Suspension Polymerization of Caprolactam

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Synopsis

The anionic polymerization of caprolactam (with sodium hydride and acetyl caprolactam as catalysts) carried out in glass ampules is reported. The effect of the catalyst concentration, polymerization temperature, and other variables was studied. Polymerization of caprolactam at temperatures around 120°C. in a paraffin suspension, in which the paraffin was introduced into a syrupy prepolymer is also reported. The influence of a few variables on conversion, molecular weight, particle size distribution, is discussed. Both viscosity and conversion are always lower in suspension than in bulk polymerization. Polymer granules of a wide range of dimensions which generally contain some residual monomer (unlike the bulk polymerization) are obtained in suspension polymerization. The above results are discussed and some interpretations are suggested.

INTRODUCTION

It is known that in conventional "hydrolytic" caprolactam polymerization, a rather high amount of monomer (ca. 10%), in equilibrium with the polymer is formed at the polymerization temperature (230–280°C.). This requires time-consuming hydroextractions and dryings of the polyamide.

With the more recent processes of ionic catalysis with alkali metals and derivatives[1] one can work at lower temperatures (120–180°C.) where the equilibrium monomer content is much lower. As a consequence of this, the polymer can be used without previous hydroextraction. As a matter of fact, this process is now industrially used for the preparation of large masses of polycaprolactam in suitable molds.

To obtain chips for injection molding, it is necessary to break such blocks and to extrude them in the form of chips. In this operation water may be easily absorbed, and if heating is too prolonged (large blocks) monomer reformation is possible in amounts which correspond to the equilibrium values at the melting temperature.

Therefore, to obtain polycaprolactam in the form of fine dust or granules at low temperature (low residual monomer) it is probable that suspension polymerization is a suitable method.

According to a recent patent,[2] AH salt (hexamethylene diammonium adipate) is suspended in paraffin and polymerized to nylon 66 at increasing temperatures up to 190°C. in order to eliminate the condensation water.

According to a Bayer patent,[3] caprolactam is polymerized in paraffin with ionic catalyst to give polycaprolactam granules in 50% yields; higher yields are obtained by using silicone oil as suspending medium.   In this method, the monomer is added to the paraffin, then suspending agents (polyamide dust or talcum) and initiators are added; the temperature is gradually raised during the course of the polymerization.

In the present work we have studied the conditions for the polymerization of caprolactam (CL) in paraffin suspension with sodium hydride and acetyl caprolactam (ACL) as catalysts.   In a few polymerizations small amounts of aniline (as regulators of the molecular weight and its distribution) were added in the ionic polymerization of caprolactam in bulk, as suggested in the patent literature.[4]

Preliminary polymerizations in glass ampules were carried out in order to determine the best formulations and these were subsequently evaluated in suspension runs.

EXPERIMENTAL

Caprolactam (Sicedison S.p.A.) had a melting point of 68.9°C.   After preliminary drying at 60°C. under vacuum for 12 hr., the necessary amount was weighed into a porcelain capsule, then further dried for 16 hr. under vacuum and kept, till the moment of use, in the dark, in a desiccator over P_2O_5.   Under such conditions the water content at the moment of use was maximally 0.007–0.1%.   Alternatively, by drying the monomer and then introducing it in a glass buret which was electrically heated, lower water values were obtained (0.005%); however, the monomer was more altered owing to the repeated heatings to which it was subjected.

The paraffin, melting at approximately 60°C., contained 0.1% water. Commercial products from C. Erba (Milan) and B.D.H. (Poole, England) products were used with similar results.

Sodium hydride (Rudi Pont, Turin) was used as received, i.e., as a 50% suspension in oil.

Acetyl caprolactam, b.p. 112°C./10 mm. Hg, was prepared from caprolactam and acetic anhydride.

Nitrogen contained oxygen in concentration less than 5 ppm.

The great importance of using products which had been very recently purified or, especially in the case of sodium hydride, taken from newly opened boxes is emphasized as, if this precaution was not observed, the reproducibility was markedly altered mainly due to the atmospheric moisture.

Polymerization in Glass Ampules

The caprolactam was weighed and charged in a small vessel which had been previously heated over direct flame, after oxygen had been removed by repeated evacuation and flushing with nitrogen.

The monomer was then melted under vacuum at 85°C.; then the sodium hydride was charged and solubilized under vacuum at the same tempera-

ture.   The glass ampules were subjected to direct flaming under nitrogen; then they were allowed to cool under nitrogen and were closed with rubber tubing and a pinch-type clamp.   Acetyl caprolactam (and aniline, if used) was charged by means of a pipet.

The caprolactam–sodium hydride solution, at the test temperature, was then charged; the glass ampule was alternately evacuated and flushed with nitrogen three times and then was flamed closed.   The polymerization was carried out in a silicone oil bath.

The polymerization time was 3 hr. in all cases.   The data (Fig. 3) show that by this time interval nearly asymototic conditions of viscosity and conversion are generally reached for all formulations.   This is also true of polymerizations carried out in the presence of aniline, which was shown to reduce the polymerization rate.[5]

Determination of Conversion

At the end of the polymerization the polymer was ground to a fine dust. It was subjected to Soxhlet hydroextraction for 16 hr. and then dried in a vacuum oven at 20 mm. Hg and 105°C. for 10 hr.[6]   Water was determined by the Fischer method on the polymer in m-cresol.

Determination of Viscosity

The relative viscosity was determined in an Ostwald viscometer for solutions of 1 g. of polymer in 100 cc. of 95.6 ± 0.2% sulfuric acid.

Suspension Polymerization

A 50-g. portion of monomer was introduced in a 500-cc. Keller glass vessel under conditions already indicated for the charging of the glass ampule.   Sodium hydride was then added under the same conditions. ACL was added by means of a pipet only when the monomer was already at the reaction temperature; this was considered the zero time.

After an interval which was variable, depending on the temperature and the catalytic charge, the mixture began to become turbid.   At this point, termed the turbidity time, the polymerization became heterophase, owing to the insolubility of the polymer in the monomer.   As soon as turbidity in the mixture was noted, the paraffin, which had been previously melted under nitrogen and was already at the reaction temperature, was rapidly introduced.

After 4 hr. the suspension was filtered hot, the polymer repeatedly washed with boiling chloroform, and then extracted with water in the Soxhlet as described above.   The relative viscosity of the extracted polymer was determined and the particle size distribution was estimated by sieving over calibrated sieves.   The optimal conditions for suspension polymerization on a laboratory scale were ascertained by a preliminary examination of the influence of various parameters.

A polymerization vessel of the Keller type equipped with a blade stirrer which almost scraped the walls operating at 350 rpm, was used.   In order

TABLE I

Run no.	Catalyst charge, mole/mole CL			Turbidity time, sec.	Ratio paraffin monomer (volume)	Conversion, %	Particle size distribution, % residual over mesh						Incrustations, %	η_r
	NaH	ACL	Aniline				20 mesh	40 mesh	60 mesh	80 mesh	100 mesh	Bottom		
						Suspension Polymerization[a]								
47	1/100	1/50	1/100	185[b]	1.5	83	27.9[e]	28.1[c]	12.8[d]	6.5[c]	9.0[e]	15.7[f]	6.1	1.63
48	1/100	1/50	1/100	185[b]	1.3	82	13.2[d]	36.3[f]	19.0[e]	8.6[f]	8.1[f]	14.8[e]	5.6	1.59
83[g]	1/100	1/50	—	150	1.3	83.4	25.2	24.6	22.2	9.2	8.7	10.1	4.0	1.59
84[g]	1/100	1/50	—	173	1.3	73.0	23.9	26.4	9.7	3.6	5.8	30.6	4.0	1.52
85[h,i]	1/100	1/50	—	135	1.3	87.5	24	21.2	22.1	9.6	11.1	12	7.8	1.63
86[h,i]	1/100	1/50	—	132	1.3	91.0	27.1	21.3	23.8	10.2	9.3	8.3	8.5	1.69
43	1/100	1/50	1/100	180	1.0	90	5.6	21.2	11.5	5.1	9.1	47.5	12.9	—
53	1/100	1/50	1/100	195	1.3	85	29.3	17.6	4.5	1.4	2.6	44.6	5.4	—
47	1/100	1/50	1/100	185	1.5	83	27.9	28.1	12.8	6.5	9.0	15.7	6.1	1.63
140	1/100	1/100[j]	—	163	1.0	94	1.0	38.0	33.7	7.6	6.8	12.9	15.0	2.3
139	1/100	1/100[j]	—	164	1.3	90	8.8	46.3	28.0	5.6	4.5	6.8	10.8	2.30
141	1/100	1/100[j]	—	183	1.5	88	17.9	47.4	22.7	4.8	3.6	3.6	13.3	2.24
						Solution Polymerization[k]								
3	1/50	1/25	—	—	—	73	63.3	20.6	7.3	2.2	2.2	4.4	4.9	1.33
3	1/50	1/25	—	—	—	70.5	57.7	22.1	6.7	2.9	2.9	7.7	24.1	1.30
6[m]	1/50	1/25	—	—	—	[n]							0	
7[m]	1/50	1/50	—	—	—	70.5	3.7	5.2	11.8	5.9	10.4	63.0	0	1.67

[a] Polymerization time 3 hr., temperature 120°C; [b] paraffin added 30 sec. after turbidity time; [c] viscosity 1.60; [d] viscosity 1.62; [e] viscosity 1.61; [f] viscosity 1.59; [g] suspending agent: silica (>100 mesh), 1%; [h] suspending agent: silica (<200 mesh), 1%; [i] cf. runs 81, 82 (Table III); [j] ampule run 343, 344; [k] polymerization time 4 hr., temperature 120°C.; [l] paraffin 105 cm.³, CL 18 g.; [m] temperature 150°C.; [n] polymer was soft and could not be filtered.

to keep the amount of incrustation as low as possible it was advisable that there be no dead spaces under the stirrer (as in the case of spherical vessels).   For the same reason it was advisable not to keep the paraffin/monomer ratio too low.   A ratio of 1.3/1.0 (by volume) was selected as the best compromise between the minimum incrustation formation and the minimum absolute amount of paraffin to avoid solubilization of the monomer (Table I).

Unless otherwise stated, the polymerization conditions which are described in the various tables were as follows: (1) introduction of the paraffin into the prepolymer at the moment turbidity is noted (turbidity time); (2) reaction carried out in a 500-cc. Keller vessel; (3) use of a blade stirrer almost scraping the walls and operating at 350 rpm (4) reaction temperature 120°C.; (5) polymerization time, 4 hr.; (6) paraffin/monomer ratio 1.3 (by volume).

RESULTS AND DISCUSSION

Polymerizations in glass ampules were carried out for 3 hr. (see Experimental) in the temperature range 116–180°C. at ACL concentrations of 1/31–1/400 mole/mole CL, and at NaH concentrations of range 1/31–1/400 mole/mole CL.   A few representative results are given in Table II.

Temperature had no pronounced effect, at least within experimental error.

The amount of water-soluble material (HS) also varied.   In Figure 1 HS is shown as a function of the catalyst concentration.

TABLE II
Polymerization in Glass Ampules

Run no.	Catalyst charge, mole/mole CL		Tempera-ture, °C.	Water Solubles (HS), %	η_r
	NaH	ACL			
176	1/100	1/50	120	3.56	1.98
177	1/100	1/50	120	3.47	1.98
343	1/100	1/100	120	3.3	2.74
344	1/100	1/100	120	3.1	2.67
224	1/200	1/100	120	3.30	3.57
225	1/200	1/100	120	3.90	3.15
234	1/150	1/100	120	2.50	3.42
235	1/150	1/100	120	2.70	3.40
300	1/31	1/100	164	3.6	2.79
301	1/31	1/100	164	3.4	2.72
290	1/47	1/25	140	5.6	1.54
291	1/47	1/25	140	6.0	1.53
315	1/100	1/400	140	89.5	3.03
316	1/100	1/400	140	87.7	3.11
349	1/100	1/150	116	8.4	4.07
350	1/100	1/150	116	8.2	3.88

The viscosity as a function of the catalyst concentration is shown in Figure 2.   The results can be expressed by eq. (1)

$$\eta_r = 15.54 - 8.08 \log (CL/ACL) - 9.35 \log (CL/NaH)$$

$$- 5.57 \log (CL/ACL) \log (CL/ACL) \pm 0.06 \quad (1)$$

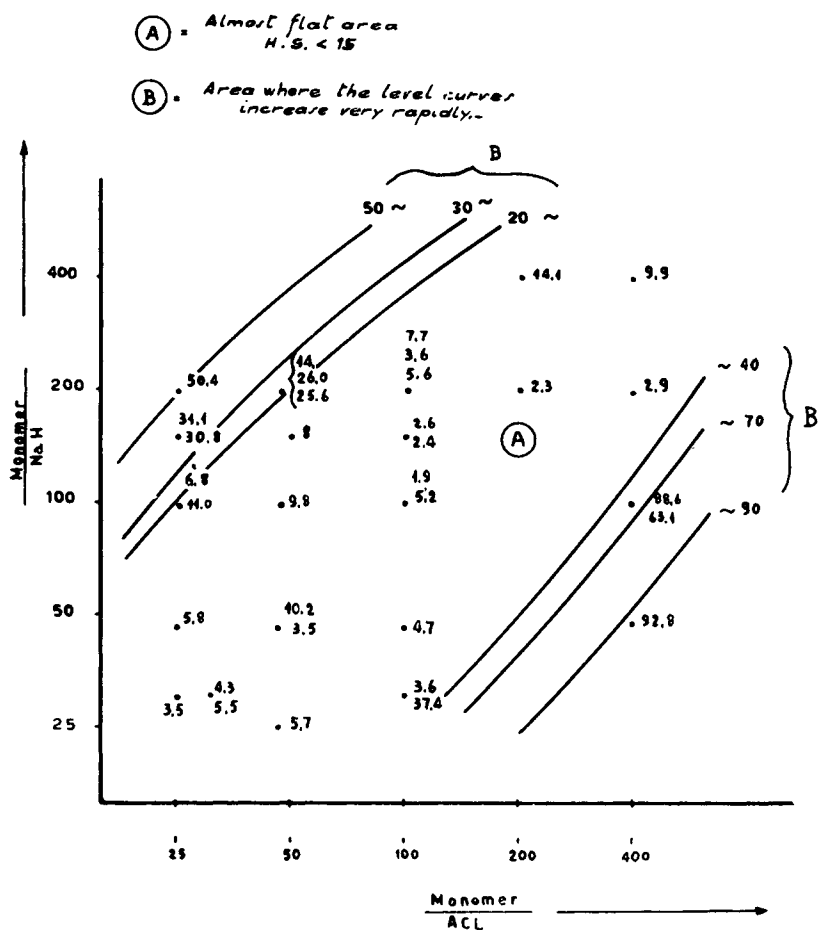where the concentration ratios are in molar ratios.

Fig. 1. Relation between water-soluble matter (HS) and catalyst concentration.

The results for polymerization carried out in the presence of amines are not shown in Figures 1 and 2.   However, it was seen[5] that aniline generally depresses both viscosity and conversion; its effect on the molecular weight distribution is presently being studied.

The suspension polymerizations were carried out with the use of those formulations which had shown the higher values of viscosity and conversion in the polymerizations in glass ampules.
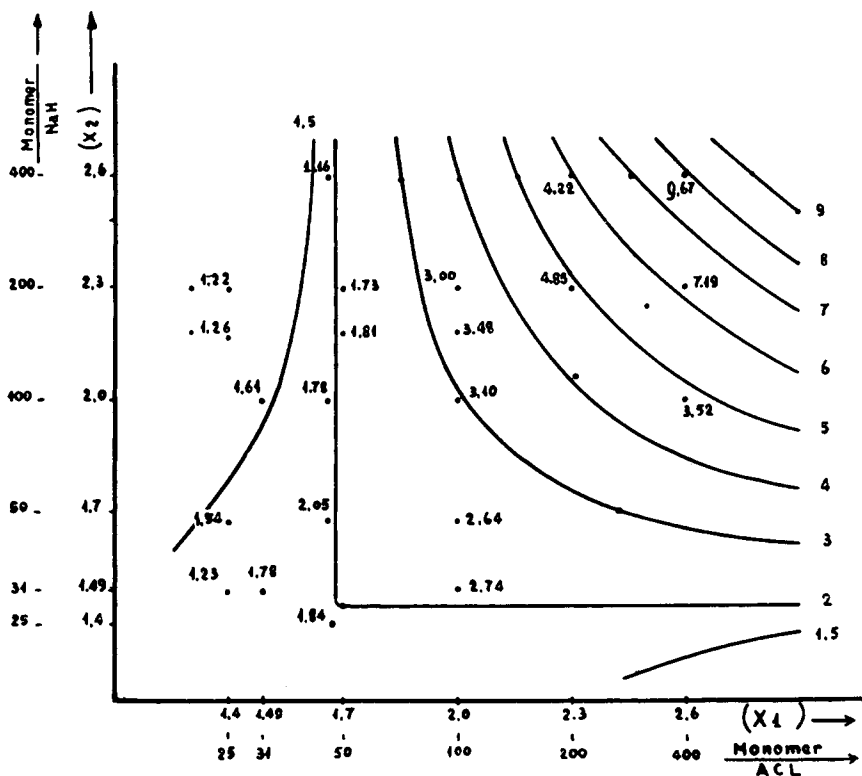
Fig. 2. Relation between viscosity of the polymer and catalyst concentration.

We examined approximately 100 materials as suspending media. We finally selected paraffin (m.p. 60°C.) for economical considerations. As a matter of fact, satisfactory insolubility of the monomer at low temperature was shown by all the hydrocarbons tested (n-hexane, n-heptane, n-nonane, vaseline oil, naphtha). However, the solubility increases very rapidly with the temperature. In the paraffin we selected the approximate solubilities (80°C., 7 g./100 cm.^{3}; 100°C., 13%; 120°C., 18%; 140°C., 36%) were lower than in the above-mentioned hydrocarbons.

We tried to carry out the suspension polymerizations by mixing the paraffin with prepolymers which had reached the highest possible conversion, the aim being to start the polymerization with a mixture of monomer and polymer particles which was relatively rich in polymer. We supposed that it would have been more difficult, especially in the case of a fast reaction, due to the extraction by the paraffin of the monomer and unconverted catalysts. Practically, paraffin, which was already at the same temperature, was mixed into the prepolymer when the latter became turbid (heterophase polymerization); in general, if we waited further we obtained granules which could not be further dispersed in the suspending medium due to their elevated viscosity.

TABLE III

Reproducibility of Suspension Polymerization[a]

Run no.	Catalyst charge, mole/mole CL			Turbidity time, sec.	Conversion, %	Particle size distribution, % residual over mesh						Incrustations, %	η_r
	NaH	ACL	Aniline			20 mesh	40 mesh	60 mesh	80 mesh	100 mesh	Bottom		
51	1/100	1/50	1/100	155	88.5	11.6	40.3	24.8	7.1	5.9	10.3	10.8	—
76	1/100	1/50	1/100	170	86	35.3	19.6	5.6	4.0	8.8	26.7	8.9	1.61
59	1/100	1/50	1/100	175	87	41.0	21.6	9.2	5.3	8.1	14.8	4.4	1.63
56	1/100	1/50	1/100	210	85	20.5	17.3	6.5	3.7	7.5	44.5	8.9	1.61
61	1/100	1/50	1/100	210	82.5	34	12.3	3.7	1.8	4.2	44.0	8.7	1.63
75	1/100	1/50	1/100	220	82.5	1.9	22.5	11.4	4.5	5.8	53.9	11.3	1.61
53[b]	1/100	1/50	1/100	195	85.0	29.3	17.6	4.5	1.4	2.6	44.6	5.4	—
57[b]	1/100	1/50	1/100	145	91.5	14.2	30.3	28.0	7.2	7.5	12.8	10.3	1.66
64[c]	1/100	1/100	1/100	405	30	—	8.0	21.3	23.3	20.7	26.7	10.2	1.55
65[c]	1/100	1/100	1/100	330	36	—	27.7	33.7	13.3	12.0	13.3	18.3	1.62
79[d,e]	1/100	1/50	—	137	71	25.6	22.8	13.8	7.2	11.3	19.3	2.1	1.48
80[d,e]	1/100	1/50	—	178	75.0	24.7	32.3	19.0	6.8	7.3	9.9	3.3	1.55
81[d,e]	1/100	1/50	—	140	87.0	19.7	28.5	28.0	7.5	7.2	9.1	3.5	1.69
82[d,e]	1/100	1/50	—	130	86	20.2	28.6	27.8	7.5	6.8	9.1	6.1	1.67
116[d]	1/100	1/50	—	100	92	28.8	20.4	18.9	10.1	10.6	11.2	6.1	1.70
90[f]	1/200	1/100	—	420	39	9.9	13.2	4.6	0.6	1.3	70.4	28.7	1.48
93[f]	1/200	1/100	—	395	50	—	1.6	1.1	1.1	1.6	94.6	28.3	1.68
91[g]	1/50	1/100	—	335	62	37.0	14.4	1.8	0.4	0.4	46.0	32.7	1.93
92[g]	1/50	1/100	—	285	72	44.8	6.6	0.3	0.3	0.3	47.7	22.7	2.21
97[g]	1/50	1/100	—	290	75	46.8	9.8	0.4	0.4	0.4	42.2	27.9	2.26
101[g]	1/50	1/100	—	320	71	31.9	13.5	1.2	0.4	1.2	51.8	32.2	1.98

[a] Polymerization time 3 hr.; [b] paraffin added 30 sec. after turbidity; [c] temperature 140°C.; [d] ampule 176; [e] NaH taken from another (older) container than that used in run 116; [f] ampules 224, 225; [g] ampules 234, 235.

The results of suspension polymerization carried out with formulations which in glass ampules gave higher values of viscosity and conversion are shown in Table III, where the reproducibility for various charge types is also shown.   Conversion and viscosity values are in the suspension polymerizations lower than those for the corresponding runs in ampules.   Furthermore the values vary, even if not too much, for the same charge on varying the turbidity time.   The differences in turbidity time for the same charge are not regular, as they probably depend on the uncontrollable presence of impurities (water) in the catalyst or in the monomer.   By considering the possible presence of various impurities, differences in the reproducibility of the purification of the monomer, catalyst, etc., it can be assumed that the conversion can be affected to a maximum relative extent of 4–5% and viscosity to 2–3%.[5]   However, in general, the reproducibility for the same formulations with the same turbidity time is good (runs 59 and 76; 61 and 75; 79, 80, 81, and 82).   Lesser consideration must be given to the reproducibility of the incrustations and the particle size distribution, which can hardly be controlled in a laboratory polymerization.   For the same charge the conversion and to a smaller extent the viscosity decrease with increasing turbidity time (runs 59, 61, and 75; 64, and 65).   The most satisfactory results (with the lower turbidity time) in viscosity (ca. 2.20) and conversion (70–75%) were obtained by the recipe of ampule 234. The particle size distribution shows two maxima at the extremes of the scale.   As it is seen from Table III, in general a rather broad particle size distribution is obtained, in which it is difficult to avoid a large-particle residue (bottom).   It is, however, possible that by working on a large scale the particle size distribution can be better defined.   However, the fractions which have different particle size distributions all show the same viscosity (Table I).   The particle size distribution was not much altered by adding an inorganic suspending agent.

The monomer which is dissolved in paraffin can polymerize to form a product with a particle size distribution which is similar to the one observed in the suspension polymerization starting from the prepolymer.   However (Table II) higher amounts of catalyst are needed, probably owing to the high solubility of acetyl caprolactam in paraffin; this is at least in part responsible for the low molecular weight which was obtained.

In order to clarify the meaning of the turbidity time in the prepolymer, with regard to the final results of the suspension polymerization, a few prepolymers were prepared and, as soon as the turbidity was reached, water was added instead of paraffin.   In this way the reaction instantaneously stopped.   The precipitated polymer was subsequently extracted by hot water in order to completely free it from the monomer, and the relative viscosity η_r of this polymer was determined.   The results (Table IV) show that for each formulation, with varying turbidity times, the conversion at that moment was inversely proportional to the length of the turbidity time. The viscosity values, on the other hand, were not very different for various formulations; however, higher values were observed for catalyst charges
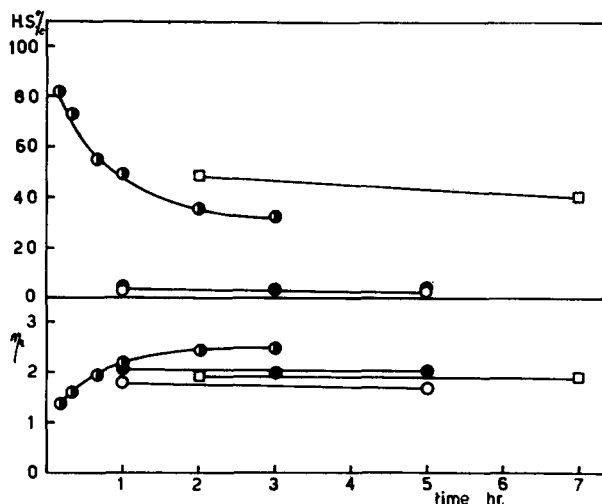
Fig. 3. Effect of polymerization time on polymerization in glass ampules at 120°C.: (◑) NaH $^1/_{200}$ mole/mole CL, aniline $^1/_{200}$ mole/mole CL, ACL $^1/_{150}$ mole/mole CL; (●) NaH $^1/_{100}$ mole/mole CL, ACL $^1/_{50}$ mole/mole CL; (○) NaH $^1/_{100}$ mole/mole CL, aniline $^1/_{100}$ mole/mole CL, ACL $^1/_{50}$ mole/mole CL; (□) NaH $^1/_{100}$ mole/mole CL, aniline $^1/_{100}$ mole/mole CL, ACL $^1/_{100}$ mole/mole CL.

which, if polymerized in suspension, would furnish the higher final results of molecular weight and conversions. The range 1.2–1.3 of the viscosity at the turbidity time probably represents the critical chain length with regard to the solubility in the monomer at the temperature (see runs 10, 11 and 13, which were poured in water before the turbidity appeared). A longer turbidity time expresses in general a lower overall reaction rate (see for example Tables II, III, VII and Fig. 3).

Therefore it appears that the differences in results between glass ampules and suspension can be attributed to the overall reaction rate. As a matter of fact, the differences which have been detected for various formulations increase with increasing turbidity time, i.e., with decreasing the overall reaction rate.

It is very probable that syrupy prepolymers with higher reaction rates (lower turbidity time) at the moment of mixing them with the paraffin had a higher viscosity due to higher conversions and higher polymer viscosity (Table IV).

Furthermore their hardening velocity could be higher. We can then suppose that either inactivation of the growing centers by the paraffin or its impurities and/or solubilization of growing active centers was more unlikely for prepolymers with higher reaction rates. At the end of the polymerization unconverted monomer is present in greater concentrations inside the granules, as shown (Table V) by its difficult extractability from the paraffin, than in solution in the suspending medium; as a consequence, monomer solubilization by the suspending medium is a relatively small

TABLE IV
Turbidity Time

Run no.	Catalyst charge, mole/mole Cl		Turbidity time, sec.[a]	Conversion, %	η_r
	NaH	ACL			
3	1/100	1/50	113	43	1.25
1	1/100	1/50	115	39	1.23
2	1/100	1/50	127	39	1.24
8	1/100	1/50	156	35	1.22
4	1/100	1/50	161	33	1.21
7	1/150	1/100	253	21	1.27
6	1/150	1/100	290	21	1.25
9	1/150	1/100	295	19	1.24
5	1/150	1/100	373	16	1.23
10	1/100	1/50	[b]	9	1.11
11	1/100	1/50	[b]	9	1.10
13	1/150	1/100	[c]	9	1.15
16	1/100	1/130	220[d]	15	1.27
17	1/100	1/130	265[d]	13	1.26
18	1/100	1/150	185[d]	16	1.28
19	1/100	1/150	210[d]	15	1.28
20	1/100	1/170	230	13	1.32
14	1/200	1/100	360	18	1.22
15	1/200	1/100	420	19	1.23

[a] Temperature 120°C.
[b] Paraffin added before the appearance of turbidity (60 sec. after ACL addition).
[c] Paraffin added before the appearance of turbidity (180 sec. after ACL addition).
[d] Temperature 116°C.

factor in incomplete conversion.   To confirm this, hot filtration of the suspension was carried out; the polymer was rapidly washed with hot paraffin. It was assumed that the amount of monomer determined in the paraffin

TABLE V
Determination of the Residual Monomer at the End of the Reaction[a]

Run no.	Catalyst charge, mole/mole CL			Turbidity time, sec.	Conversion, %	η_r	CL dissolved in paraffin, %[c]
	NaH	ACL	Pretreatment				
			[c]				
102	1/150	1/100	NaH, 1/200	330	83	2,13	30
103	1/150	1/100	NaH, 1/150	275	83	2,14	47
104	1/150	1/100	NaH, 1/100	275	86	2,10	40
92	1/150	1/100	—	285	71	2,20	40
152[b]	1/100	1/130	—	220	65	2,24	40
105	1/150	1/100	ACL, 1/200	290	73	1,62	30
109	1/150	1/100	ACL, 1/150	260	78	1,57	21
110	1/150	1/100	ACL, 1/100	310	68	1,44	25

[a] Temperature 120°C.
[b] Temperature 116°C.
[c] Calculated with regard to the residual monomer as determined from the conversion.

TABLE VI
Suspension Polymerization with Pretreatment of Paraffin

| Run no. | Catalyst charge, mole/mole CL | | | Turbidity time, sec. | Conversion, % | Particle size distribution, % residual over mesh | | | | | | Incrustations, % | η_r |
	NaH	ACL	Pretreatment[a]			20 mesh	40 mesh	60 mesh	80 mesh	100 mesh	Bottom		
97[b]	1/150	1/100	—	290	75	46.8	9.8	0.6	0.4	0.6	42.2	27.9	2.26
109[b]	1/150	1/100	ACL, 1/150	260	78.4	16.6	23.1	12.1	5.3	8.9	34.0	16.7	1.57
105[b]	1/150	1/100	ACL, 1/200	290	73.4	28.6	21.1	8.1	3.1	4.9	34.2	15.5	1.62
110[b]	1/150	1/100	ACL, 1/100	310	68.4	25	23.9	8.3	3.5	5.6	33.7	19.1	1.44
102	1/150	1/100	NaH, 1/200	330	83.2	12.7	26.3	6.6	13	36	—	26.6	2.13
103	1/150	1/100	NaH, 1/150	275	83.2	58.6	8.9	2.7	4.2	6.6	19	5.4	2.14
104	1/150	1/100	NaH, 1/100	275	86.4	29.9	38	16.1	5.1	5.1	5.8	3.8	2.10
122[c]	1/150	1/100	Metallic Na, 1/150	307	52	14.8	14.8	3.7	0.9	0.9	64.9	21.2	1.74
114	1/100	1/50	NaH, 1/100	95	93.4	33.7	21.9	9.8	5.1	9.8	19.7	11.7	1.71
116	1/100	1/50	—	100	91.6	28.8	20.4	18.9	10.1	10.6	11.2	6.1	1.70
115	1/200	1/100	NaH, 1/100	400	86.6	60.9	11.5	1.6	1.6	5.9	19.4	3.5	2.23
90	1/200	1/100	—	420	39.0	9.9	13.2	4.6	0.6	1.3	70.4	28.7	1.48

[a] All pretreatments for 30 min. at 120°C.
[b] Ampule 234.
[c] Water content before polymerization 0.04%.

TABLE VII
Suspension Polymerization[a]

Run no.	Catalyst charge, mole/mole CL		Turbidity time, sec.	Conver- sion, %	Incrusta- tions, %	η_r
	NaH	ACL				
96[b]	1/150	1/50	170	76	2.8	1.49
94[b]	1/150	1/25	135	58	4.3	1.20
95[b]	1/150	1/10	[c]	—	—	—
138	1/130	1/130	250	71	67	2.16
139[b]	1/100	1/100	164	90	10.8	2.30
129	1/100	1/100	180	87	8.1	2.25
132	1/100	1/130	175	83	15.6	2.64
137	1/100	1/130	175	85	23.7	2.68
134	1/100	1/130	215	72	45.8	2.34
136[b]	1/100	1/130	265	77	44.5	2.56
133	1/100	1/130	285	—	—	2.40
147	1/100	1/150	182	86	15.9	2.83
148	1/100	1/170	217	79	19.6	3.16
149	1/100	1/200	240	64	10.2	3.0

[a] Temperature 116°C.
[b] Temperature 120°C.
[c] No polymerization.

(by colorimetric reaction of the caprolactam as ferric hydroxammate[7]) was that effectively contained in the suspending medium at the end of the reaction. The filtered polymer was first extracted with chloroform (in which the monomer was titrated as above) and then subjected to Soxhlet extraction with hot water for 16 hr. The sum of the two results was considered to give the amount of monomer remaining at the end of the reaction within the polymer granules.

This was further verified by a series of tests in which a certain amount of catalyst was added to the paraffin before the introduction of the prepolymer. In other terms, we tried to destroy the impurities in the paraffin which would inactivate the active growing centers, by keeping it for $1/2$ hr. at 120°C. together with the polymerization catalyst. The results are shown in Table VI. Pretreating the paraffin with ACL does not increase conversion and viscosity. However, by heating the paraffin with sodium hydride and then by polymerizing it directly without filtering out the solid (analyzed water 0.04%) we had a definite improvement in the conversion alone. However, this was valid only for charges with a relatively low polymerization rate rather than for high rate charges. This suggests that such apparent positive effect arose from the fact that NaH, not being eliminated before the polymerization, actually increased the reaction velocity (cf. Fig. 2). If pretreatment of the paraffin was effected with metallic sodium by obtaining at the end the same water content (ca. 0.04%) and by filtering out the solid (an operation which was easier owing to the much more subdivided physical form), the apparent acceleration effect vanished.

TABLE VIII
Conversion in Ampule and Suspension Polymerization[a]

Catalyst charge, mole/mole CL		Ampule			Suspension				Difference in conversion between ampules and suspension, %
NaH	ACL	Run no.	η_r (average)	Conversion (average), %	Run no.	η_r (average)	Conversion (average), %	Turbidity time (average), sec.	
1/100	1/50	176, 177	1.98	96.5	116	1.7	92	135	− 4.6
1/100	1/100	343, 344	2.7	96.8	139	2.3	90	164	− 7
1/100	1/150[b]	349, 350	3.95	91.7	147	2.8	86	182	− 6
1/150	1/100	234, 235	3.41	97.4	91, 92, 97, 101	2.1	70	310	−28
1/200	1/100	224, 225	3.36	96.6	90, 93	1.6	45	400	−52

[a] Temperature 120°C.
[b] Temperature 116°C.

If we examine the data in Table V we note that a smaller quantity of monomer was dissolved in paraffin at the end of the reaction for runs where the paraffin had been pretreated with ACL, than in other runs at the same conversion which had been pretreated with NaH or which had not been pretreated at all.

The viscosity values are also appreciably lower; this could indicate that with the ACL pretreatment we had a solution polymerization which reduced the amount of monomer dissolved and lowered the average molecular weights in the final polymer(Table I).

In Table VII a series of suspension polymerizations carried out with variable amounts of ACL are reported. It is seen that with elevated values of the latter high conversions and low viscosities are obtained, very similar as in the corresponding runs in glass ampules. With decreasing amounts of ACL a maximum molecular weight and conversion are obtained, which then decrease with further decreases in the cocatalyst. By comparison of the turbidity time and even (Table VIII) of the differences between the final values of both ampules and suspension, it is seen that the positive effect of relatively small amounts of ACL is probably to be attributed to its accelerating effect on the reaction rate. The best results we obtained in this exploratory work (η_r = 2.83, conversion = 85%), considering that higher viscosities can be obtained with a concomitant decrease in the conversion, indicates that a balance was reached between sufficiently elevated reaction rate and amount of cocatalyst (large amounts of cocatalyst decreases the molecular weight). The polymer which was obtained in this way was slightly yellow in color, probably due to the oil which suspended the NaH; furthermore, it also contained some residual monomer. We did not succeed in carrying to completion polymerization of the polymer which was dissolved in paraffin as, in order to do it, it would be necessary to add an excessive amount of catalyst, and thus decrease the average molecular weight.

Polymerization at higher temperatures in order to increase the reaction rate did not appear fruitful. A run was effected at 164°C. (repetition of ampule 284) and gave a block of polymer, possibly due to the increased solubility of CL in paraffin. The residual monomer contained in the polymer particles could not be easily extracted with paraffin. Run 132 was repeated (Table VII) and the temperature was elevated at the end of the reaction to 150°C. and kept at this temperature for 1 hr. However after this treatment the polymer particles still contained 8% monomer and the conversion had not increased appreciably.[5]

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Résumé

On décrit la polymérisation anionique de la caprolactame (hydrure de sodium et acetylcaprolactame comme catalyseurs) effectuée en ampoules de verre et étudiée en fonction de la concentration en catalyseur, de la température de polymérisation etc. On décrit également la même polymérisation effectuée à des températures situées aux environs de 120°C en suspension dans la paraffine, en introduisant la paraffine dans un prépolymère sirupeux. On discute de l'influence de quelques variables sur la conversion, le poids moléculaire, la distribution de la dimension des particules etc. La viscosité et la conversion sont toujours plus basses en suspension qu'en masse: on a obtenu des granules de polymère de dimensions plutôt dispersées et qui contiennent généralement un certain résidu monomérique (contrairement à la polymérisation en masse). On discute les résultats ci-dessus et on propose quelques interprétations.

Zusammenfassung

Es wird über die anionische Caprolactampolymerisation (Katalysatoren Natriumhydrid und Acetylcaprolactam) bei Ausführung in Glasgefässen als Funktion der Katalysatorkonzentration, der Polymerisationstemperatur etc. berichtet. Die gleiche Polymerisation wird auch bei Temperaturen um 120°C in einer Paraffinsuspension durch Einführung des Paraffins in ein sirupöses Präpolymeres ausgeführt. Der Einfluss einiger Variabler auf Umsatz, Molekulargewicht, Teilchengrössenverteilung etc. wird diskutiert. Viskosität und Umsatz sind in Suspension immer niedriger als in Substanz: Polymerkörnchen mit stark streuenden Dimensionen und im allgemeinen mit einem Gehalt an Restmonomerem (im Gegensatz zur Substanzpolymerisation) werden erhalten. Diskussion und Interpretation der erhaltenen Ergebnisse werden gegeben.