# Polymerization of Acrylonitrile by Use of Potassium Alkoxides

ALBERT ZILKHA and BEN-AMI FEIT

*Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel*

In continuation of previous work[1,2] on the anionic polymerization of acrylonitrile using sodium alkoxides, we have investigated the polymerization of this monomer by potassium alkoxide catalysts.

The nature of the attached metal is important. The catalytic activity of organometallic compounds in anionic polymerization is expected to increase with the electropositivity of the attached metal, which causes a corresponding increase in the partial negative charge of the organic moiety; this causes also an increase in the ionic character of the organometallic bond, leading to a larger degree of dissociation.

Acrylonitrile was polymerized in parallel experiments by potassium and by sodium alkoxides in petroleum ether at low temperature under comparable conditions in order to determine the dependence of the catalyst activity on the attached metal (Table I). Special care was taken to use in all experiments materials purified under rigid conditions and in all cases the obtained results were reproducible. On using potassium alkoxide catalysts the yield was higher than with sodium alkoxide catalysts. Thus 1 ml. methanolic potassium methoxide (1N) gave 6.5 g. (40%) polymer, while the corresponding sodium catalyst yielded only 0.5 g. (3%). The differences in yield with potassium and sodium ethoxide catalysts were smaller than with the corresponding methoxide catalysts. Induction periods were much shorter with the potassium alkoxide catalysts. These results show that the order of the reactivity of the alkoxide catalysts in connection with the attached metal is K > Na.

Due to the high reactivity of the potassium alkoxides, it was not possible to use them in the same wide range of concentrations and amounts as with the corresponding sodium compounds. Relatively large concentrations and amounts of catalysts led to uncontrollable polymerizations.

The amount of alcohol present in the polymerization mixtures had a marked effect on the polymerization. Experiments with the same amount of catalyst and varying amounts of alcohol (Table II) showed that, up to a limit, addition of alcohol increased the yield after which a drop was noticed.

TABLE I
Dependence of Activity of Alkoxide Catalysts on the Attached Metal in Polymerization of Acrylonitrile[a]

| Run no. | Metal | Alkoxide | Catalyst solution concn., $N$ | Catalyst concn., mmole/l. | Induction period, min. | Polymerization time, min. | Polymer yield g. | Polymer yield % |
|---|---|---|---|---|---|---|---|---|
| 3 | K | Methoxide | 1 | 10 | 3.5 | 45 | 6.7 | 41 |
| 4 | K | Methoxide | 1 | 10 | 3.5 | 45 | 6.5 | 40 |
| 28 | K | Methoxide | 2 | 20 | 0.65 | 45 | 6.5 | 40 |
| 29 | K | Methoxide | 2 | 20 | 0.75 | 45 | 6.3 | 40 |
| 30 | Na | Methoxide | 1 | 10 | 10 | 45 | 0.5 | 3 |
| 31 | Na | Methoxide | 1 | 10 | 10 | 45 | 0.5 | 3 |
| 32 | Na | Methoxide | 2 | 20 | 3.5 | 45 | 1 | 6 |
| 33 | Na | Methoxide | 2 | 20 | 3.7 | 45 | 0.9 | 5 |
| 10 | K | Ethoxide | 1 | 10 | 1.0 | 45 | 6.5 | 40 |
| 11 | K | Ethoxide | 1 | 10 | 1.0 | 45 | 6.6 | 41 |
| 12 | K | Ethoxide | 1 | 10 | 0.85 | 30 | 6.2 | 39 |
| 34 | Na | Ethoxide | 1 | 10 | 7.3 | 45 | 4.4 | 28 |
| 35 | Na | Ethoxide | 1 | 10 | 7 | 45 | 4.7 | 29 |

[a] Experimental conditions: Catalyst solution (1 ml.) was added to acrylonitrile (20 ml., 3 mole/l.) and petroleum ether (79 ml.). Methanol concn., 0.249 mole/l.; ethanol concn., 0.171 mole/l. Polymerization temperature −15°.

TABLE II

Effect of Alcohol on the Polymerization of Acrylonitrile[a]

| Run no. | Vol. methanol, added ml. | Total methanol concn., mole/l. | Induction period, min. | Polymer yield | |
|---|---|---|---|---|---|
| | | | | g. | % |
| 43 | 0 | 0.249 | 0.65 | 6.4 | 40 |
| 44 | 1 | 0.498 | 6.75 | 9.5 | 60 |
| 45 | 1 | 0.498 | 6.25 | 9.2 | 58 |
| 46 | 2 | 0.747 | 19 | 10.6 | 66 |
| 47 | 2 | 0.747 | 20 | 10.5 | 66 |
| 48 | 2 | 0.747 | 19.25 | 10.3 | 64 |
| 49 | 3 | 0.996 | 39 | 8.6[b] | 54 |
| 50 | 3 | 0.996 | 39 | 9.6 | 60 |

[a] Experimental conditions: Acrylonitrile (20 ml.; 3 mole/l.), petroleum ether, and methanol were cooled to −15° and methanolic potassium methoxide (1 ml.; 2.02N; 20.2 mmole/l.) added. Total volume of petroleum ether and methanol was kept constant (80 ml.). Polymerization time 40 min. after induction period.

[b] Polymerization stopped 12 min. after induction period.

This shows the catalyst-activating effect and the inactivating polar effect of the alcohol (see Discussion). The induction period increased considerably with increasing concentration of alcohol: thus, with 1 ml. alcohol the induction period was 0.65 min. (run 43) and with 4 ml. was 39 min. (run 50).

The dependence of yield of polymer on the amount of alcoholic catalyst solution was studied under otherwise constant conditions with methanolic potassium methoxide (0.5N), the catalyst being added to the polymerization mixture. The

TABLE III

Dependence of Polymerization on Amount of Catalyst; Alcohol Concentration not Constant[a]

| Run no. | Vol. catalyst solution, ml. | Catalyst concn., mmole/l. | Methanol concn., mole/l. | Induction period, min. | Polymer yield | |
|---|---|---|---|---|---|---|
| | | | | | g. | % |
| 51 | 0.5 | 2.5 | 0.125 | 2.5 | 0.9 | 6 |
| 52 | 0.5 | 2.5 | 0.125 | 2.5 | 0.7 | 4 |
| 1 | 1 | 5 | 0.249 | 9.5 | 3 | 19 |
| 2 | 1 | 5 | 0.249 | 9.3 | 3.2 | 20 |
| 55 | 2 | 10 | 0.498 | 20.5 | 3.0 | 44 |
| 56 | 2 | 10 | 0.498 | 21 | 7.3 | 46 |
| 57 | 2 | 10 | 0.498 | 20.5 | 7.1 | 44 |
| 58 | 3 | 15 | 0.747 | 30 | 9.3 | 58 |
| 59 | 3 | 15 | 0.747 | 31 | 9.2 | 58 |

[a] Experimental conditions: Methanolic potassium methoxide (0.5N) was added to a cooled mixture of acrylonitrile (20 ml.; 3 mole/l.) and petroleum ether. Volume of catalyst solution and light petroleum was kept constant (80 ml.). Polymerization temperature −15°; time 45 min.

TABLE IV

Dependence of Polymerization on Amount of Catalyst; Alcohol Concentration Kept Constant[a]

| Run no. | Alkoxide | Catalyst solution concn., N | Catalyst concn., mmole/l. | Induction period, min. | Polymer yield | |
|---|---|---|---|---|---|---|
| | | | | | g. | % |
| 5 | Ethoxide | 0.234 | 2.34 | 5 | 2.7 | 17 |
| 6 | Ethoxide | 0.234 | 2.34 | 5.5 | 2.9 | 18 |
| 7 | Ethoxide | 0.234 | 2.34 | 5.5 | 2.2[b] | 14 |
| 8 | Ethoxide | 0.5 | 5 | 2.5 | 4.3 | 27 |
| 9 | Ethoxide | 0.5 | 5 | 2.4 | 4.5 | 28 |
| 10 | Ethoxide | 1 | 10 | 1.0 | 6.5 | 40 |
| 11 | Ethoxide | 1 | 10 | 1.0 | 6.6 | 41 |
| 12 | Ethoxide | 1 | 10 | 0.85 | 6.2[b] | 39 |

[a] Experimental conditions: Ethanolic potassium ethoxide (1 ml.) was added to a cooled mixture of acrylonitrile (20 ml.; 3 mole/l.) and petroleum ether (79 ml.). Ethanol concn., 0.171 mole/l. Polymerization temperature −15°, time 45 min.

[b] Polymerization time 30 min.

yield increased with amount of catalyst solution (Table III). The induction period increased with increasing amount of catalyst due to the increasing amount of alcohol. Thus with 0.5 ml. (run 51) and 3 ml. (run 58) catalyst solution there were induction periods of 2.5 and 30 min., respectively. This dependence was also investigated in experiments with constant quantities of alcohol and varying concentrations of ethanolic potassium ethoxide (Table IV). The yield increased continuously with increasing amount of catalyst while for the same reason the induction periods decreased.

The effect of temperature in the range between −10 and −30°C. on the polymerization of acrylonitrile by methanolic potassium methoxide was

TABLE V

Dependence of Polymerization on Temperature[a]

| Run no. | Temp., °C. | Induction period, min. | Polymer yield | |
|---|---|---|---|---|
| | | | g. | % |
| 36 | −10 | 2.5 | 4.8 | 30 |
| 37 | −15 | 3.5 | 5.8 | 36 |
| 38 | −15 | 3.5 | 5.6 | 35 |
| 39 | −25 | 20 | 6.1 | 38 |
| 40 | −25 | 20.5 | 5.8 | 36 |
| 41 | −30 | 39 | 6.4 | 40 |
| 42 | −30 | 39.5 | 6.8 | 43 |

[a] Experimental conditions: Methanolic potassium methoxide (1 ml.; 1N, 10 mmole/l.) was added to acrylonitrile (20 ml.; 3 mole/l.) in petroleum ether (79 ml.). Methanol concn., 0.249 mole/l. Polymerization time, 15 min. after induction period.

TABLE VI
Effect of Steric Factors on the Relative Reactivity of Various Alkoxide Catalysts[a]

| Run no. | Alkoxide | Catalyst solution concn., N | Catalyst concn., mmole/l. | Induction period, min. | Polyerization time, min. | Polymer yield g. | % |
|---|---|---|---|---|---|---|---|
| 18 | n-Propoxide | 1 | 10 | 0.5 | 30 | 7.6 | 48 |
| 19 | Isopropoxide | 0.5 | 5 | 2.2 | 10 | 3.1 | 20 |
| 20 | Isopropoxide | 0.5 | 5 | 2.1 | 10 | 3.2 | 20 |
| 21 | Isopropoxide | 1 | 10 | 0.4 | 30 | 6.7 | 42 |
| 22 | Isopropoxide | 1 | 10 | 0.4 | 30 | 6.4 | 40 |
| 23 | Isopropoxide | 1 | 10 | 0.5 | 30 | 6.4 | 40 |
| 24 | Isopropoxide | 1 | 10 | 0.4 | 10 | 6.1 | 38 |
| 13 | n-Butoxide | 0.5 | 5 | 1.1 | 10 | 5.5 | 34 |
| 14 | n-Butoxide | 0.5 | 5 | 1.1 | 10 | 5.5 | 34 |
| 15 | n-Butoxide | 1 | 10 | 0.35 | 10 | 7 | 44 |
| 16 | n-Butoxide | 1 | 10 | 0.3 | 10 | 7.2 | 45 |
| 17 | n-Butoxide | 1 | 10 | 0.35 | 30 | 7.8 | 49 |
| 25 | tert-Butoxide | 0.5 | 5 | 0.8 | 30 | 3.2 | 20 |
| 26 | tert-Butoxide | 0.5 | 5 | 0.85 | 10 | 2.5 | 16 |
| 27 | tert-Butoxide | 1 | 10 | 0.3 | 30 | 4 | 25 |

[a] Experimental conditions as in Table I.

TABLE VIIA
Dependence of Molecular Weight of Polyacrylonitriles on Concentration of Catalyst in a Constant Concentration of Alcohol[a]

| Monomer, ml. | Monomer concn., mole/l. | Catalyst, ml. | Catalyst concn. N | mole/l. | Total methanol ml. | mole/l. | Conversion, % | $[\eta]$, dl./g. | $\bar{M}_w$ (calc.)[b] | Wt.-avg. chain length |
|---|---|---|---|---|---|---|---|---|---|---|
| 40 | 4.62 | 3 | 5.86 | 0.135 | 15 | 2.86 | 40 | 0.063 | 1750 | 33 |
| 40 | 4.62 | 5 | 5.86 | 0.225 | 15 | 2.86 | 44 | 0.06 | 1650 | 31 |
| 40 | 4.62 | 7 | 5.86 | 0.315 | 15 | 2.86 | 37 | 0.059 | 1600 | 30 |

[a] Experimental conditions: Polymerization carried out at −15° in petroleum ether. Catalyst was diluted with methanol to 15 ml. and added to the cooled mixture of light petroleum and acrylonitrile (cf. Ref. 2, Table 2B).

[b] Weight-average molecular weights were calculated from intrinsic viscosities (measured in dimethylformamide at 30° in an Ostwald viscometer) according to the equation deduced by Cleland and Stockmayer:[13] $[\eta] = 2.33 \times 10^{-4} \bar{M}_w^{0.75}$.

investigated under otherwise constant conditions. A great increase in induction period with lowering of temperature was observed (Table V); e.g., the induction period was 2.5 min. at −10° and 39 min. at −30°C. There was a small increase in yield with lowering of temperature.

In these polymerizations it was further found that the structure and steric features of the alkoxide anion had a marked effect on the polymerization (Table VI) (see Discussion). Thus,. under comparable conditions with the use of alcoholic potassium n-butoxide (0.5N), a yield of 34% (runs 13, 14) was obtained while potassium tert-butoxide gave only 20% yield. Similarly, with n-propoxide catalyst (1N) the yield was 48% (run 18) as compared to 40% with isopropoxide catalyst (runs 22, 23).

We investigated the dependence of the weight-average molecular weights of the polyacrylonitriles on (1) the concentration of catalyst in a constant concentration of alcohol, (2) the concentration of alcohol, and (3) the concentration of monomer. Methanolic sodium alkoxide catalysts were used, as these can be used over a wide range of concentrations of reactants. Table VII shows that the molecular weight is independent of the concentration of catalyst and decreases with increasing concentration of alcohol, this decrease being linear (Fig. 1) except at low concentrations of methanol, where molecular weights considerably above linear were obtained. The molecular weights also increased linearly with increasing concentration of monomer (Fig. 2).

Some molecular weight determinations were also carried out by methoxyl endgroup analysis to obtain number-average molecular weights.

## TABLE VIIB
Dependence of Molecular Weight of Polyacrylonitriles on Concentration of Alcohol at Constant Concentrations of Catalyst and Monomer[a]

| Monomer, ml. | Monomer concn., mole/l. | Catalyst, ml. | Catalyst concn. | | Total methanol | | Conversion, % | $[\eta]$, dl./g. | $\bar{M}_w$ (calc.)[b] | Wt.-avg. chain length |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $N$ | mole/l. | ml. | mole/l. | | | | |
| 40 | 4.62 | 3 | 5.61 | 0.129 | 3 | 0.57 | 66 | 0.36 | 18,000 | 340 |
| 40 | 4.62 | 3 | 5.61 | 0.129 | 4 | 0.76 | 63 | 0.26 | 11,580 | 218 |
| 40 | 4.62 | 3 | 5.61 | 0.129 | 6 | 1.145 | 63 | 0.17 | 6,570 | 124 |
| 40 | 4.62 | 3 | 5.61 | 0.129 | 9 | 1.715 | 63 | 0.113 | 3,800 | 72 |
| 40 | 4.62 | 3 | 5.61 | 0.129 | 12 | 2.285 | 55 | 0.082 | 2,500 | 47 |
| 40 | 4.62 | 3 | 5.61 | 0.129 | 15 | 2.86 | 41 | 0.063 | 1,750 | 33 |
| 40 | 4.62 | 3 | 5.61 | 0.129 | 19 | 3.62 | 27 | 0.051 | 1,320 | 25 |

[a] Experimental conditions: A constant quantity of methanolic sodium methoxide (3 ml.; 5.61 $N$) was diluted with the required quantity of methanol and added in one portion to a cooled mixture of light petroleum (b.p. 60–80°) and acrylonitrile (40 ml.). The volume of methanol and petroleum ether was kept constant (90 ml.). Polymerization temperature −15°, time 60 min. except where otherwise indicated.

[b] Weight-average molecular weights were calculated from intrinsic viscosities (measured in dimethylformamide at 30° in an Ostwald viscometer) according to the equation deduced by Cleland and Stockmayer:[13] $[\eta] = 2.33 \times 10^{-4}\bar{M}_w^{0.75}$.

| Methanol added to catalyst, ml. | 0 | 1 | 3 | 6 | 9 | 12 | 16 |
|---|---|---|---|---|---|---|---|
| Catalyst concn. in methanol, $N$ | 5.61 | 4.21 | 2.81 | 1.87 | 1.40 | 1.12 | 1.05 |
| Yield, g. | 21 | 20 | 20 | 20 | 17.5 | 13 | 8.5 |
| Induction period, min. | 3 | 4 | 7 | 12 | 27* | 43† | 74† |
| 1/[ROH], mole/l. | 1.75 | 1.31 | 0.88 | 0.58 | 0.44 | 0.35 | 0.28 |

\* Polymerization carried out for 90 min.

† Polymerization carried out for 60 min. after the induction period.

## TABLE VIIC
Dependence of Molecular Weight of Polyacrylonitriles on Concentration of Monomer[a]

| Monomer, ml. | Monomer concn., mole/l. | Catalyst, ml. | Catalyst concn. | | Total methanol | | Conversion, % | $[\eta]$, dl./g. | $\bar{M}_w$ (calc.)[b] | Wt.-avg. chain length |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $N$ | mole/l. | ml. | mole/l. | | | | |
| 20 | 2.31 | 10 | 2.0 | 0.154 | 10 | 1.91 | 31 | 0.059 | 1600[c] | 30 |
| 30 | 3.47 | 10 | 2.0 | 0.154 | 10 | 1.91 | 54 | 0.077 | 2300 | 43 |
| 40 | 4.62 | 10 | 2.0 | 0.154 | 10 | 1.91 | 59 | 0.11 | 3650 | 69 |
| 50 | 5.78 | 10 | 2.0 | 0.154 | 10 | 1.91 | 60 | 0.13 | 4600 | 87 |
| 60 | 6.94 | 10 | 2.0 | 0.154 | 10 | 1.91 | 54 | 0.16 | 5950[d] | 112 |

[a] Experimental conditions: Methanolic sodium methoxide (10 ml., 2.0N) was added to a cooled mixture of petroleum ether (b.p. 60–80°) and acrylonitrile. The volume of acrylonitrile and petroleum ether was kept constant (120 ml.). Polymerization temperature −15°, time 60 min. except where otherwise indicated.

[b] Weight-average molecular weights were calculated from intrinsic viscosities (measured in dimethylformamide at 30° in an Ostwald viscometer) according to the equation deduced by Cleland and Stockmayer:[13] $[\eta] = 2.33 \times 10^{-4}\bar{M}_w^{0.75}$.

[c] Methoxyl = 2.5%; $\bar{M}_n = 1250$.

[d] Methoxyl = 0.95%; $\bar{M}_n = 3250$.

| Monomer, ml. | 10 | 20 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|---|
| Yield, g. | — | 5 | 13 | 19 | 24 | 26 |
| Induction period, min. | — | 40* | 22 | 16 | 10 | •8 |

\* Polymerization carried out for 60 min. after the induction period.

## DISCUSSION

From the previous[1,2] and the present results, conclusions can be drawn as to the mechanism of the anionic polymerization of acrylonitrile by alcoholic solutions of alkali metal alkoxides.

**Initiation.** Initiation is by direct interaction of the alkoxide anion with monomer, as substantiated by the following facts. (a) Alcohols add on to acrylonitrile in the presence of basic catalysts in the well-known cyanoethylation reaction.[3] (b) The
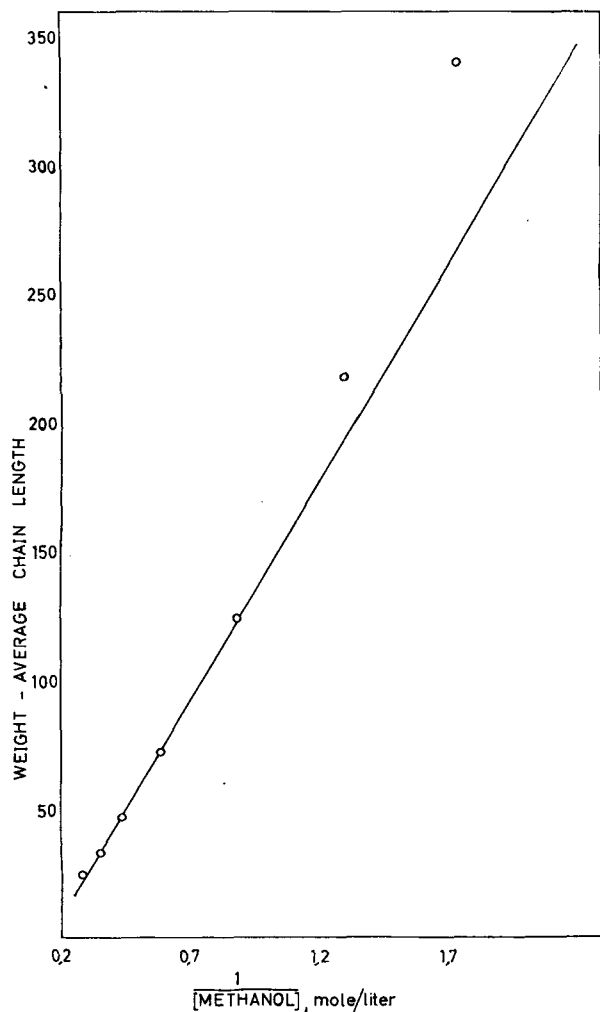
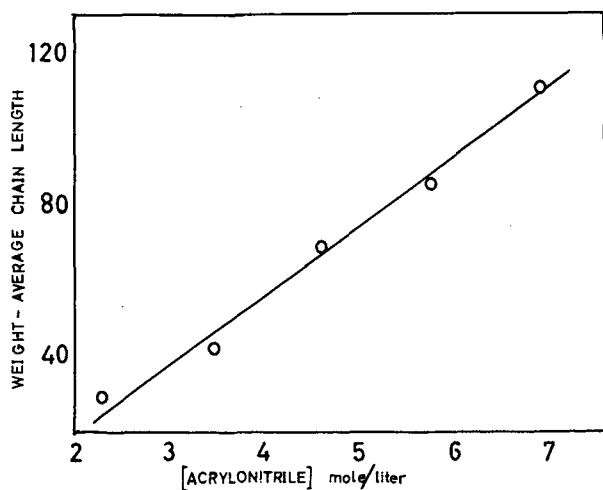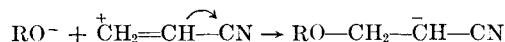Fig. 1. Dependence of molecular weight on concentration
of alcohol.



Fig. 2. Dependence of molecular weight on concentration
of monomer.

polymers contain alkoxyl groups. (c) The rate of polymerization increases with the electropositivity of the attached metal. All these facts suggest that the initiation step is:

$$RO^- + \overset{+}{C}H_2=CH\!-\!CN \rightarrow RO\!-\!CH_2\!-\!\overset{-}{C}H\!-\!CN$$

There appears to be no possibility for the formation of a cocatalyst intermediate by interaction of the alkali metal alkoxide with any component of the polymerization mixture.

The experiments were carried out under anhydrous conditions. The assumption that traces of water nevertheless present were acting as cocatalyst according to the reaction

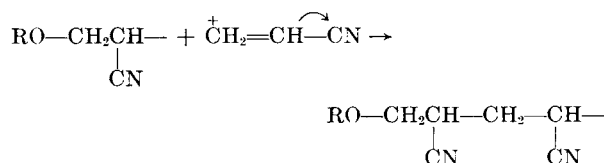$$ROK + H_2O \rightleftharpoons KOH + ROH$$
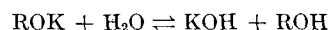
would lead to the conclusion that potassium hydroxide is the true catalyst. This is improbable for the following reasons. (a) Polymerization by KOH means that the initiator is $OH^-$; in this case the polymers should not contain alkoxyl groups. (b) It does not seem plausible that $OH^-$, being a weaker base than $RO^-$, should initiate the polymerization in preference to the stronger catalyst. (c) Initiation of the polymerization of acrylonitrile is merely a part of the cyanoethylation reaction. It is well known that the addition of alcohol to acrylonitrile can be catalyzed by aqueous alkali, the product obtained being the alkoxy cyanide.[3] (d) Caldin and Long[4] have shown that the equilibrium of the reaction:

$$OEt^- + H_2O \rightleftharpoons EtOH + OH^-$$
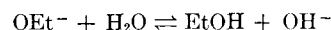
in mixtures containing ethanol and a few per cent water is strongly in favor of alkoxide and not of $OH^-$ formation.

The proposed direct interaction of alkoxide with monomer explains the fact that *tert*-butoxide anion, although being a relatively very strong base, is a relatively weak polymerization catalyst (Table VI), due to steric hindrance. This can be compared to the very difficult addition of *tert*-butanol to acrylonitrile in the cyanoethylation reaction.[3] *Tert*-butanol is even used in certain instances as solvent for this reaction. The relatively low yield obtained with potassium isopropoxide (Table VI), which is a stronger base than primary alkoxides, may also be due to steric effects, as is its behavior in cyanoethylation.[5]

**Propagation.** As is the case in other ionic polymerizations, propagation can be assumed to proceed as follows:

$$RO—CH_2CH— + \overset{+}{C}H_2=CH—\overset{\frown}{CN} →$$

$$RO—CH_2CH—CH_2—CH—$$
$$\qquad\qquad\; |\qquad\qquad\; |$$
$$\qquad\qquad CN\qquad\quad CN$$

**Termination.** The following general possibilities of chain termination are possible: (1) proton abstraction from the alcohol, (2) chain transfer to monomer, and (3) proton abstraction from solvent; this last is improbable, as petroleum ether is not a proton-donating solvent.

Bearing on the termination reaction the following was found. The molecular weight increased with decrease in concentration of alcohol. Relatively large concentrations of alcohol prevent polymerization. Within a certain range, the molecular weight increased linearly with decreasing concentration of alcohol (Fig. 1); lower concentrations of alcohol lead to molecular weights considerably above that expected for a linear relation. The molecular weight increased linearly with increasing concentration of monomer (Fig. 2). The polymers showed some weak absorption bands at 6.1 $\mu$ due to a C=C valency vibration of terminal vinyl groups (=CH$_2$).[6]

Based on the experimental evidence the choice of the mode of termination can be made with the aid of the following scheme of the polymerization steps.
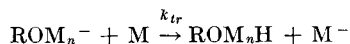
Initiation:

$$ROMe \qquad → RO^- + Me^+$$

$$RO^- + M \quad \overset{k_i}{→} ROM_1^-$$

Propagation:

$$ROM_1^- + M \overset{k_p}{→} ROM_2^-$$
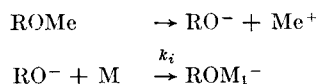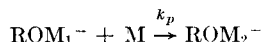
Termination:

(a) Chain transfer with monomer:

$$ROM_n^- + M \overset{k_{tr}}{→} ROM_nH + M^-$$

or proton transfer from monomer:

$$ROM^- + CH_2=CHCN → ROMH + CH_2=\overset{-}{C}—CN$$

(Here CH$_2$=$\overset{-}{C}$—CN can start a new chain and yield a polymer having a vinyl end group.)

(b) Proton transfer from the conjugated acid of the catalyst base (alcohol):

$$ROM_n^- + ROH \overset{k_t}{→} ROM_nH + RO^-$$
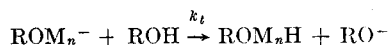
Here, the rate of propagation, $R_p$, is given by $R_p = k_p [M] [ROM^-]$, and the rate of termina-

tion, $R_t$, is given by $R_t = k_{tr}[ROM^-][M]$ or $R_t = k_t[ROM^-][ROH]$. From this the degree of polymerization is given by

$$DP = R_p/R_t$$
$$\quad = k_p[M][ROM^-]/k_{tr}[M][ROM^-] = k'$$

(in case of termination by chain transfer); and, in the case of termination by ROH, by

$$DP = R_p/R_t$$
$$\quad = k_p[M][ROM^-]/k_t[ROH][ROM^-]$$
$$\quad = k_p[M]/k_t[ROH]$$

It is thus seen that the molecular weight is independent of the concentration of catalyst, as was experimentally found. Termination by chain transfer with monomer should lead to the molecular weight being independent of monomer concentration. This, however, is not the case. If termination by ROH occurred, the molecular weight should be directly proportional to the concentration of monomer and inversely proportional to the concentration of the alcohol, according to the above equation, and a plot of the degree of polymerization against monomer concentration or against the reciprocal of the concentration of the alcohol should give a straight line. The experimental results show such a dependence of molecular weight on the concentrations of monomer and alcohol.

The fact that the linear dependence is not followed at low concentrations of alcohol may be due to the possibility that at low concentrations the alcohol is held by the insoluble alkoxide catalyst or by the precipitating polymer, thus decreasing its effective concentration in the reaction mixture. Another reason for the nonlinear dependence may be due to more termination by chain transfer to monomer at the low concentrations of alcohol. It has been shown in a previous paper[7] on the polymerization of acrylonitrile by butyllithium in petroleum ether where the termination was dominated by chain transfer that the molecular weights were of the order of 18,000–21,000; with the alkoxide catalysts, in low alcohol concentrations, the molecular weights of polymers prepared under similar conditions approach the above order of molecular weights. Also, infrared spectra of the polymers showed the presence of double bonds as consistent with chain transfer to monomer. Changes in the dielectric constant caused by changes in the concentration of alcohol may also affect the molecular weight.

Higginson and Wooding,[3] in their study of the anionic polymerization of styrene in liquid ammonia by potassium amide catalysts, found that the termination occurred by abstraction of a proton from the ammonia. Considering the high $pK_a$ of ammonia[9] (36), in the case of the alkoxides termination by alcohol ($pK_a$ between 17 and 20) seems to be much easier.

Calculation of $k_p/k_t$ for polymerization carried out at $-15°$ from the slopes of the lines of Figures 1 and 2 gave values of 36 and 35, respectively, showing good agreement between the two. Using this value of $k_p/k_t$, and with the help of the equation,

$$\text{DP} = (k_p/k_t) \, [\text{M}]/[\text{ROH}]$$

it is possible to prepare polymers whose degree of polymerization can be approximately evaluated, provided that the effective concentrations of monomer and alcohol are known.

The above scheme explains certain aspects of the polymerization of acrylonitrile by alkoxides. Thus, the activating effect of the alcohol found with alkoxide catalysts may be due in part to the increased ionization of the alkali metal alkoxide in the polar alcohol giving a higher concentration of alkoxide anions. Similarly, an increase in electropositivity of the attached metal which causes an increase in rate of polymerization may be due to a higher concentration of $RO^-$, the initiating species.

## Induction Period

The problem of the induction period observed in the heterogeneous polymerization of acrylonitrile by alkoxide solutions in petroleum ether is complicated. The induction periods, even very long ones, were highly reproducible (see runs 41, 42, in Table V and runs 49, 50 in Table II). We found that the induction periods followed the following rules:
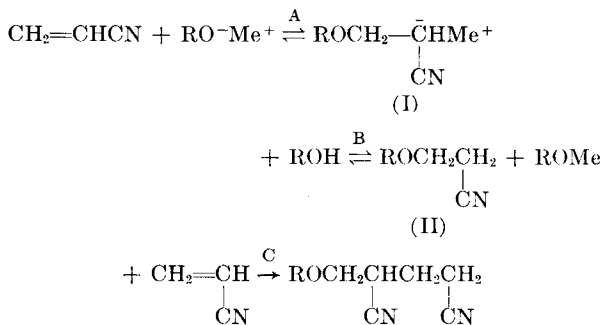
(a) Increase with increasing concentration of alcohol (Table II).

(b) Increase with increasing amount of catalyst (Table III).

(c) Decrease with increasing concentration of catalyst solution (Table IV).

(d) Decrease with increasing temperature (Table V).

(e) Decrease with increasing concentration of monomer (Table VII).

(f) Decrease with the more active catalysts (Table I).

The existence of the above rules, the reproducibility of the results, and the great care taken in the purification of materials exclude the possibility that the induction periods originate from impurities, although it is very probable that impurities may increase the induction period.

In the anionic polymerization of ethylene oxide by alkaline earth carbonates[10] it was found that the induction periods were smaller with more active catalysts. The induction periods were so definite that the authors even used them as comparative measure of activity of catalysts.

The initiation step of the polymerization of acrylonitrile by alcoholic alkoxide solutions is identical with the first step ($RO^-$ addition) in the cyanoethylation reaction. In fact, it is possible to consider the cyanoethylation reaction as "polymerization" of acrylonitrile terminated by alcohol after the addition of only one monomer molecule to the alkoxide anion.

After the initiation step, giving I, there are two simultaneous competing reactions: propagation (polymerization) or an immediate termination (cyanoethylation) as in the following scheme:

$$CH_2{=}CHCN + RO^-Me^+ \overset{A}{\rightleftharpoons} ROCH_2{-}\overset{\displaystyle |}{\underset{\displaystyle CN}{\bar{C}}}HMe^+$$

$$(I)$$

$$+ ROH \overset{B}{\rightleftharpoons} ROCH_2CH_2 + ROMe$$
$$\underset{\displaystyle CN}{|}$$
$$(II)$$

$$+ CH_2{=}CH \overset{C}{\rightarrow} ROCH_2CHCH_2CH_2$$
$$\underset{\displaystyle CN}{|} \qquad \underset{\displaystyle CN}{|} \quad \underset{\displaystyle CN}{|}$$

Reaction (B) (cyanoethylation) is, as is known, reversible, while reaction (C) (polymerization) is irreversible (the polymer being also insoluble in the reaction medium). On increasing the concentration of I, whether by increasing catalyst concentration, monomer concentration, or the basic strength of the alkoxide anion, even though it also favors reaction (B), the irreversible nature of reaction (C) will lead more to polymerization. In addition to these main considerations, the differences between the acidity of the hydroxyl hydrogen of the alcohol and that of the $\alpha$-hydrogen of the cyanoethylation product II will affect the extent of the reversibility of reaction (B) which in turn influences reaction (C) (polymerization).

From this scheme it is also seen that increasing monomer concentration favors polymerization, while increasing the alcohol concentration favors

cyanoethylation. Side reaction (B) decreases the alcohol concentration to an equilibrium concentration which may suit reaction (C) (polymerization).

In conclusion, we suppose that the induction period originates from the existence of side reaction (B) (cyanoethylation) which seems solely to take place at the start of the reaction before polymerization occurs. In support of these conclusions we have succeeded in isolating cyanoethylation products ($ROCH_2CH_2-CN$) both from polymerization reactions stopped just before the end of the induction period (before any polymerization had started) and at the end of polymerization reactions.

Yields in all experiments were only in the range of 50–60%; we have also shown that the induction period increases to high values with decreasing concentration of monomer (Table VII). The limiting yield may be explained by the fact that the concentration of monomer in the reaction mixture decreases in the course of the polymerization to such low concentrations that no polymerization occurs or that the reaction becomes very slow.

The inactivating polar effect of the alcohol at high concentrations may be due to its increasing the extent of the cyanoethylation reaction. In fact, at large concentrations of alcohol no polymerization occurs.

### EXPERIMENTAL

### Materials

Nitrogen was freed from oxygen by passage through a quartz tube containing fresh copper wire at 600°, then through a 5% alkaline permanganate solution followed by a solution of 20% pyrogallol in 20% sodium hydroxide and dried (concentrated sulfuric acid). Petroleum ether, analar grade, b.p. 60–80°, was dried over sodium, distilled, and boiled under nitrogen before use. Acrylonitrile was purified according to Bamford and Jenkins[11] by successive washings with dilute sulfuric acid (5%), dilute sodium carbonate (5%), and water. After thorough drying over calcium chloride it was fractionally distilled at atmospheric pressure and stored in the dark over calcium chloride. Immediately before use, it was filtered and fractionally distilled *in vacuo* under nitrogen; the middle fraction (about 70%) was used. Dimethylformamide was fractionally distilled.

**Alcohols.** Methanol, analar grade, was dried over magnesium and distilled. Absolute ethanol (98%) was dried over magnesium and distilled. Propanol was dried over magnesium. *n*-Butanol

was distilled over sodium and further dried by sodium and di-*n*-butyl phthalate. Isopropanol was first dried over calcium sulfate and then over calcium metal and distilled. *tert*-Butanol was first distilled over sodium and then over sodium and *tert*-butyl benzoate.

These special purifications[12] of materials gave reproducible results. We found that using different batches of acrylonitrile gave differences in quantitative results. All experiments reported in Tables I–VI were carried out with the same batch of monomer. Experiments of Table VII were carried out with a different batch.

**Alkoxide Catalysts.** These were prepared by dissolving the alkali metal 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 colored and decompose. Methoxide solutions were the most stable. The concentration of the catalyst solution was determined by titration of an aliquot portion with standard acid with phenolphthalein as indicator.

### Polymerization of Acrylonitrile

The addition of reagents and the polymerization 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 amount of acrylonitrile and petroleum ether were added. The stirred mixture was cooled to the required temperature of polymerization and kept constant. The catalyst solution was then added from a pipet. The polymerization started after an induction period and a white solid polymer formed. The polymerization was stopped after the required time by adding 100 ml. of cooled hydrochloric acid (1:1 by volume). The mixture was stirred for 20 min. and then poured into ice water. The polymer was filtered off, washed with dilute hydrochloric acid, water, methanol, and ether to remove monomer, and dried to constant weight in an electric oven at 60°.

Polymer samples were further purified and dried for molecular weight determinations. Viscosities of polymer solutions were measured in an Ostwald viscosimeter.

### Isolation of Cyanoethylation Products

A polymerization experiment carried out under the standard experimental conditions using acrylonitrile (20 ml.) petroleum ether (75 ml.) and 5 ml.

methanolic potassium methoxide (0.5*N*) was stopped 50 min. after addition of catalyst before polymerization was started by adding hydrochloric acid (100 ml.) (1:1). (In another experiment under the same conditions the induction period was 57 min.) The aqueous layer was separated and extracted with ether. The ether extract was combined with the organic layer, washed with water, and dried over sodium sulfate. On fractional distillation β-methoxy propionitrile (0.5 g.) was obtained: b.p. 158/690 mm., $n = 1.405$.[5]

## References

1. Zilkha, A., B. A. Feit, and M. Frankel, *Proc. Chem. Soc.*, **1958**, 255.

2. Zilkha, A., B. A. Feit, and M. Frankel, *J. Chem. Soc.*, **1959**, 928.

3. Adams, R., *Organic Reactions*, Vol. V, Wiley, New York, 1949, pp. 79–136.

4. Caldin, E. F., and G. Long, *J. Chem. Soc.*, **1954**, 3737.

5. Utermohlen, W. P., Jr., *J. Amer. Chem. Soc.*, **67**, 1505 (1945).

6. Dainton, F. S., and G. B. B. M. Sutherland, *J. Polymer Sci.*, **4**, 37 (1949).

7. Frankel, M., A. Ottolenghi, M. Albeck, and A. Zilkha, *J. Chem. Soc.*, **1959**, 3858.

8. Higginson, W. C. E., and N. S. Wooding, *J. Chem. Soc.*, **1952**, 760.

9. Higginson, W. C. E., and N. S. Wooding, *J. Chem. Soc.*, **1952**, 774.

10. Hill, F. N., F. E. Bailey, Jr., and J. T. Fitzpatrick, *Ind. Eng. Chem.*, **50**, 5 (1958).

11. Bamford, C. H., and A. D. Jenkins, *Proc. Roy. Soc. (London)*, **A216**, 515 (1953).

12. Vogel, A. I., *Practical Organic Chemistry*, 2nd Ed., Longmans Green, London, 1948, pp. 164–169.

13. Cleland, R. L., and W. H. Stockmayer, *J. Polymer Sci.*, **17**, 473 (1955).

## Synopsis

The heterogeneous anionic polymerization of acrylonitrile in petroleum ether by potassium alcoholic alkoxide solutions at low temperature was studied. Alkoxides of the more electropositive metal were more active catalysts, ROK > RONa. Increasing amount of alcohol in the polymerization mixture up to a limit, had an activating effect. Yield of polymer increased with catalyst concentration. The mechanism of the polymerization consists of initiation by direct interaction of alkoxide anion with monomer, with no cocatalyst; this is substantiated by the presence of alkoxyl groups in the polymers and by the existence of steric effects of bulky alkoxide groups. Termination is by proton abstraction from alcohol. In accordance with this, the degree of polymerization was found to be independent of catalyst concentration, directly proportional to monomer, and inversely to alcohol concentrations, according to the equation, $DP = k_p[M]/k_t[ROH]$. Plot of DP versus monomer and the reciprocal of the alcohol concentrations gave values for $k_p/k_t$ of about 35. All polymerizations showed an induction period with the following regularities. It increased with increasing concentration of alcohol and with lowering of temperature, and decreased with increasing catalyst and monomer concentrations and was smaller with the more active potassium catalysts. Induction periods seem to originate from the competing side-reaction of cyanoethylation, the initiation step of the polymerization being identical with the first step (RO⁻ addition) in the cyanoethylation reaction. Cyanoethylation products were isolated from polymerization mixtures.

## Résumé

On a étudié la polymérisation anionique de l'acrylonitrile dans l'éther de pétrole par des solutions d alcoyloxyde de potassium en milieu alcoolique à basse température. Les alcoyloxydes des métaux les plus électropositifs constituent les catalyseurs les plus actifs: ROK > RONa. Jusqu'à une certaine limite, des quantités croissantes d'alcool dans le mileu de polymérisation causent un effet activant. Le rendement en polymère augmente avec la concentration du catalyseur. Le mécanisme de la polymérisation consiste en une initiation par interaction directe de l'anion alcoyloxyde avec le monomère sans aucun co-catalyseur; ceci est mis en èvidence par la présence de group alcoyloxyde dans les polymères et par l'existence d'effet stérique des groups alcoyloxydes volumineux. La terminaison se fait par abstraction d'un proton de l'alcool. En accord avec ceci, le degré de polymérisation est indépendant de la concentration en catalyseur et est directement proportionnel à la concentration en monomère et inversement proportionnel à celle de l'alcool, suivant l'équation $DP = k_p[M]/k_t[ROH]$. En portant DP en fonction de $[M]/[ROH]$ on obtient des valeurs de $k_p/k_t$ d'environ 35. Toutes les polymérisations présentent une période d'induction avec les régularités suivantes: celle-ci croît avec la concentration en alcool et avec l'abaissement de la température et décroît quand augmentent les concentrations en catalyseur et monoère; elle est plus petite avec les catalyseurs au potassium les plus actifs. Les périodes d'induction semblent être dues à la compétition de la réaction secondaire de cyanéthylation, l'étape d'initiation de la polymérisation étant identique à la première étape (addition d'RO⁻) de la réaction de cyanéthylation. Les produits de cyanéthylation ont été isolés du milieu de polymérisation.

## Zusammenfassung

Die heterogene, anionische Polymerisation von Acrylnitril wurde in Petroläther mit alkoholischen Kaliumalkoxydlösungen bei niedriger Temperatur untersucht. Alkoxyde des stärker elektropositiven Metalls bildeten die wirksameren Katalysatoren, ROK > RONa. Eine steigende Menge von Alkohol in der Polymerisationsmischung hatte bis zu einem Grenzwert einen aktivierenden Einfluss. Die Ausbeute an Polymerem nahm mit der Katalysatorkonzentration zu. Für den Polymerisationsmechanismus charakteristisch ist eine Startreaktion, bei der das Alkoxydanion ohne Kokatalysator direkt mit dem Monomeren reagiert; dieser Mechanismus wird durch die Gegenwart von Alkoxylgruppen im Polymeren und durch das Auftreten sterischer Effekte bei sperrigen Alkoxydgruppen belegt. Kettenabbruch erfolgt durch Protonenentzug vom Alkohol. In Übereinstimmung damit erwies sich der

Polymerisationsgrad als unabhängig von der Katalysator-konzentration, direkt proportional zur Monomer- und umgekehrt proportional zur Alkoholkonzentration, entsprech-end der Gleichung, DP $= k_p[\text{M}]/k_t[\text{ROH}]$. Das Dia-gramm DP gegen die Monomerkonzentration und gegen den Reziprokwert der Alkoholkonzentration lieferte für $k_p/k_t$ Werte um 35. Alle Polymerisationen zeigten eine Induktionsperiode mit folgenden Gesetzmässigkeiten: Mit steigender Alkoholkonzentration und mit Herabsetzung der Temperatur nahm die Induktionsperiode zu und mit zuneh-mender Katalysator- und Monomerkonzentration ab und sie war bei den aktiveren Kaliumkatalysatoren kürzer. Die Induktionsperioden scheinen durch Cyanoäthylierung als kompetitive Nebenreaktion bedingt zu sein; die Start-reaktion der Polymerisation ist mit dem ersten Schritt (RO⁻-Addition) bei der Cyanoäthylierungsreaktion iden-tisch. Die Reaktionsprodukte der Cyanoäthylierung konn-ten aus der Polymerisationsmischung isoliert werden.