

Anionic Homogeneous and Heterogeneous Polymerizations of Acrylonitrile by Alkali Metal Alkoxides*

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INTRODUCTION

The anionic homogeneous polymerization of acrylonitrile in dimethylformamide by aqueous solutions of quaternary ammonium hydroxide catalysts¹ and the heterogeneous polymerization by alcoholic alkali metal alkoxides in petroleum ether^{2,3} have been investigated in previous works. One other anionic homogeneous polymerization of acrylonitrile in dimethylformamide, briefly reported recently,⁴ involved sodium diethylmalonate as catalyst.

It was found that under heterogeneous conditions, with $\text{CH}_3\text{ONa}/\text{CH}_3\text{OH}$ as polymerization catalyst, the degree of polymerization is given by $\overline{DP} = K[M]/[\text{ROH}]$.

As a continuation of this work, we have studied the polymerization of this monomer using methanolic solutions of potassium, sodium, and lithium methoxides as catalysts, under homogeneous conditions in dimethylformamide, and also its polymerization, with methanolic solutions of sodium and potassium methoxides, under heterogeneous conditions in petroleum ether.

The mechanisms of polymerization were investigated by studying the dependence of molecular weight on initiator, monomer, and alcohol concentrations. The dependence of molecular weight on temperature and the positive counterion was studied under homogeneous and heterogeneous conditions, and explanations of the experimental results are given here. A general comparison of the homogeneous and heterogeneous polymerization is given in accordance with the results obtained in the present and previous works.

RESULTS

Dependence of Molecular Weight on Monomer Concentration

Homogeneous Polymerization

This dependence was investigated with $\text{CH}_3\text{ONa}/\text{CH}_3\text{OH}$ catalyst in the presence of two different constant concentrations of methanol (0.149 and

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0.496 mole/l.), and two different concentrations of catalyst were used: 18 and 6 mmole/l., respectively. The molecular weight in the two series was equal, constant, and independent of monomer concentration within experimental error. In the first case, there was a decrease in yield with increasing monomer concentration, but an increase in yield was found in the presence of greater concentration of methanol. The polymerization temperature was -10° and the polymerization time was 30 min. See Table I.

TABLE I
Dependence of Molecular Weight on Concentration of Monomer, Homogeneous Polymerization

Run no.*	[M], mole/l.	Yield, g.	Conversion, %	$[\eta]$, dl./g.	\bar{M}	\bar{DP}
55A	0.604	0.80	50	0.037	860	16
58A	0.604	0.80	50	0.051	1320	25
59A	1.510	1.50	37.5	0.045	1110	21
56A	2.230	2.30	36	0.045	1110	21
57A	2.230	2.00	30	0.051	1320	25
60A	3.620	2.70	28	0.053	1390	26
93A	0.906	0.80	33	0.050	1280	24
94A	0.906	0.75	31	0.045	1110	21
90A	1.812	1.80	37	0.046	1150	22
91A	1.812	1.80	37	0.047	1180	22
92A	1.812	2.30	48	0.045	1110	21
96A	2.416	2.65	41	0.048	1220	23
97A	2.416	2.60	40	0.044	1080	20
98A	2.416	2.90	45	0.044	1080	20

* Runs 55A-60A: concentration of CH_3ONa , 0.018 mole/l.; concentration of methanol, 0.149 mole/l. Runs 93A-98A: concentration of CH_3ONa , 0.006 mole/l.; concentration of methanol 0.496 mole/l.

TABLE II
Dependence of Molecular Weight on Concentration of Monomer,* Heterogeneous Polymerization

Run no.	[M], mole/l.	$[\text{CH}_3\text{OK}]$, mmole/l.	Ind. period, min.	Yield, g.	Conversion, %	$[\eta]$, dl./g.	\bar{M}	\bar{DP}
125A	1.51	41.6	4.0	2.70	68	0.047	1180	22
130A	1.51	41.6	4.0	2.25	56	0.049	1250	24
169A	1.51	41.6	3.5	2.25	56	0.042	1020	19
16Y	1.51	40.0	3.3	2.20	55	0.044	1080	20
17Y	3.02	20.0 ^b	6.0	4.50	56	0.068	1940	37
20Y	3.02	20.0 ^b	7.5	4.40	55	0.067	1900	36
21Y	3.02	20.0 ^b	7.0	3.75	47	0.071	2050	39

* Experimental conditions: Concentration of methanol, 0.496 mole/l.; polymerization temperature, -10° ; polymerization time, 30 min. (after induction period).

^b Comparable conditions are being kept since molecular weight is independent of catalyst concentration.

Heterogeneous Polymerization

In a previous work³ a linear dependence of molecular weight on acrylonitrile concentration, with $\text{CH}_3\text{ONa}-\text{CH}_2\text{OH}$ as catalyst, was reported. In the present work, too, molecular weight of the polyacrylonitrile increased with increasing monomer concentration. Methanolic solutions of potassium methoxide were used as catalyst. Experimental difficulties were encountered in the determination of this dependence over a wide range of monomer concentrations, because of the high reactivity of the potassium methoxide catalyst, leading to uncontrollable exothermic polymerizations (see Table II).

Dependence of Molecular Weight on Catalyst Concentration*Homogeneous Polymerization*

A methanolic solution of sodium methoxide was used as catalyst. The catalyst concentration was varied in the range 0.01–0.03 mole/l., while constant concentrations of methanol (0.248 mole/l.) and monomer (0.906 mole/l.) were present in the polymerization mixture. Molecular weight was independent of catalyst concentration and remained constant in this range, within experimental error. Polymer conversion increased a little with catalyst concentration (52–65%). See Table III.

TABLE III
Dependence of Molecular Weight on Concentration of Catalyst,* Homogeneous Polymerization

Run no.	$[\text{CH}_3\text{ONa}]$, mole/l.	Yield, g.	Conversion, %	$[\eta]$, dl./g.	\bar{M}	\bar{DP}
48A	0.010	1.25	52	0.032	710	13
49A	0.010	1.35	56	0.031	680	13
50A	0.010	1.35	56	0.041	990	19
51A	0.015	1.50	63	0.031	680	13
52A	0.015	1.50	63	0.036	830	16
47A	0.030	1.55	65	0.035	800	15
53A	0.030	1.50	64	0.034	770	15
54A	0.030	1.60	67	0.042	1020	19

* Experimental conditions: polymerization temperature, -5° ; polymerization time, 30 min.

Heterogeneous Polymerization

It is seen from the results given in Table IV that the molecular weight is independent of catalyst concentration. A methanolic solution of potassium methoxide was used as catalyst. Under otherwise constant conditions the molecular weight remained constant as the catalyst concentration varied in the range 0.04–0.101 mole/l. A similar independence of molecular weight and catalyst concentration has been found in previous work³ in which $\text{CH}_3\text{ONa}-\text{CH}_2\text{OH}$ was catalyst. See Table IV.

TABLE IV
Dependence of Molecular Weight on Catalyst Concentration,^a Heterogeneous Polymerization

Run no.	[CH ₃ OK], mole/l.	Ind. period, min.	Yield, g.	Conversion, %	[η], dl./g.	\bar{M}	\bar{DP}
1Y	0.040	3.50	2.30	58	0.036	830	16
9Y	0.040	3.30	2.10	53	0.036	830	16 ^b
16Y	0.040	3.30	2.35	59	0.044	1080	20
8Y	0.060	0.55	2.20	55	0.047	1180	22
5Y	0.074	0.25	3.70	93	0.042	1020	19
6Y	0.074	0.15	3.70	93	0.040	950	18
4Y	0.101	0.08	3.60	90	0.042	1020	19

^a Experimental conditions: concentration of monomer, 1.51 moles/l.; concentration of methanol, 0.496 mole/l.; polymerization temperature, -10°; polymerization time 30 min. (after induction period).

^b Polymerization time, 20 min.

Dependence of Molecular Weight on Methanol Concentration

Under otherwise homogeneous constant conditions the molecular weights of acrylonitrile polymers obtained with sodium methoxide catalyst (6 mmoles/l.) were independent of methanol concentration (49.5–792 mmoles/l.). A great decrease in polymer conversion with increasing concentration of methanol was observed (63–6.5%). There was no induction period with the low methanol concentrations, while with the highest concentration an induction period of 40 sec. was observed. See Table V.

TABLE V
Dependence of Molecular Weight on Methanol Concentration,^a Homogeneous Polymerization

Run no.	[CH ₃ OH], mmole/l.	Ind. period, sec.	Conversion, %	Un-reacted AN, % ^b	[AN], mmole/l. ^c	[η], dl./g.	\bar{M}	\bar{DP}
164A	49.5	0	60.0	36.3	33.5	0.042	1020	19
157A	148.5	0	48	34	163.0	0.042	1020	19
161A	297.0	3–5	31	33	328.3	0.042	1020	19
165A	297.0	5	46	—	—	0.034	770	15
162A	420.8	—	27	—	—	0.040	950	18
163A	420.8	—	21	—	—	0.040	950	18
158A	544.5	5–10	10.5	—	—	0.037	860	16
159A	544.5	—	15.5	—	—	0.039	920	17
166A	668.3	20	17	—	—	0.039	920	17
160A	792.0	40	6.3	1.8	823.0	0.039	920	17

^a Experimental conditions: concentration of monomer, 0.906 mole/l.; concentration of catalyst CH₃ONa, 6 mmoles/l.; polymerization temperature, -5°; polymerization time, 15 min. The catalyst solution was added to the cooled (-5°) solution consisting of monomer, methanol, and dimethylformamide.

^b As determined quantitatively by titration with *n*-dodecyl mercaptan.

^c This is the amount of acrylonitrile that reacted with methanol, as calculated from the amounts of polymer obtained and unreacted monomer.

In previous work³ the dependence of molecular weight on methanol concentration under heterogeneous conditions (in petroleum ether) was studied, sodium methoxide being initiator. The molecular weight was proportional to the reciprocal of the alcohol concentration.

Dependence of Molecular Weight on Temperature

Homogeneous Polymerization

The effect of temperature on the polymerization and the dependence of molecular weight on it were studied under comparable conditions with methanolic solutions of potassium methoxide, sodium methoxide, and lithium methoxide catalysts.

With potassium methoxide as initiator in the presence of constant concentrations of monomer (0.906 mole/l.) and methanol (0.248 mole/l.), the molecular weight of the polyacrylonitrile remained constant with

TABLE VI
Effect of Temperature on the Molecular Weight,^a Homogeneous Polymerization

Run no.	Init.	Polym. temp., °C.	Yield, g.	Conversion, %	$[\eta]$, dl./g.	\bar{M}	\bar{DP}
116A	CH ₃ OK	-50	1.75	73	0.039	920	17
118A		-50	—	—	0.041	980	18
120A		-35	1.70	71	0.034	770	15
119A		-15	1.65	69	0.035	800	15
117A		-5	1.45	60	0.041	980	18
108A	CH ₃ ONa	-50	3.40	85	0.040	950	18 ^b
109A		-50	3.50	88	0.039	920	17 ^b
110A		-50	1.95	81	0.029	620	12 ^c
115A		-50	1.80	75	0.038	890	17
113A		-35	1.80	75	0.029	630	12 ^d
114A		-35	2.15	89	0.037	860	16
111A		-20	1.90	79	0.031	680	13
112A		-20	1.80	75	0.030	650	12
48A		-5	1.25	52	0.031	680	13
49A		-5	1.35	56	0.031	680	13
50A		-5	1.35	56	0.041	990	19
104A	CH ₃ OLi	0	3.00	75	0.046	1150	22
105A		0	3.00	75	0.040	950	18
106A		15	2.95	74	0.046	1150	22
100A		15	2.95	74	0.040	950	18
102A		30	2.70	68	0.038	880	17
103A		30	2.65	66	0.036	830	16
107A		40	2.40	60	0.037	860	16

^a Experimental conditions: concentration of initiator CH₃OK, 10 mmoles/l., CH₃ONa, 10 mmoles/l.; CH₃OLi, 28 mmoles/l.; polymerization time, 30 min.

^b Concentration of monomer, 1.51 moles/l.; induction period, 1 min.

^c Induction period, 1.5 min.

^d Induction period, 10 sec.

polymerization temperature decreasing from -5 to -50°C . Conversion increased from 60 to 73% with decrease in temperature.

With sodium methoxide as initiator under the same conditions, there was no change in the molecular weight within experimental error. The yield increased with decrease in temperature (55–80%).

Because of the relatively lower reactivity of lithium methoxide as an anionic initiator, higher concentrations of it (0.028 mole/l.) and of monomer (1.51 mole/l.) were used, while the same methanol concentration (0.248 mole/l.) was used. The polymerizations were carried out at higher temperatures (0 – 40°), as no polymerization occurred at lower temperatures. The molecular weight remained relatively constant over this temperature range. Conversion decreased slightly with increase of temperature (75–60%). Irrespective of the polymerization temperature and of the different types of initiators, the molecular weights obtained were of the same order. See Table VI.

Heterogeneous Polymerization

In contrast to the homogeneous polymerization, there was an increase of molecular weight with decrease of temperature under heterogeneous conditions in which $\text{CH}_3\text{OK}-\text{CH}_3\text{OH}$ was catalyst. Decrease of polymerization temperature from -10 to -40° caused an increase in molecular weight from about 1100 to 4500. Induction period increased from 1.5 min. to 8 min., under comparable conditions.

A semilogarithmic plot of molecular weight versus the reciprocal of the polymerization temperature gave a straight line whose slope corresponds to a difference in activation energy between propagation and termination of 5.2 kcal./mole. See Table VII.

Effect of Alkali Metal Counterion on Molecular Weight

Homogeneous Polymerization

As seen in Table VI, the molecular weights obtained with potassium, sodium, and lithium methoxide catalysts were of the same order, irrespec-

TABLE VII
Effect of Temperature on the Molecular Weight,* Heterogeneous Polymerization

Run no.	Polym. temp., $^{\circ}\text{C}$.	$[\text{CH}_3\text{OK}]$, mmole/l.	Ind. period, min.	Yield, g.	Conversion, %	$[\eta]$, dl./g.	\bar{M}	\bar{DP}
125A	-10	41.6	4.0	2.70	68	0.047	1180	22
130A	-10	41.6	4.0	2.25	56	0.049	1250	24
16Y	-10	40.0	—	2.20	55	0.044	1080	20
140A	-25	74.0	1.5	2.50	63	0.080	2400	45
141A	-25	74.0	1.5	2.45	61	0.076	2260	42
142A	-40	74.0	8.0	2.55	64	0.128	4500	85
143A	-40	74.0	8.0	2.80	70	0.125	4350	82

* Experimental conditions: concentration of methanol, 0.496 mole/l.; concentration of monomer, 1.51 mole/l.; polymerization time, 30 min. (after induction period).

tive of monomer and catalyst concentrations and polymerization temperature.

Heterogeneous Polymerization

The molecular weights of the polyacrylonitriles obtained with sodium methoxide catalyst were considerably higher than those obtained by initiation with potassium methoxide catalyst. The molecular weights of polymers obtained by initiation with potassium methoxide were of the order of those obtained in the homogeneous system (molecular weight about 1000). It was impossible to study the effect of the lithium positive counterion because of the inability of lithium methoxide to initiate polymerization. See Table VIII.

TABLE VIII
Dependence on Molecular Weight on the Alkali Positive Counterion,* Heterogeneous Polymerization

Run no.	Init.	[Init.], mmole/l.	Ind. period, min.	Yield, g.	Conversion, %	$[\eta]$, dl./g.	\bar{M}	\bar{DP}
125A	CH ₃ OK	41.6	4.0	2.70	68	0.047	1180	22
130A		41.6	4.0	2.25	56	0.049	1250	24
131A		41.6	5.0	2.60	65	0.042	1020	19
127A	CH ₃ ONa	84.5	1.0	2.60	65	0.086	2640	50
128A		84.5	1.1	2.65	66	0.091	2830	53
129A		84.5	1.0	2.60	65	0.095	3020	57

* Experimental conditions: concentration of monomer, 1.51 mole/l.; concentration of methanol, 0.496 mole/l.; polymerization temperature, -10° ; polymerization time, 30 min. (after induction period).

DISCUSSION

Mechanisms of Homogeneous and Heterogeneous Polymerizations

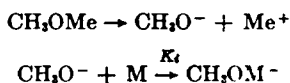
The mechanism of the present anionic homogeneous polymerization of acrylonitrile by methanolic solutions of alkali metal alkoxides was determined from the independence of molecular weights on the concentrations of monomer and initiator. The proposed mechanism is similar to that which has already been given in a previous work¹ for the anionic polymerization of acrylonitrile by aqueous solutions of quaternary ammonium hydroxides in dimethylformamide; the same independence was found there.

The expression obtained in the present work for the degree of polymerization is:

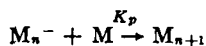
$$DP = R_p/R_t = K_p[M][M_n^-]/K_t[M][M_n^-] = K_p/K_t = K'$$

where $[M]$ and M_n^- have their usual meanings. This expression was derived from the following scheme of the polymerization steps:

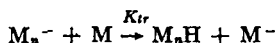
Initiation:



Propagation:



Termination, by chain transfer to monomer:



where M^- is $\text{CH}_2=\text{C}^--\text{CN}$.

The presence of terminal double bonds and ether groups in the polymers as found from their infrared spectra support the steps of initiation and termination described above.

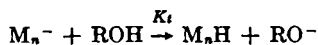
The effect of alcohol on the polymerization was investigated in order to establish the mode of termination. The independence of molecular weight on methanol concentration over a wide range of concentrations undoubtedly proves that termination is indeed by chain transfer to monomer.

Cundall et al.⁴ reported recently a similar mechanism for the anionic polymerization of acrylonitrile in dimethylformamide, initiated by sodiomalonic ester, based on kinetic studies and molecular weight determinations.

The molecular weight increased with increasing concentration of monomer, in the heterogeneous polymerization in petroleum ether catalyzed by methanolic solutions of potassium methoxide. This dependence of molecular weight on concentration of monomer was not investigated over a wide range because of experimental difficulties; for the same reason we have also not investigated the effect of methanol on the heterogeneous polymerization.

The increase of molecular weight with monomer concentration shows the absence of termination by chain transfer to monomer; accordingly, no double bonds have been found in the infrared spectra of polymers thus obtained.

It may be therefore concluded that the mechanism of the $\text{CH}_3\text{OK}-\text{CH}_3\text{OH}$ -catalyzed anionic polymerization of acrylonitrile in petroleum ether is identical with that of the intensely investigated system acrylonitrile-petroleum ether- $\text{CH}_3\text{ONa}-\text{CH}_3\text{OH}$ ³. In this system termination was by the acidic hydrogen atoms of the methanol present in the polymerization mixture. Based on this fact and on the already described steps of initiation and propagation and on termination, according to the reaction



$\overline{\text{DP}}$ is given by:

$$\overline{\text{DP}} = R_p/R_t = K_p[M][M_n^-]/[ROH] = K'[M]/[ROH]$$

Increase of molecular weight with monomer concentration, with $\text{CH}_3\text{OK}-\text{CH}_3\text{OH}$ catalyst, is in accord with this expression of $\overline{\text{DP}}$. The polymerization system acrylonitrile-polyacrylonitrile-dimethylformamide- $\text{CH}_3\text{OMe}-\text{CH}_3\text{OH}$ is a homogeneous one. The ion pairs of the growing polymer chains ---C-Li⁺, ---C-Na⁺, and ---C-K⁺ dissociate com-

pletely or almost completely in dimethylformamide, which has a very high dielectric constant (37.6) and acts also as a powerful solvating agent. Thus, only "free"⁵ polymer anions and not ion pairs exist in the polymerization mixture. The dissociated alkali cations are highly solvated by the great excess of dimethylformamide.

Kinetic rate studies of the cyanoethylation reaction of methanol in methanol-dimethylformamide mixtures, catalyzed by the derived alkali metal alkoxides, and of the anionic homogeneous polymerization of acrylonitrile by methanolic solutions of alkali metal alkoxides⁶ have shown that the methanol is completely consumed in a very fast cyanoethylation reaction before polymerization starts. This explains the results given in Table V, whereby cyanoethylation products were obtained, and an approximately equivalent amount of acrylonitrile has reacted with the methanol present in the polymerization mixture (cyanoethylation). The absence of methanol in the reaction mixture during the polymerization explains the fact that termination was by chain transfer to monomer, leading to a constant degree of polymerization independent of the methanol concentration.

The "free" growing anions whose positive counterions have been separated can be solvated by acrylonitrile molecules, owing to the acidic character of their double bond. The α -hydrogen atoms of the acrylonitrile monomers may thus be the sole free source of acidic hydrogen atoms for termination. Thus, termination is by chain transfer to monomer in accord with the experimental results and with the proposed mechanism for the homogeneous polymerization of acrylonitrile.

The phenomenon of induction period in the heterogeneous polymerization has already been discussed in a previous work.³

Effect of the Positive Alkali Counterion

Results concerning the influence of the positive counterion on the molecular weight in anionic polymerization were reported⁷ but no explanation for this influence has been given. We have shown in a previous work¹ that under comparable conditions the molecular weight of polyacrylonitrile polymerized in dimethylformamide with R_4NOH as an initiator was greater with the $(CH_3)_4N^+$ than with the $(C_2H_5)_4N^+$ positive counterion. We have explained there that increase in size or electropositivity (or both) of the positive counterion increases the ionic character of the growing ion pair, leading to a greater attraction of protons by the carbanion of the growing chain.

It may be assumed that this phenomenon will be much affected by the solvent in which the polymerization is carried out.

The positive counterion is relatively very near the growing end, in a solvent of low dielectric constant and low solvation ability. In such a medium, changes in the size and electropositivity of the positive counterion will therefore have an influence on the molecular weight, according to the above explanation. As long as the growing positive counterion is not in the

vicinity of the growing carbanion there will be no difference whether it is large or small or whether its electropositivity is different from that of another positive counterion, because it leaves behind the same free growing anion.

The experimental results given (Table VI) are in full agreement with these assumptions. There were no differences in the molecular weights of the acrylonitrile polymers obtained by the initiation with CH_3OLi , CH_3ONa , and CH_3OK in dimethylformamide.

On the other hand, petroleum ether has a very low dielectric constant (about 2) and no solvating ability, so that the ion pairs do not undergo solvation and the dissociation of the carbon metal bond $---\text{C}-\text{Me}^+$ of the ion pairs is minimal. Under these conditions any change in size and electropositivity of the positive counterion will lead to different molecular weights. Accordingly, the molecular weights of the acrylonitrile polymers obtained in petroleum ether under comparable conditions with CH_3ONa initiator were higher (3×10^3) than those obtained by initiation with CH_3OK (about 1000) (Table VIII).

The ionic dissociation of CH_3OLi in petroleum ether, and the basic strength of the methoxide anion in this partially covalent compound, are so small in comparison with the sodium and potassium methoxides, that polymerization of acrylonitrile with this initiator and investigation of the effect of the lithium positive counterion on the molecular weight were thus impossible.

"Limiting Anionic Behavior"⁵

Results have been reported concerning the effect of the positive counterion on the structure of polymers such as polyisoprene, polybutadiene, polystyrene, etc., obtained by anionic catalysts. Organolithium compounds yielded polydiolefins of a *cis*-1,4 structure only in aliphatic hydrocarbon solvents, in which the C—Li bond has a covalent character.⁸ Organolithium compounds undergo solvation in the presence of Lewis bases^{9,10} and the C—Li bond is largely converted to an ionic bond, behaving in polymerization reactions as the other more ionic organo alkali metal compounds, such as organosodium compounds.¹¹

Kelley and Tobolsky¹² showed in copolymerization studies of styrene and isoprene that the composition of the copolymers obtained with sodium as positive counterion was much less dependent on the solvent than that obtained with lithium. The separation of ions in the $---\text{C}-\text{Na}^+$ ion pair is much greater than in the $---\text{C}-\text{Li}^+$ ion pair. In passing from a dissociating solvent to a nondissociating solvent, such as benzene, the ionization of the $---\text{C}-\text{Na}^+$ ion pair is not greatly decreased as in the case of the $---\text{C}-\text{Li}^+$ ion pair. Copolymers of the same composition were obtained in tetrahydrofuran with both lithium and sodium catalysts. The $---\text{C}-\text{Li}^+$ ion pair approaches under these conditions the "limiting anionic behavior" of the $---\text{C}-\text{Na}^+$ ion pair. Potassium, when used as a catalyst for the polymerization of isoprene, yielded polyisoprene of the same structure in various solvents, while with lithium and sodium the

structure was affected by the solvent. In ethers lithium, too, shows the limiting anionic behavior, giving a polyisoprene of the same structure as that obtained with the sodium and potassium catalysts.⁵

The above-mentioned results and explanations are in full agreement with our experimental results concerning the molecular weight of the polyacrylonitriles. It was found that potassium, sodium, and even lithium methoxides yield polymers having molecular weights of the same order in dimethylformamide. It is obvious that the growing ion pairs $---C-K^+$, $---C-Na^+$, and $---C-Li^+$ show here their limiting anionic behavior in this solvent of high dielectric constant and powerful solvating properties.

In order to study the influence of different positive counterions on the molecular weights one must work under suitable conditions. A positive counterion of relatively greater size and high electropositivity will show its limiting behavior even in solvents of low dielectric constants and poor solvation ability.

Actually, this was the case when potassium methoxide was used as an initiator in petroleum ether. Molecular weights of the polymers thus obtained were of the same order (about 1000) as those obtained in dimethylformamide.

Effect of Temperature

Increase of molecular weight with decrease in polymerization temperature in anionic polymerization has been reported for various monomers, catalysts, and solvents under homogeneous and heterogeneous conditions.¹³

In the present work, too, molecular weight increased with decrease of polymerization temperature when CH_3OK-CH_3OH was used as catalyst under heterogeneous conditions in petroleum ether. An increase in temperature should increase the dissociation of carbon—alkali metal bond, making it more ionic. Increasing temperature has an influence parallel to that of increasing electropositivity of the positive counterion: both lead to a decrease in molecular weight. This decrease in molecular weight ceases when the "limiting" conditions characteristic of the particular system studied are reached. It may be thus assumed that the molecular weight of polymers obtained in a polymerization system being in its "limiting" conditions will not be affected by changes of polymerization temperature.

Indeed, in the present homogeneous polymerization in dimethylformamide, under the polymerization conditions used, the lithium, sodium, and potassium ion pairs show their limiting anionic behavior, and no change in molecular weight was observed over the polymerization temperature range used.

EXPERIMENTAL

Materials

Acrylonitrile (British Drug Houses) was purified according to the method of Bamford and Jenkins.¹⁴

Dimethylformamide (British Drug Houses) was subjected to an azeo-

tropic distillation with benzene,¹⁵ and then fractionally distilled *in vacuo* under nitrogen; the fraction boiling at 65–66° at 35 mm. was used.

Methanol (British Drug Houses), Analar grade, containing no more than 0.01% water was used without any further purification.

Oxygen-free nitrogen was used.

Petroleum ether (British Drug Houses), Analar grade, b.p. 60–80°, was refluxed over sodium wire and distilled before use.

Alkali methoxide catalysts were prepared as previously described.³

Polymerization and Isolation Procedures

Polymerization and isolation procedures for the homogeneous and heterogeneous polymerizations were the same as used before¹ for the homogeneous polymerization of acrylonitrile by aqueous solutions of quaternary ammonium hydroxides. In all experiments the overall volume of the polymerization mixture was kept constant (50 ml.). Under the homogeneous conditions in dimethylformamide, polymerization occurred in most cases instantaneously as catalyst was added, and was accompanied with an immediate development of yellow-brown color. In petroleum ether, initiation occurred after an induction period.

The purification of polymers for the molecular weight determinations and the viscosity measurements were carried out as previously described.¹

Molecular weights determined from intrinsic viscosities were calculated according to the equation of Cleland and Stockmayer¹⁶ in dimethylformamide solutions at 30°:

$$[\eta] = 2.33 \times 10^{-4} M_w^{0.75}$$

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Synopsis

The homogeneous (in dimethylformamide) and heterogeneous (in petroleum ether) polymerizations of acrylonitrile by methanolic solutions of alkali metal methoxides were compared. In the homogeneous system termination of polymerization was by chain transfer to monomer and degree of polymerization (\overline{DP}) was constant, while in the heterogeneous system termination was by the acidic hydrogen of the alcohol and \overline{DP} increased with monomer concentration according to the equation $\overline{DP} = K_p[M]/K_t[ROH]$. Decrease in temperature led to increase in molecular weight in the heterogeneous polymerization but not in the homogeneous. The positive counterion influenced the molecular weight only under the heterogeneous conditions; the more electropositive potassium gave smaller molecular weights than the sodium catalyst. Owing to the high dielectric constant of dimethylformamide and its high solvating power, the growing ion pairs $---C-Li^+$, $---C-Na^+$, and $---C-K^+$ in this solvent were fully dissociated and showed their "limiting anionic behavior," leading to the molecular weights' being constant irrespective of polymerization temperature and alkali metal counterions. Because of the high ionic character of the $---C-K^+$ bond, the potassium catalyst shows its "limiting anionic behavior" even under heterogeneous conditions, leading to molecular weights of the same order in both the homogeneous and the heterogeneous systems.

Résumé

On a comparé les polymérisations homogènes (dans le diméthylformamide) et hétérogènes (dans l'éther de pétrole) de l'acrylonitrile initiées par des solutions méthanoliques de méthoxydes des métaux alcalins. Dans le système homogène la terminaison de la polymérisation se faisait par transfert de chaîne sur le monomère et le degré de polymérisation \overline{DP} était constant; par contre dans le système hétérogène la terminaison se fait par l'hydrogène acide de l'alcool et le \overline{DP} augmente avec la concentration du monomère suivant l'équation $\overline{DP} = K_p[M]/K_t[ROH]$. Une diminution de la température provoque une augmentation du poids moléculaire dans la polymérisation hétérogène mais pas dans la polymérisation homogène. C'est uniquement dans des conditions hétérogènes que le contre-ion positif avait une influence sur le poids moléculaire. Le dérivé potassique, plus électropositif, a donné des poids moléculaires plus bas que le dérivé sodique. A cause de la constante diélectrique élevée du diméthylformamide et de son grand pouvoir de solvation, les paires d'ions $---C-Li^+$, $---C-Na^+$, $---C-K^+$ dans ce solvant sont entièrement dissociées et montrent leurs comportements anioniques limites. Ceci cause des poids moléculaires constants indépendant de la température de polymérisation et des contre-ions des métaux alcalins. A cause du caractère ionique élevé du lien $---C-K^+$ la catalyse au dérivé potassique montre un comportement anionique limite même dans des conditions hétérogènes menant à des poids moléculaires du même ordre dans les deux systèmes homogènes et hétérogènes.

Zusammenfassung

Die homogene (in Dimethylformamid) und heterogene (in Petroläther) Polymerisation von Acrylnitril mit methanolischer Alkalimethoxydlösung wurde verglichen. Im homogenen System erfolgte die Kettenbeendigung durch Übertragung zum Monomeren und DP war konstant; im heterogenen System fand jedoch der Kettenabschluss durch den sauren Wasserstoff des Alkohols statt und \overline{DP} nahm mit der Monomerkonzentration nach der Gleichung: $\overline{DP} = K_p[M]/K_t[ROH]$ zu. Temperaturabnahme führt bei der heterogenen Polymerisation, aber nicht bei der homogenen, zu einem Anstieg des Molekulargewichts. Die positiven Gegenionen hatten nur unter heterogenen Bedingungen einen Einfluss auf das Molekulargewicht; das elektropositivere Kalium lieferte kleinere Molekulargewichte als der Natriumkatalysator. Wegen der hohen Dielektrizitätskonstanten von Dimethylformamid und seines hohen Solvatisierungsvermögens sind die wachsenden Ionenpaare $---C-Li^+$, $---C-Na^+$, und $---C-K^+$ in diesem

Lösungsmittel vollständig dissoziiert und zeigen ihr "anionisches Grenzverhalten," das zu einem konstanten Molekulargewicht, unabhängig von Polymerisationstemperatur und Alkalimetall-Gegenion führt. Auf Grund des stark ionischen Charakters der $---C-K^+$ -Bindung zeigt der Kaliumkatalysator sein "anionisches Grenzverhalten" auch unter heterogenen Bedingungen und liefert Molekulargewichte von gleicher Grössenordnung in homogenen und heterogenen Systemen.

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