Anionic Heterogeneous Polymerization of Acrylonitrile by Butyllithium.   I

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Synopsis

The anionic heterogeneous polymerization of acrylonitrile in petroleum ether by *n*-butyllithium was studied under various experimental conditions.   The dependence of the molecular weight on the total concentrations of the monomer and initiator was strongly affected by the momentary concentration of monomer in the polymerization mixture and by the order of their addition to it.   Two polymerization mechanisms were found to operate simultaneously.   When monomer was added to the catalyst solution at low rates, nonterminated "living" polymerization was essentially dominant, as was evident from the linear dependence of $\overline{DP}$ on [monomer] and 1/[BuLi].   Under such conditions $\overline{DP}$ was independent of the rate of monomer addition.   Chain transfer to monomer was the dominant mechanism at high rates of monomer addition, as was evident from the independence of the degree of polymerization of both monomer and initiator concentrations.   At intermediate rates of monomer addition the extent of each of the two mechanisms was appreciable, and $\overline{DP}$ increased with decreasing the rate of monomer addition.   A two-stage propagation step in which the growing carbanion of the $\sim\!\!\sim C^-Li^+$ ion-pair was solvated by monomer, was suggested to be responsible for the dependence of the polymerization mechanism on the momentary concentration of monomer in the polymerization mixture.

INTRODUCTION

In the heterogeneous polymerization of acrylonitrile in petroleum ether initiated by butyllithium, termination was by chain transfer to monomer,[1] but no evidence for such a termination was found when the polymerization was carried out in toluene[2] at $-78°C$.   Different types of termination were found for the homogeneous polymerization of acrylonitrile in dimethylformamide (DMF) initiated by butyllithium,[3] depending on the catalyst concentration: namely, chain transfer to monomer, monomolecular termination, and nonterminated "living" polymerization.   In anionic polymerizations of acrylonitrile carried out in the absence of acidic substances, termination was by chain transfer to monomer.   This was the case with alkali metal alkoxide initiators in DMF,[4] metal ketyls in tetrahydrofuran,[5] and sodiomalonic ester in DMF.[6]

At present the mechanism of the anionic polymerization of acrylonitrile is not clear enough, since different mechanisms operate, irrespective of the

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type of initiator and solvent used and of the heterogenity of homogenity of the polymerization mixture.[1-6]

In the present work the anionic heterogeneous polymerization of acrylonitrile in petroleum ether by n-butyllithium was studied to find out the different polymerization mechanisms operating under various experimental conditions.

RESULTS

Dependence of Molecular Weight on Rate of Addition of Monomer

The dependence of molecular weight on the rate of addition of monomer (R_{addn}) to the polymerization mixture consisting of a solution of butyllithium in petroleum ether, was investigated at 0°C. Four distinct regions of $\overline{DP}$ existed, depending on R_{addn} (Table I and Fig. 1) as follows. (a) At relatively very high addition rates of monomer, polymers having relatively low and essentially constant $\overline{DP}$ values were obtained. These limiting $\overline{DP}$ values (300–400) were obtained on adding the initiator to the monomer in petroleum ether (J24, J25, J26, Table I). In these experiments the value of R_{addn} might be considered the highest possible, since all the monomer was present at the start of the polymerization. (b) On lowering R_{addn} in the range of about 200–40 mmole/sec., $\overline{DP}$ increased continuously. The increase in the range of 200–100 mmole/sec. was relatively small. It may be noted that even when the monomer was added in one portion (runs M1, N1, Table I), the molecular weight obtained was not as low as the limiting values (runs J24, J25, J26). (c) On further lowering R_{addn} in the range of 40–3 mmole/sec., $\overline{DP}$ was essentially constant, independent of R_{addn} and relatively high ($\overline{DP}$ = 1100–1400). (d) At lower rates of addition, the molecular weights decreased.
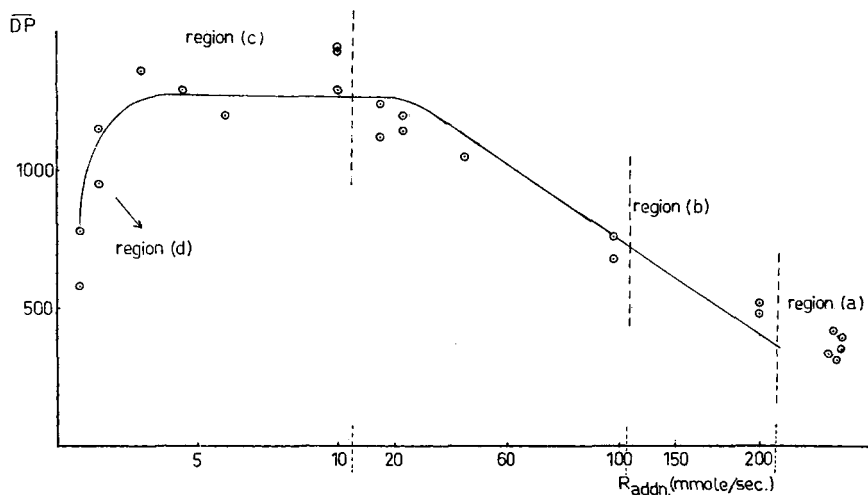

Fig. 1. Dependence of molecular weight on the rate of addition of monomer.

The dependence of $\overline{DP}$ on R_{addn} was influenced by the temperature of the polymerization (Table I, Series B). Thus at $-55°C.$, $\overline{DP}$ remained constant on varying R_{addn} from 200 to 10 mmole/sec.

TABLE I
Dependence of Molecular Weight on the Rate of Addition of Monomer[a]

Run no.	R_{addn}, mmole/sec.	Yield, %	$[\eta]$, dl./g.	$\overline{M}_w$	$\overline{DP}$
Series A[b]					
J23	c	80	0.360	17,800	336
J24	c	85	0.373	18,700	349
J25	c	85	0.426	22,300	419
J26	c	85	0.413	21,400	392
J27	c	87	0.340	16,500	312
M1	200[d]	—	0.510	27,500	519
N1	200[d]	—	0.470	25,400	479
J10	98	83	0.613	36,300	682
J11	98	87	0.666	40,500	764
B23	45	—	0.845	55,700	1051
J12	23	90	0.933	63,500	1196
J13	23	83	0.893	60,100	1138
J14	15	87	0.961	66,000	1242
J15	15	83	0.880	58,700	1118
B3	10	83	1.075	76,500	1443
R13	10	89	0.986	68,400	1291
R14	10	85	1.065	75,800	1430
J16	6	87	0.933	63,500	1198
B33	4.5	—	0.985	68,300	1289
B35	3	—	1.026	72,100	1360
B36	1.5	—	0.796	50,600	955
B37	1.5	—	0.906	61,100	1151
B38	0.8	88	0.540	30,600	577
B39	0.8	85	0.676	41,350	780
Series B[e]					
J30	200[d]	83	1.373	106,450	2007
J31	200[d]	95	1.373	106,450	2007
J28	10	80	1.326	101,600	1918
J29	10	90	1.426	111,800	2109

[a] Experimental conditions: acrylonitrile (0.909 mole/l.) was added at different rates to a solution of butyllithium (0.05 mole/l.) in petroleum ether.
[b] Series A: polymerization temperature 0°C.
[c] Butyllithium (0.05 mole/l.) was added to a solution of acrylonitrile (0.909 mole/l.) in petroleum ether.
[d] Monomer was added in one portion.
[e] Series B: polymerization temperature $-55°C.$

These results indicated that the effect of the rate of addition of monomer and of the order of addition of reagents on $\overline{DP}$, should be considered in investigating the dependence of $\overline{DP}$ on the variables of the polymerization system. In order to eliminate this factor, suitable R_{addn} of monomer, which did not affect the molecular weights (region c) were used.

Dependence of Molecular Weight on Rate of Addition of Initiator

The molecular weights were independent of the rate of addition of butyllithium to the monomer in petroleum ether at 0°C., but increased largely on decreasing it at −50°C. (Table II).

TABLE II
Dependence of Molecular Weight on the Rate of Addition of Initiator[a]

Run no.	R_{addn}, mmole/sec.	Yield, %	$[\eta]$, dl./g.	$\bar{M}_w$	$\overline{DP}$
Series A[b]					
J26	5.0	83	0.413	21,400	392
J27	5.0	87	0.340	16,500	312
J23	0.5	80	0.360	17,800	336
J24	0.25	83	0.373	18,700	349
J25	0.25	85	0.426	22,300	419
Series B[c]					
J35	5.0	83	0.593	34,600	652
J37	5.0	90	0.686	41,600	785
J34	0.25	70	1.180	86,900	1640
J36	0.25	87	1.213	90,100	1700

[a] Experimental conditions: butyllithium (0.05 mole/l.) in petroleum ether was added to acrylonitrile (0.909 mole/l.) in petroleum ether.
[b] Series A: polymerization temperature 0°C.
[c] Series B: polymerization temperature −50°C.

Dependence of Molecular Weight on Monomer Concentration

When the monomer was added to the catalyst solution at rates which were found not to affect the molecular weight (3–30 mmole/sec.), $\overline{DP}$ was directly proportional to monomer, except at relatively high concentrations (3.33 mole/l.) (Table IIIA and Fig. 2). But when it was added at relatively high rates, the molecular weights were essentially constant and independent of monomer concentration (Table IIIB).

Dependence of Molecular Weight on Catalyst Concentration

The molecular weights were inversely proportional to the butyllithium concentration and increased about tenfold on decreasing its concentration in the range of 0.1–0.02 mole/l. (Table IV and Fig. 3). Molecular weights as high as 330,000 were obtained at the lowest catalyst concentration and leveled off at the highest one.

Dependence of Molecular Weight on [Acrylonitrile]/[Butyllithium]

Although $\overline{DP}$ was directly proportional to monomer and inversely proportional to initiator (Tables III and IV), different values of $\overline{DP}$ were obtained for the same (or comparable) values of [acrylonitrile]/[butyllithium], under comparable experimental conditions. The molecular weights were lower with the higher monomer concentrations (Table V).

TABLE III
Dependence of Molecular Weight on Monomer Concentration[a]

Run no.	[Monomer], mole/l.	R_{addn} of monomer, mmole/sec.	Yield, %	$[\eta]$, dl/g.	$\bar{M}_w$	$\overline{DP}$
Series A						
B1	0.303	3	75	0.906	61,100	1151
B2	0.303	3	87	0.920	62,300	1175
R1	0.303	3	95	0.933	63,500	1198
B3	0.909	10	83	1.075	76,500	1443
R13[b]	0.909	10	87	0.986	68,400	1291
R14	0.909	10	83	1.065	75,800	1430
B6[c]	1.515	15	87	1.333	102,300	1930
R15	1.515	13	87	1.298	98,800	1864
Y19	1.515	15	—	1.533	125,000	2358
B9	2.121	21	80	1.860	159,200	3004
B10	2.121	21	—	1.653	136,100	2568
R6	2.121	21	87	1.794	152,100	2870
B11	3.030	34	78	1.920	166,300	3138
B12	3.030	30	—	2.160	194,500	3669
B20	3.030	30	—	2.313	213,300	4024
R8	3.030	30	85	2.144	192,800	3640
Y17	3.030	25	—	2.420	226,500	4274
R9	3.330	34	78	1.860	159,500	3010
R10	3.330	34	—	1.940	168,700	3183
Series B						
B13	0.303	30	75	0.826	53,900	1020
B14	0.303	30	—	0.906	61,100	1158
J10	0.909	98	83	0.613	36,300	685
J11	0.909	98	87	0.666	40,500	764
B16	1.515	152	82	0.993	69,000	1303
B18	3.030	300	75	0.820	53,600	1013
B19	3.030	300	—	0.693	42,700	805

[a] Experimental conditions: monomer was added at various rates to the catalyst (0.05 mole/l.) solution in petroleum ether. Reaction temperature 0°C.

[b] The same experiment stopped immediately after addition of monomer gave 78% conversion.

[c] The same experiment stopped immediately after addition of monomer gave 81% conversion.

Thus, for example, with [acrylonitrile]/[butyllithium] = 42–45, a molecular weight of about 300,000 was obtained with [acrylonitrile] = 0.909 mole/l. (runs B24, B25, I15), whereas a molecular weight of about 150,000 was obtained with [acrylonitrile] = 2.121 mole/l. (runs R6, B9, B10).

Effect of Temperature on the Molecular Weight

$\overline{DP}$ increased with lowering the temperature (Tables I, II), this being characteristic of other anionic polymerizations. The extent of this increase was affected by the rates of addition of reagents to the polymerization mixture. A relatively large increase of molecular weight was observed
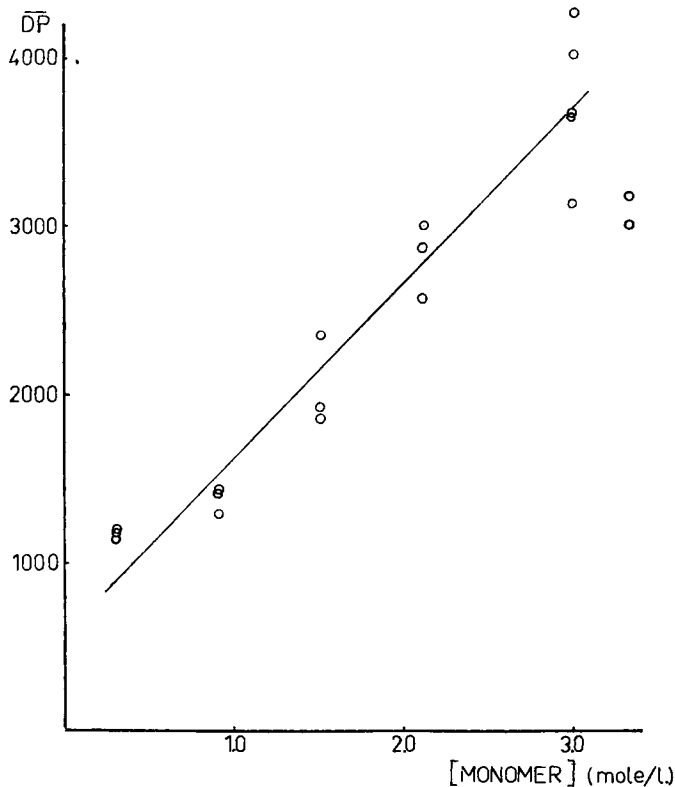
Fig. 2. Dependence of molecular weight on monomer concentration.

when monomer was added at high rates (compare runs M1, N1 with runs J30, J31, Table I), while its change was smaller at low rates (compare runs B3, R13, R14 with runs J28, J29, Table I).

The reverse was found when the initiator was added to the monomer solution. On lowering the temperature from 0 to −50°C., the molecular weights increased from 20,000 to 40,000 when the rate of addition of catalyst was 5 mmole/sec., and from 20,000 to 90,000 when the rate was 0.25 mmole/sec. (Table II).

DISCUSSION

The main observation of the present work was that the dependence of the molecular weight on the concentrations of monomer and catalyst was considerably affected by the rate and the order of their addition to the polymerization mixture.

It will be shown that the experimental results are consistent with two different mechanisms for the presently investigated polymerization of acrylonitrile, namely, nonterminated "living" polymerization and polymerization involving chain transfer to monomer. The fact that at rel-
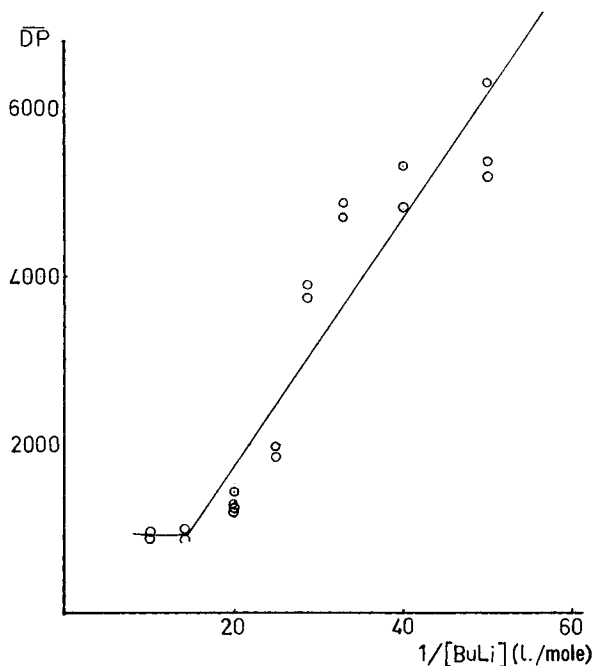
Fig. 3. Dependence of molecular weight on catalyst concentration.

atively low rates of monomer addition $\overline{DP}$ was directly proportional to [monomer] (Table III and Fig. 2) and inversely proportional to [initiator] (Table IV and Fig. 3) is in accordance with a nonterminated "living" polymerization.[7]

Termination by chain transfer to monomer results in a constant $\overline{DP}$ ($=k_p/k_{tr}$), independent of the concentrations of monomer and catalyst.[8] Molecular weights were constant under the following experimental conditions: (A) when the initiator was added in one portion or at different rates to the monomer solution (Table III, A); (B) when the monomer was added in one portion or at high rates to the initiator solution (Tables I, IIIB). It follows that chain transfer to monomer was dominant only when relatively high monomer concentrations were present during the polymerization. Deviations from the above experimental conditions resulted in the formation of polymers whose $\overline{DP}$ was not constant but proportional to the concentrations of monomer and catalyst (Tables IIIA and IV).

The constant $\overline{DP}$ found in previous anionic polymerizations of acrylonitrile,[1,3−6,8] was a result of carrying out the polymerizations exclusively according to the above-mentioned experimental conditions (A).

The dependence of $\overline{DP}$ on the rate of addition of monomer, (Fig. 1) reflects the different operating mechanisms.   In region (a) of the curve, which represents very high addition rates, chain transfer to monomer is the sole mode of termination.   The low limiting values of $\overline{DP}$ (300–400) in this

TABLE IV
Dependence of Molecular Weight on Catalyst Concentration[a]

Run no.	[BuLi], mmole/l.	Yield, %	[η], dl/g.	$\bar{M}_w$	$\overline{DP}$
I15	20	79	2.873	284,000	5355
B24	20	80	3.240	334,200	6306
B25	20	—	2.806	275,400	5196
R11	25	83	2.860	283,600	5350
R12	25	87	2.653	255,900	4828
B26	30	—	2.673	258,200	4873
B27	30	—	2.640	254,100	4790
I17	35	83	2.266 ·	207,500	3915
I18	35	—	2.193	198,600	3740
I37	40	70	1.300	98,800	1864
I38	40	—	1.353	104,500	1978
J14	50	83	0.961	66,000	1243
J16	50	—	0.933	63,500	1199
B3	50	—	1.073	76,500	1442
R13	50	89	0.986	68,400	1291
R14	50	83	1.065	75,800	1430
B28	70	—	0.460	24,700	466
B29	70	90	0.553	31,600	596
B30	100	—	0.460	24,700	466
B31	100	95	0.527	29,400	553

[a] Experimental conditions: acrylonitrile (0.909 mole/l.) was added at a rate of 10 mmole/sec. to the butyllithium in petroleum ether. Polymerization temperature 0°C.

TABLE V
Dependence of Molecular weight on [Acrylonitrile]/[Butyllithium][a]

Run no.[b]	[Acrylonitrile], mole/l.	[BuLi], mole/l.	$\dfrac{[AN]}{[BuLi]}$	[η], dl/g.	$\bar{M}_w$	$\overline{DP}$
I15	0.909	0.02	45.4	2.873	284,000	5355
B24	0.909	0.02	45.4	3.240	334,200	6306
B25	0.909	0.02	45.4	2.806	275,400	5196
B9	2.121	0.05	42.1	1.860	159,200	3004
R6	2.121	0.05	42.1	1.794	152,100	2870
B10	2.121	0.05	42.1	1.653	136,100	2568
B26	0.909	0.03	30.3	2.673	258,200	4873
B27	0.909	0.03	30.3	2.640	254,100	4790
B6	1.515	0.05	30.3	1.333	102,000	1930
Y19	1.515	0.05	30.3	1.533	125,000	2358
R4	0.606	0.05	12.1	1.026	72,100	1358
B28	0.909	0.07	13.0	0.460	24,700	466
B29	0.909	0.07	13.0	0.553	31,600	596
B1	0.303	0.05	6.1	0.906	61,000	1152
R2	0.303	0.05	6.1	0.920	62,300	1175
B30	0.909	0.10	9.1	0.460	24,700	466
B31	0.909	0.10	9.1	0.527	29,400	553

[a] Comparable conditions were kept as regards rate of addition of monomer, which was in the range which did not affect the molecular weights (3–21 mmole/sec.).
[b] The run numbers are the same as given in Tables III and IV.

region give the value of k_p/k_{tr} (the ratio of the propagation and transfer rate constants). The existence of a low limiting value of $\overline{DP}$ was observed in other anionic polymerizations of acrylonitrile, the values being dependent on the type of the system. In the homogeneous polymerization in DMF catalyzed by methoxides[4] or by sodium diethylmalonate[6] this value of $\overline{DP}$ was 15–20, and in the heterogeneous polymerization in tetrahydrofuran catalyzed by sodium benzophenone[5] it was about 100. In region (c) of the curve (R_{addn} 40–3 mmole/sec.) the molecular weights were approximately constant and independent of R_{addn}. The molecular weights in this region were directly proportional to [monomer] (Table III) and inversely proportional to [catalyst] (Table IV), this being characteristic of a "living" polymerization system.[7] Region (b) of the curve was intermediate between regions (a) and (c). The continuous increase of $\overline{DP}$ with decrease of R_{addn} might be explained by a simultaneous operation of the two mechanisms: lowering of R_{addn} towards region (c) increased the extent of the nonterminated polymerization which caused an increase of $\overline{DP}$, while with rates of addition near the chain transfer region, chain transfer was dominant as was evident from the independence of $\overline{DP}$ of monomer concentration (Table IIIB). However, $\overline{DP}$ although constant, was higher than the limiting values, indicating that chain transfer to monomer was not the sole operating mechanism. Region (d) of the curve will be discussed later.
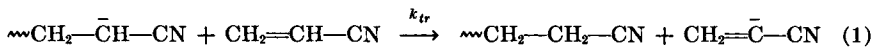
A closer examination of Table IIIB revealed the reason for the independence of molecular weight of monomer concentration. In the case of the lowest monomer concentration used (runs, B13, B14,) R_{addn} of monomer was that of region (c) (Table I), where essentially a "living" mechanism was shown to operate, and the molecular weight was the maximal for this monomer concentration. Increasing the monomer concentration should have increased linearly the molecular weights if the "living" mechanism were dominant. The fact that the molecular weights remained essentially constant showed that there was actually a termination by chain transfer to monomer, whose extent increased with increasing the momentary monomer concentration (higher R_{addn}), leading to a lowering of the molecular weights towards the low limiting values. This effect seems to cancel the increase of molecular weight with increasing the monomer concentration, which is due to the simultaneous "living" mechanism operating at these rates of addition.

The presence of different momentary concentrations of monomer was responsible for the above mentioned changes of $\overline{DP}$. In region (a) where excess monomer was present during the polymerization, only chain transfer to monomer occurred, while in region (c), where its momentary concentration was relatively small, essentially non-terminated polymerization took place.

Further support for the effect of increasing monomer concentration in causing termination by chain transfer is seen from Figure 2 and Table IIIA, where at the highest monomer concentration investigated (3.33 mole/l.), the molecular weight decreased instead of increasing.

Conversions of about 80% were obtained when monomer was added over 4–5 sec. and the polymerization stopped immediately afterwards (Table III), showing that the polymerization was very fast so that monomer could not be accumulated in the polymerization mixture. Had this not been the case, the concepts "rate of addition of monomer" and "momentary" concentration of monomer, would have been meaningless.

From the above it is seen that the momentary concentration of monomer, if it exceeds a certain value, seems to be the cause for termination by transfer to monomer:

$$\text{\textasciitilde\textasciitilde CH}_2\text{—}\overset{-}{\text{CH}}\text{—CN} + \text{CH}_2\text{=CH—CN} \overset{k_{tr}}{\longrightarrow} \text{\textasciitilde\textasciitilde CH}_2\text{—CH}_2\text{—CN} + \text{CH}_2\text{=}\overset{-}{\text{C}}\text{—CN} \quad (1)$$

It follows from the simple relationship which applies to polymerization involving chain transfer to monomer,[9] $DP = k_p[M] \, [\text{\textasciitilde\textasciitilde C}^-]/k_{tr}[M][\text{\textasciitilde\textasciitilde C}^-]$, where M is monomer and $\text{\textasciitilde\textasciitilde C}^-$ is growing end, that the monomer concentration, no matter how small it is, cannot affect the molecular weight. Hence, a different effect of the monomer, which should be dependent on its concentration, must be considered to account for the dependence of the polymerization mechanism on the momentary concentration of the monomer. We think that such effects as solvation of the growing chain ends by the monomer, are responsible for this dependence.

Solvation of the growing ion-pairs might be through the acidic α-hydrogen of the monomer, or through its β-carbon atom:

$$\text{CH}_2\text{=CH—C}\equiv\text{N} \quad \leftrightarrow \quad \overset{+}{\text{CH}}_2\text{—CH=C=N}^-$$
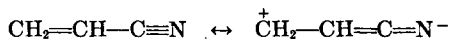
It is obvious that β-carbon type solvation will be in favor of propagation, whereas solvation through the α-acidic hydrogen will be in favor of termination by chain transfer to monomer. The experimental results showed that the extent of solvation of growing carbanions through the acidic α-hydrogen and therefore of chain transfer to monomer, increased up to a maximum with increasing the momentary concentration of monomer (Table I). On the other hand, "living" nonterminated polymerization occurred at relatively low momentary concentrations of monomer (Tables IIIA and IV). This suggests that solvation through the α-hydrogen competes effectively with the β-carbon type solvation only at relatively high momentary concentrations of monomer.

Molecular weights decreased with decreasing R_{addn} below about 3 mmole/sec. (Fig. 1). In the polymerizations of acrylonitrile in petroleum ether[1] and in DMF[3] catalyzed by butyllithium, low molecular weights of the order of those obtained under chain transfer conditions were realized when monomer was added at low rates of addition (0.75 and 0.15 mmole/sec., respectively). In region (c) of the curve where the polymerization was essentially of the "living" type and the monomer was added over a period of a few seconds (1–15 sec.), the "living" ends persisted, and added monomer was essentially polymerized on them. In addition the fact that plots of $\overline{DP}$ versus [monomer] and versus 1/[butyllithium] were linear

(Figs. 2 and 3) for this region, showed that essentially no other butyllithium in addition to that which had initiated polymerization was further consumed during the polymerization.   It might therefore be that the molecular weights decreased with lower R_{addn} values, i.e., region (d), because the polyacrylonitrile "living" ends die, for example, by a spontaneous monomolecular termination,[3,11] due to their transient character,[3,10] before combining with added monomer, which is in turn consumed in a new initiation by free butyllithium.

The k values calculated from the slopes of the lines of Figures 2 and 3 by using the equation: $\overline{DP}$ = $[M]/k$ [BuLi], were somewhat different $(1.9 \times 10^{-2}$ from Fig. 2 and 0.6×10^{-2} from Fig. 3).   If the polymerization were exclusively of the non-terminated "living" type, k would be the fraction of the butyllithium that was effective in initiation.   If both the "living" and chain transfer mechanisms were operating simultaneously, however, this would not be the case, since some of the polymeric chains were initiated by monomer anions (CH$_2$ = C̈—CN) according to eq. (1).

Dependence of Molecular Weight on [Acrylonitrile]/[Butyllithium]

As was shown, relatively high momentary monomer concentrations increased the extent of chain transfer to monomer, this was also observed previously in the presence of relatively high butyllithium concentrations,[3] which might be due to its participation in the transfer reaction, possibly by a four-centered mechanism as shown in I:

$$\text{Li}^+ \quad \text{Bu}^- \text{—Li}^+$$
$$\text{P —CH}^- \quad \text{H—C} = \text{CH}_2$$
$$\text{CN} \qquad \text{CN}$$
$$\text{I}$$
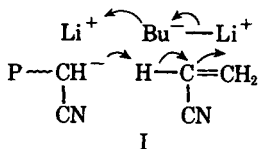
Thus, although "living" polymerization was essentially occurring in region (c), it seems that there was some simultaneous chain transfer termination, which was negligible with the low monomer and catalyst concentrations, but became appreciable with relatively high ones.   This was evident from the decrease of molecular weight found with high monomer concentrations (runs R9, R10. Table IIIA) and from the levelling off of molecular weights, near the low limiting values of $\overline{DP}$, found with the high catalyst concentrations (runs B28–B31, Table IV).

The simultaneous occurrence of the "living" and the chain transfer mechanisms together with the effect of increasing monomer and catalyst concentrations on the extent of the chain transfer reactions, explain well the results of Table V.   Indeed, for the same [acrylonitrile]/[butyllithium] values, lower molecular weights were obtained with the higher monomer and catalyst concentrations.   These same factors seem to be responsible for the difference found in the k values which were calculated from the straight lines of Figures 2 and 3.   However, the analogous polymerization of methacrylonitrile[12] (which has no α-acidic hydrogen atom for chain

transfer) in petroleum ether by butyllithium, was exclusively of the "living" type, and the k values obtained from the plots of $\overline{DP}$ versus [monomer] and versus 1/[butyllithium] were the same; also the plot of $\overline{DP}$ versus [monomer]/[BuLi] was linear.

The low efficiency of the butyllithium found in initiating the polymerization ($k = 0.6 \times 10^{-2}$–1.9×10^{-2}, i.e., 0.6–1.9% consumption of total catalyst) might be due to the low degree of dissociation of the polymeric butyllithium, $(BuLi)_n \rightleftharpoons nBuLi$, assuming that only monomeric butyllithium is the effective initiator.[13] Such low values of k were also reported for the butyllithium-initiated polymerization of acrylonitrile in toluene[2] at $-78°C$. ($k \leq 5 \times 10^{-2}$) and for the butyllithium-initiated polymerization of methacrylonitrile in petroleum ether[12] ($k = 2 \times 10^{-2}$).

Effect of Temperature on the Molecular Weight

In the polymerization of acrylonitrile with petroleum ether by butyllithium,[1] where termination was by chain transfer to monomer, molecular weights increased with lowering the temperature. The increase of molecular weight found on lowering the polymerization temperature from 0 to $-55°C$. (Table I, runs M1, N1, J30, J31) and on adding the monomer at high rates (200 mmole/sec.) was undoubtedly due to a high extent of chain transfer at region (b) (Fig. 1). With lower R_{addn} (10 mmole/sec.), the increase of molecular weight was comparatively small (Table I, runs B3, R13, R14, J28, J29), probably because the polymerization was essentially of the "living" type. This increase might however be ascribed to the decrease in the concentration of monomeric butyllithium caused by lowering the temperature.
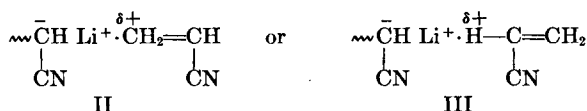
When the catalyst was added at low rates to the monomer (0.25 mmole/sec., runs J24, J25, J34, J36, Table II), there was a fourfold increase of molecular weight on lowering the temperature from 0 to $-55°C$., whereas with the higher rates of addition (5 mmole/sec. runs J26, J27, J35, J37, Table II) only a twofold increase was obtained. The increase in the former case might be due in part to the chain transfer mechanism and in part to a possible partial "living" polymerization, which was made possible by the momentary concentration of monomeric butyllithium being reduced to such a low value, which was insufficient to participate in both the initiation and transfer reactions.[3] In the latter case, the momentary concentrations of monomeric butyllithium, even though it was reduced by the same extent on lowering the temperature, its value was high enough to participate also in the chain transfer.

Solvation of the Growing Ends by Monomer

The growing ends of polymer chains in aliphatic hydrocarbon solvents are ion-pairs of the type $-C^-Li^+$.[14] This was found to be responsible for the stereoregular polymerization of vinyl,[15] acrylic,[16,17] and diene monomers.[18,19] Decreasing the high covalent character of these ion-pairs either
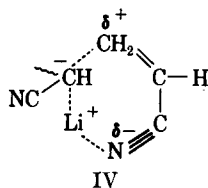
by solvating the Li^+ counter-ion[18,20,21] or by replacing it by more electro-positive alkali metal cations[19] reduced the degree of isotacticity. It is therefore apparent that the electric and the steric features of the $—C^-Li^+$ growing ion-pairs have some unique stereochemical effects as regards the nucleophilic attack of the growing ion-pair on the acidic double bond of the monomer.

We propose, in an attempt to explain the dependence of the polymerization mechanism on the momentary monomer concentration, that the propagation step is a two-stage propagation[21,22] in which the acrylonitrile monomer, having both an acidic double bond and an acidic α-hydrogen, is loosely associated in the first stage with the growing $—C^-Li^+$ growing ion-pair by charge transfer forces, the monomer being the electron acceptor. The structure of the monomer-solvated ion-pair, might be (schematically) either II or III:

$$\text{\textasciitilde\textasciitilde}\overset{-}{C}H\ Li^+\cdot\overset{\delta+}{C}H_2\!\!=\!\!CH \quad\text{or}\quad \text{\textasciitilde\textasciitilde}\overset{-}{C}H\ Li^+\cdot\overset{\delta+}{H}\!-\!C\!\!=\!\!CH_2$$
$$\ \ \ |\qquad\qquad\ \ |\qquad\qquad\ \ \ \ |\qquad\qquad |$$
$$\ \ CN\qquad\qquad CN\qquad\qquad\ \ \ CN\qquad\qquad CN$$
$$\qquad\quad\text{II}\qquad\qquad\qquad\qquad\qquad\qquad\text{III}$$

The number of associated monomer molecules might be more than one.

Some reasonable driving forces leading to a preferred formation of solvate (II), might be the great contribution of the dipolar form of acrylonitrile ($\overset{+}{C}H_2\!\!-\!\!C\!\!=\!\!C\!\!=\!\!N^-$) to its resonance structure and the plausible solvation of the Li^+ counterion by the nitrile group, as it is solvated by Lewis bases.[23] These electrostatic interactions might also lead to the formation of a relatively stable six-membered cyclic solvate (IV):

$$\begin{array}{c}
\overset{\delta+}{CH_2}\\
\diagup\qquad\diagdown\\
NC\diagdown\overset{-}{C}H\qquad\quad C\!-\!H\\
\vdots\qquad\qquad |\\
Li^+\quad\overset{\delta-}{N}\diagdown C
\end{array}$$
$$\text{IV}$$

The solvated ion-pairs (IV) are rapidly converted to nonsolvated ones in the second stage of the propagation, which consists of the formation of a covalent carbon–carbon bond between the carbanion and a monomer molecule. With low momentary monomer concentrations (low R_{addn} values), added monomer molecules will essentially face unsolvated $--C^-Li^+$ ion-pairs, and β-type solvates (II) will again be formed, so that an essentially nonterminated polymerization will take place.

On the other hand, when the rate of monomer consumption does not exceed the rate of its addition (high R_{addn} values), added monomer molecules will first face essentially solvated ion-pairs of type II, which will be further solvated by monomer more easily through its small acidic α-hydrogen atom than through the bulkier β-carbon atom due to steric factors. This will lead to solvated ion-pairs similar to type III, which are

of course susceptible to termination by chain transfer to the solvating monomer. Addition of nucleophiles to a double bond is strongly affected by steric factors, e.g., the extent of the base-catalyzed addition of *tert*-butanol to acrylonitrile is very small compared to that of primary alcohols, although its conjugated base is much stronger.[24]

Rates of nucleophilic substitution[25] and addition[26] reactions involving hydrogen-solvated nucleophiles, are very slow as compared to those involving nonsolvated ones. At a certain high enough momentary concentration of monomer, limiting conditions might be attained in the polymerization system, where essentially all the growing ends might be solvates of type III. The rate constant of propagation involving such hydrogen-solvated growing ends ($K_{p(H)}$) is plausibly much smaller than that of the free growing ion-pair $\sim\!\!C^-Li^+$ and than that of solvates of type II. The low limiting values of $\overline{DP}$ found (Fig. 1) are thus determined by the low value of this propagation rate constant, and are given by $k_{p(H)}/k_{tr}$.

EXPERIMENTAL

The purification of acrylonitrile,[27] petroleum ether, the preparation of butyllithium,[28] and the polymerization procedure[3] were as previously described.

Intrinsic viscosities were determined from one viscosity measurement in DMF (0.1 g./100 ml.) by using the equation given by Ham:[29]

$$10\,\eta_{sp} = [\eta] + 0.075\,[\eta]^2$$

Weight-average molecular weights were determined from the intrinsic viscosity by use of the equation of Cleland and Stockmayer.[30]

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Résumé

On a étudié la polymérisation anionique hétérogène de l'acrylonitrile dans l'éther de pétrole, au moyen de *n*-butyllithium dans diverses conditions expérimentales. La dépendance du poids moléculaire vis-à-vis des concentrations totales en monomère et en initiateur est fortement influencée par la concentration momentanée en monomère dans le mélange de polymérisation et par l'ordre de leur addition à celui-ci. On a trouvé deux mécanismes simultanés de polymérisation. Quand le monomère est ajouté à la solution catalytique à de faibles vitesses, une polymérisation "vivante" non-terminée est essentiellement dominante, comme cela est mis en évidence par la dépendance linéaire du $\overline{DP}$ vis-à-vis de la concentration et de l'inverse de la concentration en BuLi. Dans de telles conditions le $\overline{DP}$ est indépendant de la vitesse d'addition de monomère. Le transfert de chaîne sur monomère est le mécanisme dominant pour des vitesses élevées d'addition de monomère, comme cela est mis en évidence par l'indépendance du degré de polymérisation vis-à-vis des concentrations en monomère et en initiateur. Pour des vitesses intermédiaires d'addition de monomère, l'importance relative de chacun des deux mécanismes est appréciable et le $\overline{DP}$ augmente avec la diminution de la vitesse d'addition du monomère. On a suggéré qu'une étape de propagation en deux stades, dans laquelle le carbanion croissant de la paire ionique $\sim\sim C^- Li^+$ est solvaté par le monomère, est responsable de la dépendance du mécanisme de la polymérisation vis-à-vis de la concentration momentanée en monomère dans le mélange polymérisant.

Zusammenfassung

Die anionische heterogene Polymerisation von Acrylnitril in Petroläther unter Einwirkung von *n*-Butyllithium wurde unter verschiedenen Versuchbedingungen untersucht. Die Abhängigkeit des Molekulargewichts von der totalen Monomer- und Initiatorkonzentration wurde durch die Momentankonzentration des Monomeren im Polymerisationsgemisch und durch die Art des Monomerzusatzes stark beeinflusst. Es zeigte sich, dass gleichzeitig zwei Polymerisationsmechanismen wirksam sind. Bei Zusatz des Monomeren zur Katalysatorlösung mit kleiner Geschwindigkeit trat im wesentlichen, wie die lineare Abhängigkeit von $\overline{DP}$ von [Monomer] und 1/[BuLi] zeigte, eine abbruchsfreie "living"-Polymerisation auf. Unter diesen Bedingungen war $\overline{DP}$ von der Geschwindigkeit des Monomerzusatzes unabhängig. Bei hoher Geschwindigkeit des Monomerzusatzes war, wie die Unabhängigkeit des Polymerisationsgrades von Monomer- und Initiatorkonzentration zeigte, die Kettenübertragung zum Monomeren der vorwiegende Mechanismus. Bei mittlerer Geschwindigkeit des Monomerzusatzes traten beide Mechanismen in merklichem Ausmass auf, und $\overline{DP}$ stieg mit fallender Zusatzgeschwindigkeit des Monomeren an. Ein Zweistufen-Wachstumsschritt, bei welchem das wach-

sende Carbanion des ⁓C⁻Li⁺-Ionenpaares durch das Monomere solvatisiert wurde, wurde zur Erklärung der Abhängigkeit des Polymerisationsmechanismus von der Momentankonzentration des Monomeren in der Polymerisationsmischung angenommen.