer even at low temperatures gave violent reactions yielding red low polymers. The ratio of the amount of light petroleum to monomer affected the yield (Table 5). An optimal range of ratios was found.

TABLE 5. *Dependence of yield on amount of light petroleum.*

Experimental conditions: Methanolic sodium methoxide (5 ml.; 5·3N) was added to a cooled mixture of acrylonitrile (40 ml.) and light petroleum (b. p. 40—60°). Polymerisation temp. −15°, time 1 hr.

Light petroleum (ml.)	50	100	150
Yield (g.)	12 *	17	14·5
Induction period (min.)	8	14	13

* The polymer obtained was lightly coloured.

Temperature was important. Experiments with sodium methoxide under the conditions of Table 1 showed that below about −30° to −40° no polymerisation occurred while temperatures higher than about −5° to 0° led to uncontrolled polymerisation yielding coloured sticky low polymers.

Using solid sodium methoxide (Matheson, U.S.A.) under otherwise constant conditions (Table 6), we obtained very low yields, showing the great difference in the catalytic reactivity as compared with methanolic sodium methoxide. However, addition of methanol to a stirred suspension of solid sodium methoxide in light petroleum followed by addition of monomer gave very high yields (Table 6). The low yields obtained with solid sodium methoxide seem to be due to the surface area of the catalyst and the presence of alcohol. The latter has a solvent effect on the solid sodium methoxide, and a catalyst-activating effect which will be considered later. Precipitation of the catalyst from solution by light petroleum gave particles of much greater surface area than that of the solid sodium methoxide.

TABLE 6. *Polymerisation by solid sodium methoxide.*

Experimental conditions: Solid sodium methoxide (Matheson, U.S.A.) was added to cooled light petroleum (b. p. 40—60°; 75 ml.) and stirred for 5 min. Acrylonitrile (40 ml.) was then added. Polymerisation temp. −15°, time 2 hr.

Catalyst (g.)	1·4	2·25	2·81	4·22
Equivalence to 5·2N methanolic solution (ml.)	5	8	10	15
Yield (g.)	1 *	2·5	3 †	5

* This run, stopped after 3·5, hr. gave 2 g. polymer.

† Experiment carried out with addition of 10 ml. of methanol to the suspension of the solid sodium methoxide in light petroleum. This was stirred for 5 min. and then monomer added. The yield was 20 g. of polymer.

The amount of alcohol had a marked effect on the polymerisation; further experiments (Table 7) with the same amount of catalyst and various amounts of alcohol showed that the yield was greatly affected. Up to a limit, addition of alcohol increased the yield, after which a sharp drop was noticed; this shows the catalyst-activating effect and the inactivating polar effect of the alcohol. With more acidic alcohols the latter effect is more pronouned.

Comparable experiments with sodium alkoxides dissolved in the parent alcohol showed (Table 8) good agreement with the order of the basic strength of alkoxides. The strongly basic alkoxides worked even at relatively low concentrations and gave very high yields in a short time. The induction period with strong catalysts was very short. With sodium allyloxide in allyl alcohol, no polymerisation occurred: this may be due to the high acidity of allyl alcohol as shown by its strong reaction with sodium. Under basic conditions, the inductive effect (− *I*) of the double bond would dominate the resonance effect (the anionotropy of the hydroxyl group) and so enhance the acidity of the hydrogen.

TABLE 7. *Effect of alcohol on the polymerisation.*

A. Experimental conditions: A constant quantity of methanolic sodium methoxide (3 ml., 5·86N) was diluted with the required quantity of methanol and added in one portion to a cooled mixture of light petroleum (b. p. 40—60°; 75 ml.) and acrylonitrile (40 ml.); polymerisation temp. −15°, time 90 min.

Methanol added to catalyst (ml.)	0	5	7	12	17
Concn. of catalyst in methanol (N)	5·86	2·19	1·76	1·17	0·88
Yield (g.)	15	19·5	19	13	5·5
Induction period (min.)	8	8	7·5	34	50

B. Experimental conditions: Methanolic sodium methoxide (5 ml.; 5·3N) was added to a cooled solution of methyl alcohol and light petroleum (b. p. 40—60°). Catalyst, stirred for 5 min. with monomer (40 ml.), was added in one portion from a pipette; polymerisation temp. −15°, time 90 min.

Added methanol (ml.)	0	10	25
Light petroleum (ml.)	75	65	50
Yield (g.)	26	13 *	0 †

* Induction period 15 min.

† Even at room temperature no polymerisation occurred.

TABLE 8. *Comparison of the relative reactivity of various alkoxides in the polymerisation of acrylonitrile.*

Experimental conditions: Sodium alkoxide solutions dissolved in the derived alcohol (2·5N) were added to a cooled mixture of light petroleum (b. p. 40—60°; 75 ml.) and acrylonitrile (40 ml.). Polymerisation temp. —15°.

	Catalyst 3 ml., time 60 min.		Catalyst 5 ml., time 30 min.	
Alkoxide	Yield (g.)	Induction period (min.)	Yield (g.)	Induction period (min.)
Methoxide	0	—	0[a][b]	—
Ethoxide	2·5	16	6·5	8
n-Propoxide	0·5	—	7	4
*iso*Propoxide	—	—	explosive polym.[c]	0
Allyloxide	0	—	0[d]	—
n-Butoxide	5·5	4	explosive polym.[c]	0
n-Pentyloxide	2·5	4	14·5[e]	4
Benzyloxide	—	—	10·5[f]	3

[a] The induction period was more than 30 min. This experiment carried out for 2 hr. gave 14 g. of polymer. [b] Use of methoxide catalyst (10 ml.) gave 19·5 g. of polymer after 2 hr. [c] In these " explosive reactions " the polymerisation is very fast and goes out of control. The polymer, as fine particles, and reaction mixture burst out violently from the apparatus; otherwise the polymerisation would have been quantitative in a few minutes. [d] Even sodium allyloxide in allyl alcohol (10 ml.) gave no polymerisation after 2 hr. [e] Using sodium *n*-pentyl oxide catalyst (10 ml.) gave a rather " explosive polymerisation " and part of the polymerisation mixture evaporated; yield 20·5 g. after 5 min. [f] Use of sodium benzyloxide catalyst (10 ml.) gave an " explosive polymerisation."

Preliminary experiments on the specific activating effect of alcohol in the anionic polymerisation of vinyl monomers were carried out. Use of catalyst solutions prepared from sodium alkoxides dissolved in different alcohols of various acidities gave very important results. Small additions of relatively weakly or strongly acidic alcohols, such as phenol, allyl alcohol, butan-1-ol, propan-2-ol and *tert.*-butyl alcohol to methanolic sodium methoxide increased strongly the reactivity of the catalyst (Table 9). For example, the catalyst prepared by addition of propan-2-ol (1 ml.) to methanolic sodium methoxide (3 ml., 5·86N) gave a violently explosive polymerisation after 45 sec. Even weak catalysts such as sodium allyloxide show great reactivity on addition of another alcohol such as methanol. Whereas sodium allyloxide in allyl alcohol gave no polymerisation, its methanolic solution was a strong catalyst (Table 9).

TABLE 9. *Effect of addition of alcohols to methanolic sodium methoxide catalyst.*

Experimental conditions: A solution of methanolic sodium methoxide (3 ml., 5·86N) in various amounts of different alcohols was added in one portion to a cooled mixture of acrylonitrile (40 ml.) and light petroleum (b. p. 40—60°; 75 ml.); reaction temperature —15°.

Added alcohol	Added alcohol (ml.)	Yield (g.)	Time of polymn. (min.)	Induction period (min.)
—	—	2·5	30	—
Allyl	1	8	5	1·5
Allyl	2	explosive	5	4
Phenol	0·5 g.	14	30	2·5
Phenol	1 g.	0	30	—
Butan-1-ol	0·5	7	30	1
Propan-2-ol	1	explosive	—	0·75
Propan-2-ol	2	explosive	—	2·5
tert.-Butyl alcohol	0·5	9	30	1·5

Note: A solution of sodium allyloxide (10 ml., 2·5N) in allyl alcohol was evaporated to dryness *in vacuo* and dissolved in 10 ml. of methanol and added to acrylonitrile (40 ml.) and light petroleum (b. p. 40—60°; 75 ml.) at —15°. After 30 min., 11 g. of polymer were obtained; induction period 17 min.

EXPERIMENTAL

Purification.—Light petroleum (b. p. 40—60°) was dried over sodium and boiled under nitrogen before use. The alcohols were dried over sodium and distilled. Acrylonitrile was dried and distilled to free it from inhibitors. Nitrogen was purified from oxygen by passing it through a quartz tube containing fresh copper wire at 600°, then through a solution of 20% of pyrogallol in 20% sodium hydroxide, and dried over concentrated sulphuric acid.

Sodium Alkoxide Catalysts.—These were prepared by dissolving sodium in the respective alcohol under reflux; care was taken to avoid moisture. The alcoholic alkoxide solutions were kept in brown bottles. They must be fresh as they tend to become coloured and decompose. Methanolic sodium methoxide is the most stable. It is difficult to prepare concentrated solutions of the long- or branched-chain alcohols as the solubility of their sodium alkoxides is limited. The concentration of the catalyst solution was determined by titrating an aliquot portion with standard acid with phenolphthalein as indicator.

Polymerisation of Acrylonitrile.—The addition of reagents and the polymerisation were carried out under nitrogen. Into a three-necked flask fitted with a high-speed stirrer and a gas adaptor for introducing nitrogen, the required amounts of acrylonitrile and light petroleum were added. The stirred mixture was cooled (ice–salt bath) to −15° and the temperature kept constant. The catalyst solution was then added from a pipette. The polymerisation started after an induction period and a white solid polymer formed. The polymerisation was stopped after the required time by adding 100 ml. of cooled hydrochloric acid (1 : 1 v/v). The mixture was stirred for 20 min. and then poured into ice-water. The polymer was filtered off, and washed with alcohol and then with water until the filtrate was neutral to litmus and dried to constant weight in an electric oven at 60°. The polymer was obtained as fine white granules because the acrylonitrile was dispersed as fine droplets in the cold light petroleum.

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