

Anionic Heterogeneous Polymerization of Acrylonitrile by Butyllithium. II. Effect of Lewis Bases on the Molecular Weight

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Synopsis

The heterogeneous polymerization of acrylonitrile in petroleum ether by butyllithium in the presence of Lewis bases was investigated. Molecular weights increased sharply on addition of small amounts of Lewis bases. High, maximal molecular weights were obtained at optimal values of $[\text{Lewis base}]/[\text{BuLi}] = 1-2$. Beyond this optimum a sharp decrease of molecular weights was observed. The optimal $[\text{Lewis base}]/[\text{BuLi}]$ ratio was dependent on the Lewis base used and was specifically related to the structure of the complex $\text{Li}^+\cdot\text{Lewis base}$. The effectiveness of the Lewis bases in obtaining high molecular weights was as follows: $\text{DMF} \gg \text{THF} \sim \text{dioxane} > \text{dimethylacetamide}$. A nonterminated "living" polymerization for which $\overline{\text{DP}} = R_p/R_t$ was observed with low rates of monomer addition, whereas chain transfer to monomer occurred with high rates. This behavior was qualitatively the same as that found in the absence of any Lewis base. However, under comparable conditions, higher molecular weights were always obtained in the presence of a Lewis base, except for relatively high ratios of $[\text{Lewis base}]/[\text{BuLi}]$. It was suggested that at the optimal ratio of $[\text{Lewis base}]/[\text{BuLi}]$ and beyond it, all the positive Li^+ ions in the polymerization mixture were solvated by the Lewis base. This solvation increased the nucleophilic reactivity of the carbanions. On increasing the Lewis base concentrations up to the optimal value of $[\text{Lewis base}]/[\text{BuLi}]$, R_p increased much more than R_t , which resulted in a sharp increase of molecular weights. Beyond the optimal value of $[\text{Lewis base}]/[\text{BuLi}]$ where all the positive counterions of the propagating ends were completely solvated, added Lewis-base might cause further dissociation of the associated $[\text{BuLi}]_n$, leading to a larger increase of R_t as compared to R_p , and consequently to a decrease of $\overline{\text{DP}}$.

INTRODUCTION

Lewis bases have been found to have a marked effect on the rate¹ and stereospecificity¹⁻⁴ of diene polymerizations catalyzed by lithium alkyls. The rate of the anionic polymerization of styrene by butyllithium in hydrocarbon solvents increases strongly on addition of small quantities of Lewis bases⁵⁻⁷ and is maximal at a molar ratio⁵ of $[\text{butyllithium}]/[\text{Lewis base}] = 2$, while the molecular weights are independent of the Lewis base concentration.⁵

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The presence of relatively small amounts of tetrahydrofuran decreases the molecular weights in the polymerization of styrene by phenyllithium in petroleum ether,⁸ while in the presence of large amounts, the molecular weights increase linearly with the volume per cent of tetrahydrofuran or with the dielectric constant of the polymerization mixture. In the polymerization of acrylonitrile by butyllithium in various solvents⁹ the molecular weights obtained are the highest in petroleum ether and decrease strongly on passing to solvents having a greater dielectric constant, such as tetrahydrofuran or dimethylformamide.

Accordingly it was of interest to study the effect of Lewis bases on the heterogeneous polymerization of acrylonitrile by butyllithium in petroleum ether, a system which was studied before¹⁰ in the absence of a Lewis base.

RESULTS

The molecular weights of the polyacrylonitriles obtained in petroleum ether with butyllithium as initiator, increased in the presence of only small quantities of Lewis bases, such as dimethylformamide, tetrahydrofuran, dioxane and dimethylacetamide. Acrylonitrile was added to the solution of the butyllithium and Lewis base in petroleum ether, at relatively low rates which were found¹⁰ not to affect the molecular weights.

With all the Lewis bases used the molecular weights increased sharply up to a maximum on increasing the concentration of Lewis base, (starting from [Lewis base] = 0), whereafter further addition of Lewis base caused a de-

TABLE I
Polymerization of Acrylonitrile in the Presence of Dimethylformamide^a

Run no.	$\frac{[\text{DMF}]}{[\text{BuLi}]}$	Conversion, %	$[\eta]$, dl./g.	\bar{M}_w
R13	0	87	0.986	68,390
R24	0.5	83	1.353	104,500
R25	1	83	3.013	303,400
W18	1	87	2.780	272,000
W19	1	95	3.253	335,000
R27	2	91	3.533	378,400
R28	2	87	3.806	414,000
Z1	2	—	3.986	440,000
R35	3	87	3.466	365,000
R36	3	—	3.046	307,600
D42	4	71	2.880	285,800
D43	4	84	2.930	292,000
D52	8	90	1.480	117,500
D53	8	92	1.970	172,200
D62	15	88	1.290	97,700
D63	15	83	1.430	112,200
D72	50	87	0.130	4,500

^a Experimental conditions: acrylonitrile (0.909 mole/l.) was added at a rate of 9.1 mmole/sec. to a solution of butyllithium (0.05 mole/l.) and dimethylformamide in petroleum ether. Polymerization temperature 0°C.

crease in molecular weights. The optimal values of the ratio, [Lewis base]/[butyllithium], and of the maximal molecular weights were dependent on the type of the Lewis base.

Dimethylformamide (DMF)

Of all the Lewis bases investigated, DMF was the most effective in increasing the molecular weight. On increasing [DMF]/[BuLi] from 0 to 2, the molecular weights increased sharply from 68,000 to a maximum of 440,000, and decreased gradually after (Table I and Fig. 1). At [DMF]/[BuLi] = 50 (about 20% DMF by volume) where the polymerization was homogeneous, a polymer having a molecular weight of 4,500 was obtained, which was of the order of that obtained in the homogeneous polymerization in DMF.¹¹

Tetrahydrofuran (THF)

Maximal molecular weights of about 220,000 were obtained at [THF]/[BuLi] = 2-4 (Table II and Fig. 1).

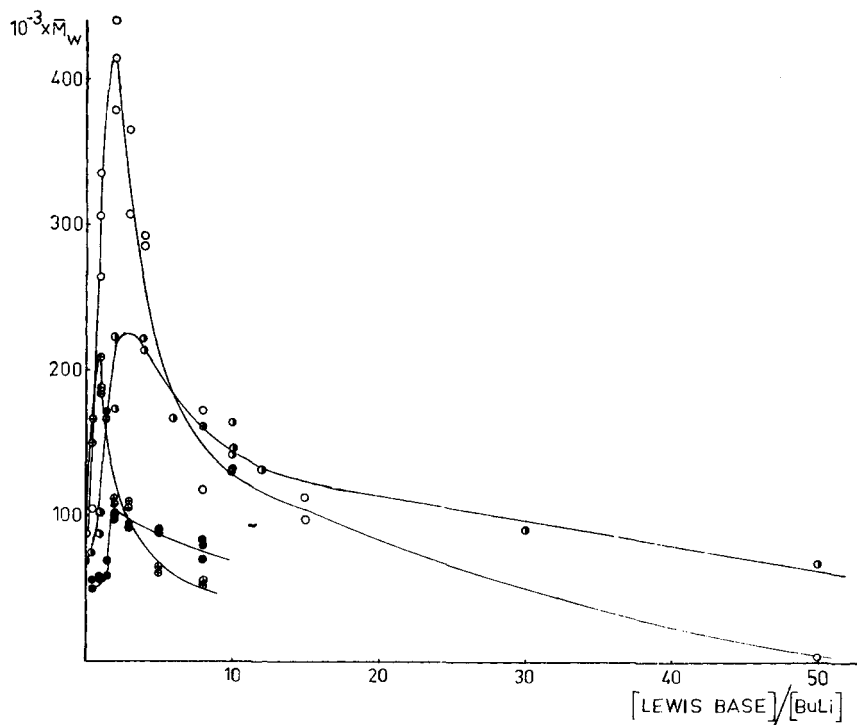


Fig. 1. Dependence of molecular weight on the ratio [Lewis base]/[BuLi]: (O) DMF; (●) THF; (⊕) dioxane; (●) dimethylacetamide.

Dioxane

Maximal molecular weights of about 200,000 were obtained with [dioxane]/[BuLi] = 1 (Table III and Fig. 1).

TABLE II
Polymerization of Acrylonitrile in the Presence of Tetrahydrofuran*

Run no.	$\frac{[\text{THF}]}{[\text{BuLi}]}$	Conversion, %	$[\eta]$, dl./g.	\bar{M}_w
R13	0	88	0.986	68,390
A4	0.5	83	1.050	74,420
K10	1	80	1.325	101,500
R29	1	84	1.180	86,900
R32	2	95	1.980	173,400
D34	2	85	2.386	222,500
K12	4	63	2.311	213,000
T24	4	75	2.375	220,900
K13	6	75	1.924	167,000
K25	8	79	1.880	161,800
P6	10	—	1.900	164,000
P7	10	80	1.746	146,000
P9	10	—	1.700	141,000
T12	10	—	1.580	130,000
T50	12	67	1.620	132,600
A17	30	88	1.227	91,600
D57	50	67	0.987	68,500
D18	80	76	0.632	37,800
D16	160	60	0.359	17,800
D11	220	40	0.335	16,200

* Experimental conditions as in Table I.

TABLE III
Polymerization of Acrylonitrile in the Presence of Dioxane*

Run no.	$\frac{[\text{Dioxane}]}{[\text{BuLi}]}$	Conversion, %	$[\eta]$, dl./g.	\bar{M}_w
I1	0.5	95	1.766	149,000
I2	0.5	—	1.920	166,300
I3	1	79	2.296	209,000
I4	1	80	2.113	188,800
I17	1	—	2.070	183,700
Z16	1	85	2.020	177,800
I5	1.5	79	1.920	166,300
I6	1.5	82	1.960	171,100
I7	2	83	1.386	107,700
I8	2	88	1.420	111,200
I9	3	80	1.393	108,400
I10	3	79	1.394	108,800
I11	5	83	0.946	64,700
I12	5	78	0.933	63,700
X20	8	90	0.848	56,100
X21	8	—	0.855	56,600

* Experimental conditions as in Table I.

Dimethylacetamide (DMAc)

In contrast to the great influence of DMF, dimethylacetamide caused but a relatively small increase in molecular weight. The maximal molecular weight (about 100,000) was obtained at $[\text{DMAc}]/[\text{BuLi}] = 2$ (Table IV and Fig. 1).

TABLE IV
Polymerization of Acrylonitrile in the Presence of Dimethylacetamide^a

Run no.	$[\text{DMAc}]/[\text{BuLi}]$	Conversion, %	$[\eta]$, dl./g.	M_w
I19	0.5	—	0.773	49,400
I20	0.5	75	0.846	55,700
I21	1.0	75	0.861	57,000
I22	1.0	80	0.867	57,600
I23	1.5	—	0.993	69,000
I24	1.5	83	0.880	58,700
I25	2	80	1.286	97,500
I26	2	—	1.300	98,800
C3	2	84	1.320	100,100
I27	3	75	1.253	94,200
I29	3	—	1.233	92,400
I30	5	82	1.193	88,100
I31	5	75	1.200	88,900
I32	8	78	1.140	82,900
I34	8	—	1.126	81,200
C9	8	90	0.990	68,700

^a Experimental conditions as in Table I.

TABLE V
Dependence of Molecular Weight on Monomer Concentration in the Presence of Dioxane^a

Run no.	$[\text{AN}]$, mole/l.	R_{addn} , mmole/sec. ^b	Conversion, %	$[\eta]$, dl./g.	\bar{M}_w	\bar{DP}	\bar{M}_w^c
Y1	0.303	3.0	87	1.180	86,900	1640	62,300
Y4	0.303	3.0	88	1.273	96,100	1813	
Y7	0.909	9.1	83	1.386	107,700	2032	76,500
I8	0.909	9.1	—	1.420	111,200	2100	
Y11	1.515	15.1	85	2.326	214,800	4052	102,300
Y13	1.515	15.1	88	2.633	253,500	4783	
Y9	2.120	21.2	—	3.013	303,400	5724	152,100
Y10	2.120	21.2	90	2.906	289,100	5455	
Y6	3.030	30.3	80	2.926	291,700	5503	194,500
Y8	3.030	30.3	84	2.746	267,900	5040	
Y5	3.303	33.0	82	2.946	294,400	5554	

^a Experimental conditions: monomer was added into a cool solution (0°C.) of butyllithium (0.05 mole/l.) and dioxane (0.1 mole/l.) in petroleum ether. Polymerization time: 15 min.

^b Rate of monomer addition.

^c Molecular weights of polymers obtained in the absence of a Lewis base.¹⁰

Dependence of Molecular Weight on Monomer and Catalyst Concentrations in the Presence of a Lewis Base

The molecular weights obtained in the presence of dioxane at $[\text{dioxane}]/[\text{BuLi}] = 2$ were directly proportional to monomer concentration in the range of 0.303–2.120 mole/l., but remained constant up to 3.030 mole/l. (Table V and Fig. 2). They were considerably higher than those obtained in the absence of a Lewis base over the whole range of the monomer concentrations investigated.

The molecular weights were inversely proportional to the catalyst concentration, this being the same as was found in the absence of any Lewis

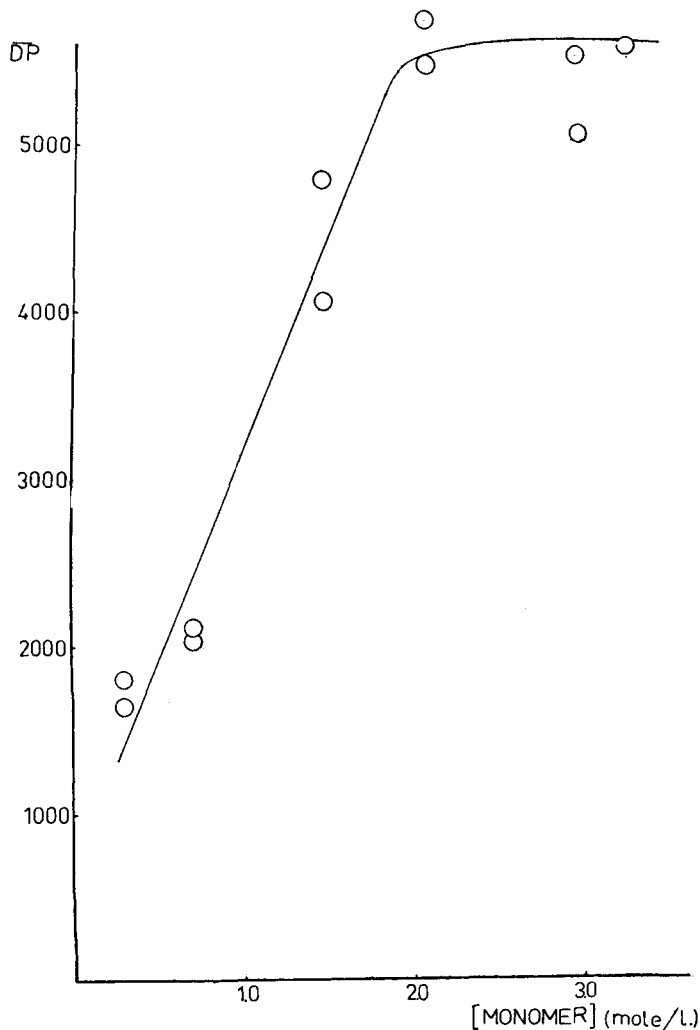


Fig. 2. Dependence of molecular weight on monomer concentration in presence of dioxane.

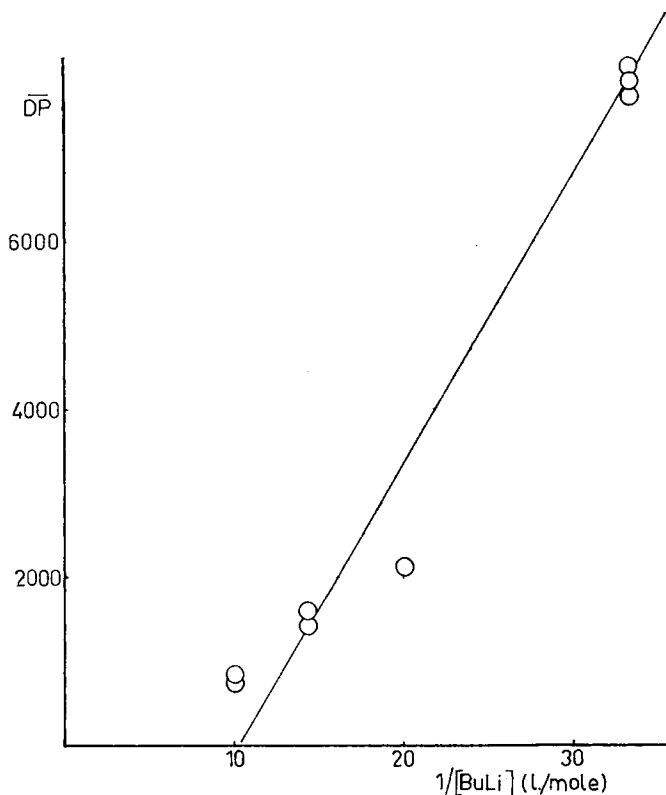


Fig. 3. Dependence of molecular weight on catalyst concentration in presence of dioxane.

TABLE VI
Dependence of Molecular Weight on Concentration of Butyllithium in the Presence of Dioxane^a

Run no.	$10^2 \times$ [BuLi], mole/l.	Conver- sion, %	$[\eta]$, dl./g.	\bar{M}_w	\bar{DP}	\bar{M}_w^b
Y21	3	—	3.753	406,400	7670	254,200
Y22	3	91	3.693	398,100	7508	
Y23	3	86	3.620	387,300	7310	
I8	5	83	1.422	111,200	2100	66,000
Y24	7	90	1.153	84,100	1592	31,600
Y25	7	84	1.086	77,800	1464	
Y26	10	79	0.666	40,500	764	24,700
Y27	10	—	0.720	44,900	845	

^a Experimental conditions: monomer (0.909 mole/l.) was added at a rate of 9.1 mmole/sec. to a solution of butyllithium and dioxane in petroleum ether. [Dioxane]/[BuLi] = 2. Polymerization temperature 0°C.

^b Molecular weights of polymers obtained under comparable conditions in the absence of dioxane.¹⁰

base, where the molecular weights were considerably lower¹⁰ (Table VI and Fig. 3).

Effect of Experimental Conditions on the Molecular Weight

The order and rate of addition of reactants to the polymerization mixture had in principle the same influence on the molecular weight as was found before¹⁰ in the absence of a Lewis base (Table VII). The molecular weights obtained in the presence of a Lewis base were higher. In the presence of THF, the lowest molecular weights were obtained when either the catalyst (runs K1, K2) or monomer (runs P1, P2) were added at the end in one portion, but were much higher when monomer was the one added at the end. The molecular weights increased from about 35,000 (runs P1, P2) to about 150,000 (runs P6, P7, P9) on decreasing the rate of addition of monomer (Table VII).

TABLE VII
Effect of Experimental Conditions on the Molecular Weight^a

Run no.	Lewis base	[Lewis base] [BuLi]	Conversion, %	R _{addn} , mmole/ sec.	[η], dl./g.	\bar{M}_w
K1	THF	10	82	b	0.266	12,000
K2	THF	10	79	b	0.266	12,000
P1	THF	10	90	c	0.626	37,330
P2	THF	10	85	c	0.573	33,190
P6	THF	10	83	9.1	1.900	164,000
P7	THF	10	92	9.1	1.746	146,000
P9	THF	10	78	9.1	1.700	141,000
W1	DMF ^d	2	94	45.5	2.566	245,000
W2	DMF ^d	2	82	45.5	2.866	283,000
W3	DMF	2	74	45.5	2.562	244,000
W5	DMF	2	93	45.5	2.680	259,000
W6	DMF	2	88	1.5	3.140	321,000
W7	DMF	2	84	1.5	3.873	423,000

^a Experimental conditions: monomer (0.909 mole/l.) was added to a solution of butyllithium (0.05 mole/l.) and the Lewis base in petroleum ether. Polymerization temperature 0°C.

^b Butyllithium was added in one portion to the solution of monomer and Lewis base in petroleum ether.

^c Monomer was added in one portion.

^d Polymerization temperature -20°C.

With the most effective Lewis base investigated, DMF, polymers having high molecular weights were obtained even at high rates of monomer addition (Table VII, runs W1, W2, W3, W5). On decreasing the rate of addition of monomer there was also an increase in the molecular weight (runs W6, W7).

Some polymerizations were carried out in the presence of diethyl ether and diethylamine. Under comparable conditions, at [diethyl ether]/[Bu-

Li] = 2, a polymer having a molecular weight of 296,000 was obtained, and with [diethylamine]/[BuLi] = 2 a molecular weight of 194,000 was obtained.

DISCUSSION

The main results of the present work were the following: (a) \overline{DP} was linearly dependent on [monomer] and on $1/[\text{BuLi}]$ at relatively low rates of monomer addition; (b) molecular weights increased to a certain maximum with increasing [Lewis base], at an optimal value of [Lewis base]/[BuLi] ratio.

This dependence of \overline{DP} on [monomer] and [catalyst] showed that the polymerization was of the "living" type¹² at the low rates of monomer addition employed. At relatively high rates, low molecular weights were obtained. On addition of the initiator in one portion to the solution of acrylonitrile and THF in petroleum ether, in the case of which all the monomer was present at the start of the polymerization and its rate of addition might therefore be considered the maximal (Table VII, runs K1, K2), the molecular weight was the low limiting one—about 12,000. Lower rates of monomer addition resulted in a large increase of the molecular weight (Table VII, runs P6, P7, P9). In principle, this behavior as regards the dependence of \overline{DP} on the experimental conditions was the same as in the absence of a Lewis base,¹⁰ showing that its presence did not affect the general mechanism of the polymerization.

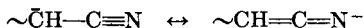
The present polymerization proceeded with two simultaneously operating mechanisms. At high momentary concentrations of monomer, termination by chain transfer to monomer was dominant, leading to low molecular weights; at low concentrations, non-terminated "living" polymerization was dominant. The only effect of the Lewis base present was to increase the molecular weights.

Lithium alkyls exist in nonpolar solvents as associates $(\text{BiLi})_n$,¹³⁻¹⁶ having a low nucleophilic reactivity because of this association.¹⁵ Basic solvents cause disruption of associated lithium alkyls^{15,17} and of other alkali metal organic compounds. Rates of reactions in nonpolar solvents involving butyllithium¹⁵ and other alkali metal alkyls¹⁸⁻²² were therefore highly accelerated on addition of basic solvents such as ethers, amines, amides, etc. Lewis acid-base solvation of the alkali metal cation accounted for this rate-accelerating effect of Lewis bases.¹⁸⁻²⁵

Three general species of lithium alkyls were mainly present in the presently investigated polymerization system: polymeric butyl-lithium, monomeric butyllithium (which is the effective initiator^{6, 26}, and $\sim\text{CH}(\text{CN})\text{Li}^+$ ion-pairs of growing chain ends. Also, dimeric growing ends inactive in propagation might be present, as was found in the case of polyisoprene in hydrocarbon solvents,²⁷ but no experimental evidence was given for this. In this connection it might be mentioned that the polymer structure affected the degree of association of "living" lithiated growing ends.

Thus, "living" polystyrene was less associated than "living" polyisoprene and polybutadiene.^{28,29} In the present polymerization system, the per cent ionic character of all the above-mentioned species of lithium alkyls was an important factor, since they participated in the initiation and propagation steps of the polymerization. It was therefore obvious that both dielectric constant and solvation would affect the rates of these steps. It was also obvious that increasing the degree of depolymerization of $(\text{BuLi})_n$ would increase the rate of initiation. This could be accomplished by increasing the dielectric constant.

However the small amounts of the Lewis bases in the presence of which high, maximal molecular weights were obtained, could make no measurable difference in the dielectric constant. It follows, therefore, that essentially solvation factors were responsible for the relatively high molecular weights obtained at $[\text{Lewis base}]/[\text{BuLi}]$ ratios of 1-2 (Fig. 1), and in view of the known structures of Lewis bases—solvated alkali metal cations,^{5,6,18,21,22,26} might reasonably be assumed that all the positive lithium ions in the polymerization mixture, including those of $(\text{BuLi})_n$, were solvated by the Lewis base, thus increasing the effective negative charge of the carbanions of both the $\sim\text{CH}_2\text{Li}^+$ and $\sim\text{C}(\text{CN})\text{Li}^+$ ion-pairs, and with it the rates of the initiation and propagation reactions. The solvation is greater with the propagating ion-pair since it is resonance stabilized, i.e., and is more



ionizable.³⁰⁻³² Consequently, R_p would increase more than R_t on carrying out the polymerization in the presence of a small amount of a Lewis base. Since the polymerization was of the "living" type where $\overline{\text{DP}}$ could be given by $\overline{\text{DP}} = R_p/R_t$ (provided that the rate of initiation was relatively low and catalyst was slowly consumed), this explains why relatively high molecular weights were obtained under such conditions.

In view of this explanation it might be concluded that up to the optimal $[\text{Lewis base}]/[\text{BuLi}]$ ratios (Fig. 1), R_p increased much more than R_t under the influence of the Lewis base. Just beyond the optimal $[\text{Lewis base}]/[\text{BuLi}]$ ratios, where there was a maximal possible solvation of the Li^+ ions,^{5,6,18,21,22,26} and where the Lewis base would be in small excess not affecting the dielectric constant, the relatively sharp decrease of molecular weights found could be accounted for by a larger dissociation of $(\text{BuLi})_n$ caused by this excess, thus increasing R_t . R_p would not be appreciably affected, since the propagating chain ends were already completely solvated. As a result the value of R_p/R_t would be relatively smaller, leading to a decrease in molecular weights.

At the high $[\text{Lewis base}]/[\text{BuLi}]$ ratios where the molecular weights became relatively small and tended to level off, there was already a large change in the dielectric constant of the polymerization medium. The influence of the dielectric constant would be of considerable importance, since all the lithium alkyls had undergone maximum solvation. An analogous levelling off of the polymerization rate with relatively high ratios

of $[\text{THF}]/[\text{BuLi}]$ after a sharp increase with low ratios was already found for the butyllithium-initiated polymerization of styrene in benzene.^{5, 7} The fact that the molecular weights decreased and became relatively low showed that R_t increased more than R_p . This might be due at least in part to a maximal depolymerization of polymeric butyllithium $(\text{BuLi})_n$, caused by the relatively high dielectric constant of the Lewis bases. In addition, the low molecular weights obtained at the very high ratios of $[\text{Lewis base}]/[\text{BuLi}]$ investigated (Table II, runs D16, D11) approached the order of those obtained under chain transfer to monomer conditions (Table VII, runs K1, K2), indicating that these low molecular weights obtained might be due to an appreciable increase in the extent of the simultaneously operating chain transfer mechanism although low rates of monomer addition were used.

In support of these considerations concerning the effect of the dielectric constant, it was found for the butyllithium-initiated polymerization of acrylonitrile in various solvents⁹ that the molecular weights obtained were much higher when the polymerization was carried out in petroleum ether (dielectric constant⁸ = 1.915) than when THF (dielectric constant³³ = 7.58) or DMF (dielectric constant³⁴ = 37.6) were used as polymerization solvents.

It was reported that rates of anionic polymerizations in nonpolar solvents were highly accelerated when carried out in the presence of small amounts of Lewis bases^{28, 35} ($[\text{Lewis base}]/[\text{BuLi}] = 0-2$).^{5-7, 26} It is our opinion that an increased rate of the propagation step was an important factor in the acceleration of the polymerization rate observed under such conditions. Also Bywater and Worsfold⁷ in a kinetic study of the butyllithium-initiated polymerization of styrene in benzene in the presence of THF, pointed out that the rate of polymerization increased sharply on increasing the $[\text{THF}]/[\text{BuLi}]$ ratio up to 10, whereafter a sharp decrease of rate was observed. They suggested that this sharp increase of polymerization rate was due mainly to an increase in the rate of propagation caused by formation of a reactive monoetherate complex, $\sim\text{CH}(\text{C}_6\text{H}_5)\text{Li}^+\cdot\text{THF}$.

Such behavior in the presence of small amounts of Lewis bases was also reported for nucleophilic substitution reactions involving butyllithium¹⁵ and other alkali metal alkyls.^{20, 21}

Optimal $[\text{Lewis base}]/[\text{BuLi}]$ ratios were suitable for obtaining high molecular weights, high rates of anionic polymerizations^{5, 6, 26} and for obtaining stereospecific characteristics of polymers in anionic polymerization.³ Thus, for example, in hydrocarbon solvents when butyllithium was used as initiator and THF as Lewis base, maximal molecular weights of polyacrylonitriles (Table II), maximal rates of polymerization^{5, 6, 26} and a minimal content of polyisoprene of 1,4-structure³ were all obtained at the same ratio of $[\text{THF}]/[\text{BuLi}] = 2$. This was strongly in favor of the existence of one common THF-solvated propagating ion-pair of the structure $\sim\text{C}^-\text{Li}^+\cdot 2\text{THF}$.^{5, 6} for these systems. When diethers such as monoglyme or dioxane were used as basic additives, the Li^+ ion was solvated on

the average by only one molecule of an ether.^{21,22} This explains why in the case of dioxane, maximal molecular weights were obtained at $[\text{dioxane}]/[\text{BuLi}] = 1$ (Table III and Fig. 1).

The differences found in the optimal molecular weights obtained in the presence of the various Lewis bases investigated should be due mainly to the relative polarity and the steric requirements of the Lewis base solvated growing ends $\sim\text{CH}(\text{CN})\text{Li}^+$. (Lewis base_n). This polarity cannot be correlated solely with the basic strength of the Lewis base, as steric factors were found to have a major influence.^{36,37} The highest optimal molecular weights were obtained with DMF, which is known to have a strong solvating power for cations. The relatively low optimal molecular weights obtained with dimethyl-acetamide may be due to steric factors involved in complex formation.

The "living" mechanism found (Tables V and VI) with relatively low $[\text{Lewis base}]/[\text{BuLi}]$ ratios, and the dependence of molecular weight on the rate of monomer addition (momentary concentration of monomer) (Table VII) in the presence of a Lewis base, were qualitatively the same as were found in its absence.¹⁰ This might lead to the conclusion that the solvation of the Li^+ counterion by the Lewis base had in principle no effect on the mechanism of the polymerization and did not interfere appreciably with the solvation of the carbanion of the propagating ion-pair by monomer molecules which was the first stage in the two-stage propagation¹⁰ in the present polymerization system.

In this connection it may be mentioned that for the homogeneous butyllithium-initiated polymerization of styrene in benzene in the presence of THF, Bywater and Worsfold⁷ found the order in butyllithium to be one-half at low $[\text{THF}]/[\text{BuLi}]$ ratios, which indicated that the chain ends were ion-pairs associated as dimers. Accordingly in the presently investigated polymerization of acrylonitrile, it might well be assumed that the Lewis base-solvated propagating ends were ion-pairs at least at the low $[\text{Lewis base}]/[\text{BuLi}]$ ratios. This assumption may be further strengthened by the fact that the polymerization system was heterogeneous.

EXPERIMENTAL

The purification of acrylonitrile, preparation of catalyst, polymerization procedure, and the determination of intrinsic viscosities were as described in part I.¹⁰ Dioxane was purified similarly to tetrahydrofuran⁸ and dimethylacetamide similarly to dimethylformamide.⁸

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Résumé

On a étudié la polymérisation hétérogène de l'acrylonitrile dans l'éther de pétrole par le butyl-lithium en présence de bases de Lewis. Les poids moléculaires augmentent fortement par addition de petites quantités de bases de Lewis. On a obtenu des poids moléculaires élevés et maxima pour des valeurs optima du rapport [base de Lewis]/[BuLi] = 1-2. Au-delà de cet optimum, on observe une nette diminution des poids moléculaires. Le rapport optimum [base de Lewis]/[BuLi] dépend de la base de Lewis utilisée et est lié spécifiquement à la structure du complexe Li⁺.base de Lewis. L'effica-

cit  des bases de Lewis pour l'obtention de poids mol culaires  lev s est la suivante: DMF \gg THF \sim dioxane $>$ dim thylac tamide. On a observ  une polym risation "vivante" dans laquelle $\overline{DP} = R_p/R_t$ pour de faibles vitesses d'addition de monom re, tandis qu' un transfert de cha ne sur monom re se produit   des vites es  lev es. Ce comportement est qualitativement le m me que celui trouv  en l'absence de toute base de Lewis. Cependant, dans des conditions comparables des poids mol culaires plus  lev s sont toujours obtenus en pr sence d'une base de Lewis, except  pour des rapports relativement  lev s [base de Lewis]/[BuLi]. On a sugg r  que pour un rapport optimum [base de Lewis]/[BuLi] et au-del  de celui-ci, tous les ions positifs Li^+ dans le m lange polym risant sont solvat s par la base de Lewis. Cette solvation augmente la r activit  nucl ophile des carbonions. En augmentant les concentrations en base de Lewis jusqu'  la valeur optimum du rapport [base de Lewis]/[BuLi], R_p augmente beaucoup plus que R_t , ce qui se traduit par une forte augmentation des poids mol culaires. Au-del  de la valeur optimum du rapport [base de Lewis]/[BuLi] o  tous les contre-ions positifs des fins de cha nes en croissance sont compl tement solvat s, l'addition de base de Lewis peut causer une nouvelle dissociation des $[BuLi]_n$ associ s, conduisant   une plus importante augmentation de R_t compar    R_p et par cons quent   une diminution du \overline{DP} .

Zusammenfassung

Die heterogene Polymerisation von Acrylnitril in Petrol ther durch Butyllithium in Gegenwart von Lewisbasen wurde untersucht. Die Molekulargewichte nahmen bei Zusatz kleiner Mengen von Lewisbasen scharf zu. Maximale Molekulargewichte wurden bei optimalen Werten von $[Lewisbase]/[BuLi] = 1-2$ erhalten. Oberhalb dieses Optimums wurde eine scharfe Abnahme des Molekulargewichts beobachtet. Das optimale Verh ltnis von $[Lewisbase]/[BuLi]$ hing von der verwendeten Lewisbase ab und stand in spezifischer Beziehung zur Struktur des Komplexes Li^+ -Lewisbase. Die Wirksamkeit der Lewisbasen bei der Erzielung hoher Molekulargewichte folgende Reihenfolge: DMF \gg THF \sim Dioxan $>$ Dimethylacetamid. Bei geringer Geschwindigkeit des Monomerzusatzes wurde eine abbruchsfreie "living"-Polymerisation mit $\overline{DP} = R_p/R_t$ beobachtet, w hrend bei hoher Geschwindigkeit Ketten bertragung zum Monomeren auftrat. Dieses Verhalten war qualitativ dem in Abwesenheit einer Lewisbase gefundenen gleich. Es wurden jedoch unter vergleichbaren Bedingungen in Gegenwart einer Lewisbase immer h here Molekulargewichte erhalten, ausgenommen f r relativ hohe Werte des Verh ltnisses $[Lewisbase]/[BuLi]$. Es wird angenommen, dass beim optimalen Verh ltnis $[Lewisbase]/[BuLi]$ und dar ber alle positiven Li^+ -Ionen in der Polymerisationsmischung durch die Lewisbase solvatisiert werden. Diese Solvatisierung nahm mit der nukleophilen Reaktivit t des Carbanions zu. Beim Anstieg der Lewisbasenkonzentration zum optimalen Wert von $[Lewisbase]/[BuLi]$ nahm R_p viel st rker zu als R_t , was zu einer scharfen Molekulargewichtszunahme f hrte. Oberhalb des optimalen Wertes von $[Lewisbase]/[BuLi]$, wo alle positiven Gegenionen der wachsenden Enden vollst ndig solvatisiert waren, kann der Zusatz einer Lewisbase eine weitere Dissoziation des assoziierten $[BuLi]_n$ verursachen und zu einer st rkeren Zunahme von R_t im Vergleich zu R_p und damit zu einer Abnahme von \overline{DP} f hren.

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