

Some Effects of Cocatalyst Structure on the Anionic Polymerization of ϵ -Caprolactam. II.*

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Synopsis

A study of the effect of catalyst (base) concentration and *N*-acylcaprolactam cocatalyst size and substitution on the fast anionic polymerization of caprolactam indicated that a steric effect due to cocatalyst size exists, and perhaps an electronic effect due to cocatalyst substitution was noted. The rate of polymerization, degree of polymerization, and yield of polymer are related to these effects. It was also noted that at high base concentrations, the rate and degree of polymerization along with the product yields all decrease. These latter observations suggest that reinterpretation of some of the reaction mechanism data may be important if polymer degradation is not an appreciable factor during the reaction.

INTRODUCTION

In a previous publication, an initial report was made concerning the effect of cocatalyst size and substitution on the anionic polymerization of caprolactam.¹ These preliminary studies indicated that when *N*-acylcaprolactams were employed as cocatalysts, the size of the acyl group effected the rate of polymerization, the degree of polymerization, and the yield of polymer. Indications that the electronegativity of the *N*-acyl group might also effect the magnitude of the same quantities were also reported. The initial data was based upon *N*-acetyl-, *N*-butyryl-, *N*-stearyl-, *N*-benzoyl-, and *N*-4-methoxybenzoyl- caprolactams being employed as polymerization cocatalysts. We have now investigated all the normal acyl groups from acetyl through myristoyl plus stearyl, and in addition the benzoyl, 4-cyanobenzoyl, 4-chlorobenzoyl, 4-bromobenzoyl, and 4-iodobenzoyl groups. The *N*-acylcaprolactams were prepared as described in previous publications.² The data obtained from the investigations to be described herein are displayed in Tables I-III.

EXPERIMENTAL

Polymerizations

The polymerization reactions were carried out in vapor baths. For reactions at 142°C., *o*-xylene (b.p. 142°C.) was employed; at 154°C., cyclo-

* From the theses of R. P. Scelia and S. E. Schonfeld which were submitted in partial fulfillment of the requirements for the degree of Master of Science.

hexanone (b.p. 155°C.) was used; and at 175°C., 2-octanol (b.p. 179°C.) was the heat exchanger.

Caprolactam (0.1 mole; 11.3 g.) was melted in a test tube and sparged with dry nitrogen at the appropriate reaction temperature for 30 min. to remove any traces of moisture present. Sodium hydride (as a 50% oil dispersion) was added at the desired concentration, and the reaction mixture sparged with dry nitrogen for an additional 10 min. The cocatalyst was then added at a constant concentration of 0.05 mole-%, and the mixture was heated at the desired temperature with dry nitrogen bubbling through the mixture until solidification occurred (until the reaction mixture was immobile at the temperature being employed) or until it was apparent that solidification would not occur.

Yields

The samples of 6-nylon were ground in a Waring Blendor and extracted with chloroform to remove any monomer present. The samples were then dried and weighed.

Inherent Viscosities

One-half gram samples of the polymers were dissolved in 100 ml. of concentrated sulfuric acid and allowed to flow through a No. 200 Ostwald viscosimeter, and the inherent viscosities determined in the usual fashion.

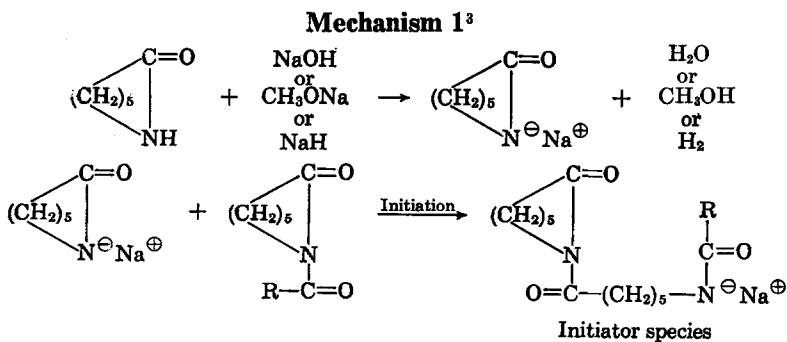
Degradation Reactions

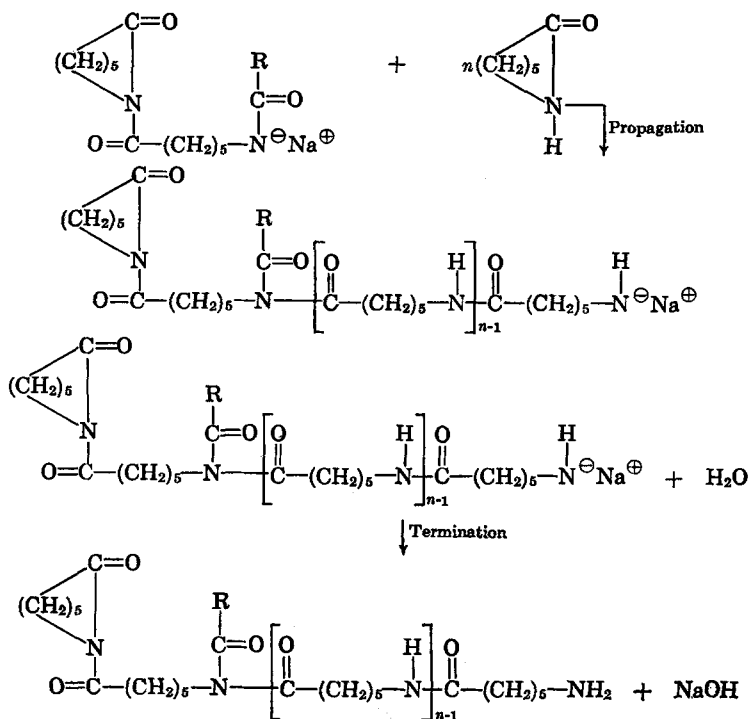
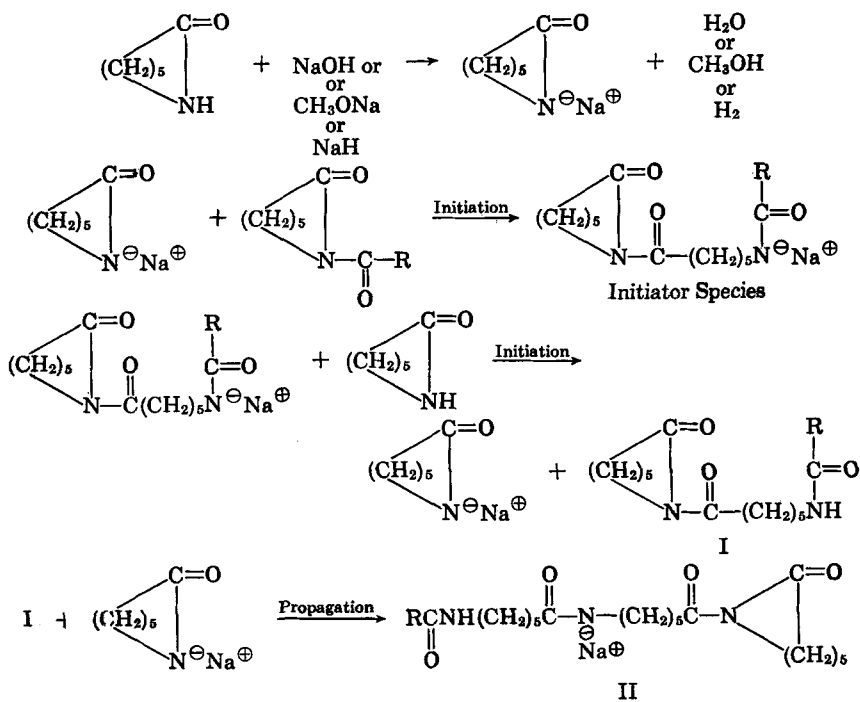
N-Sodiocaprolactam was prepared by adding an excess of caprolactam to powdered sodium in refluxing xylene under dry nitrogen.

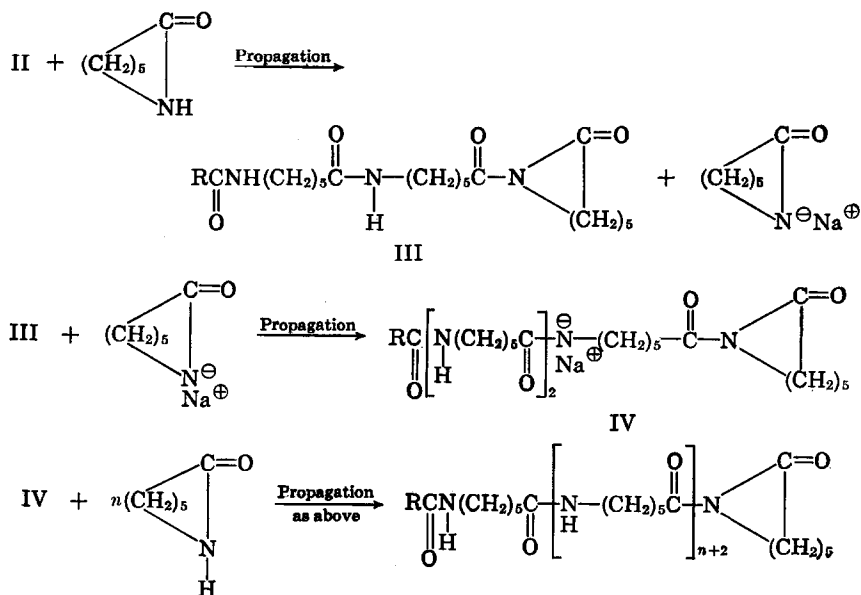
Samples of 6-nylon previously prepared under the conditions listed in Table I were heated above their melting points (230°C.). The desired amount of *N*-sodiocaprolactam was added to the melt under dry nitrogen. The mixtures were heated and sparged with dry nitrogen for the required time. The samples were immediately cooled to room temperature, ground, and extracted with chloroform. Inherent viscosities were then determined in the usual manner.

RESULTS AND DISCUSSION

Two mechanisms might be considered for the fast anionic polymerization of lactams.



Mechanism 2⁴



Of the two mechanisms shown above, mechanism 2 may be the most generally accepted. This is logical because the addition of each caprolactam moiety to the growing polymer chain involves attack of a caprolactam anion at the imide linkage. In mechanism 1, no such extensive use of the imide linkage is required. In looking at both mechanisms, it is possible to speculate that the concentration of catalyst (base) in the polymerization mixture would perhaps exert a profound effect upon the rate and degree of polymerization.

In mechanism 1, it might be expected that as the base concentration increases, the rate of polymerization would increase up to a point and then become constant at or above the *N*-acylcaprolactam concentration because each growing chain is initiated by attack of the caprolactam anion on the *N*-acyllactam cocatalyst and if no base-catalyzed degradation is taking place, at this point, in this scheme, the basic catalyst will have fulfilled its function and should exert no further effects on the polymerization. Similarly, the degree of polymerization might be expected to be inversely proportional to the base concentration until the amount of base added was equimolar with the amount of cocatalyst employed, at which point it too would remain constant if no base-catalyzed degradation is occurring.

It seems logical that in mechanism 2, the rate and degree of polymerization should be directly proportional to the base concentration, provided that degradation of the growing polymer chains is not an appreciable factor, due to the requirements that the cocatalyst must be activated by the attack of the caprolactam anion and because chain propagation occurs by the reaction of the anion with the terminal imide rings. If these conclusions are valid, a high base concentration would be most advantageous to the reaction process.

Table I shows data which indicate that regardless of the nature of the cocatalyst employed, neither mechanism seems to be quite correct with regard to the effects of base concentration if chain degradation is unimportant. The nature of chain degradation by caprolactam anion might be depicted as shown below:

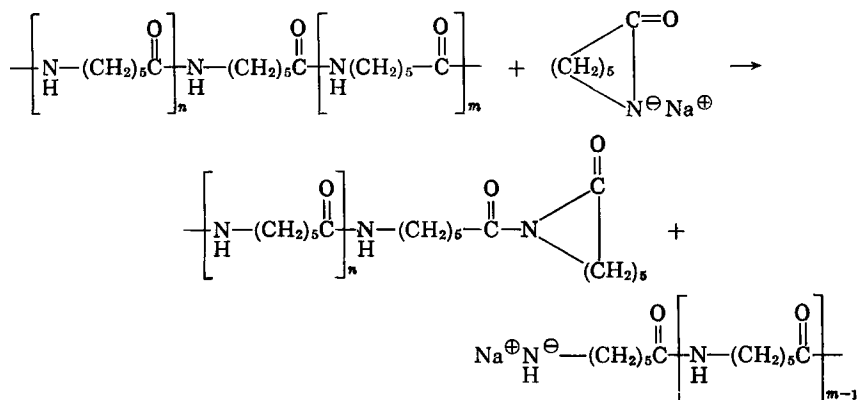


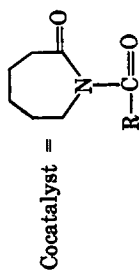
Table II displays results which were obtained from attempts to degrade 6-nylon above its melting point with *N*-sodiocaprolactam. As the table indicates, no appreciable degradation occurred when reaction times comparable to polymerization times employed in this work were used. Those experiments where much longer reaction times were utilized showed significant amounts of degradation.

If degradation is not an important factor, then it is possible that neither mechanism is quite correct as a model to explain the effects of base concentration. As can be seen in Table I, reaction rates, yields, and molecular weights proceed from a minimum at low base concentrations through a maximum at intermediate base concentrations to a second minimum at higher base concentrations. At present we are trying to carry out experiments which will resolve these anomalies.

Table I shows the effect of base concentration on the time necessary to produce solid polymer, holding the temperature at 154°C. and the concentration of various cocatalysts constant at 0.05 mole-%. The time necessary to produce solid polymer decreased with increasing base concentration to a point and then increased greatly as the base concentration was further increased. The table also shows the effect of base concentration on the inherent viscosity of the polymers produced at constant cocatalyst concentrations of 0.05 mole-%. The inherent viscosities of the samples remained high at low base concentrations and either increased or decreased only slightly as the base concentration was raised to about 2 mole-%. As the base concentration was increased further the inherent viscosities of the polymers decreased greatly.

The effect of base concentration on the yields of polymer holding the concentration of cocatalyst constant at 0.05 mole-% also is displayed in Table I.

TABLE I
Data Concerning the Effect of Cocatalyst Size and Substitution and Base Concentration
on the Anionic Polymerization of ϵ -Caprolactam^a



Cocatalyst ^b	Base concentration in mole-% NaH									
	0.29	0.57	1.15	2.29	3.44	4.58	5.73	6.88		
R = CH ₃										
Polymerization time, sec. ^c	232	201	93	74	56	52	435	637		
Yield of polymer, % ^c	94	98	96	100	98	95	40	33		
Inherent viscosity ^c	1.17	1.09	1.08	0.80	0.68	0.63	0.44	0.42		
R = C ₂ H ₅										
Polymerization time, sec.	405	345	124	98	98	115	541	751		
Yield of polymer, %	72	99	100	98	92	88	34	19		
Inherent viscosity	0.76	0.99	1.03	1.02	0.93	0.79	0.46	0.10		
R = n-C ₄ H ₉										
Polymerization time, sec.	443	262	118	83	95	108	457	>1,000		
Yield of polymer, %	72	94	97	97	88	81	29	7		
Inherent viscosity	0.88	0.96	1.03	1.03	0.94	0.88	0.39	<0.01		
R = n-C ₈ H ₁₇										
Polymerization time, sec.	305	187	94	56	60	88	456	>1,000		
Yield of polymer, %	83	100	100	100	94	85	34	16		
Inherent viscosity	1.01	1.10	1.14	1.03	1.00	0.81	0.39	0.11		
R = n-C ₁₀ H ₂₁										
Polymerization time, sec.	222	136	95	60	62	86	469	>1,000		
Yield of polymer, %	90	100	98	96	91	79	33	24		
Inherent viscosity	1.07	1.12	1.16	1.03	1.02	0.80	0.42	0.26		

R = n -C ₈ H ₁₈																			
Polymerization time, sec.	119	111	84	72	56	82	619	>1,000											
Yield of polymer, %	100	100	100	100	93	86	33	22											
Inherent viscosity	1.07	1.12	1.16	1.04	1.05	0.81	0.48	0.41											
R = n -C ₇ H ₁₆		0.57	1.15	2.29	3.44	4.58	5.73	6.88											
Polymerization time, sec.	156	121	86	80	61	80	622	>1,000											
Yield of polymer, %	99	100	100	100	89	75	32	20											
Inherent viscosity	1.08	1.11	1.14	1.11	1.10	0.87	0.46	0.37											
R = n -C ₈ H ₁₇																			
Polymerization time, sec.	163	127	88	82	64	80	597	>1,000											
Yield of polymer, %	96	100	100	100	90	66	29	20											
Inherent viscosity	1.10	1.10	1.13	1.15	1.16	0.89	0.54	0.33											
R = n -C ₉ H ₁₈																			
Polymerization time, sec.	170	130	90	86	67	74	599	>1,000											
Yield of polymer, %	97	100	100	100	87	60	28	14											
Inherent viscosity	1.14	1.12	1.13	1.18	1.18	0.92	0.59	0.28											
R = n -C ₁₀ H ₂₀																			
Polymerization time, sec.	205	135	101	87	71	78	572	>1,000											
Yield of polymer, %	80	94	95	97	84	56	25	13											
Inherent viscosity	1.16	1.15	1.13	1.00	1.00	0.80	0.41	0.25											
R = n -C ₁₁ H ₂₂																			
Polymerization time, sec.	262	160	113	89	84	93	485	>1,000											
Yield of polymer, %	74	91	94	97	79	54	22	14											
Inherent viscosity	1.20	1.19	1.13	0.95	0.93	0.71	0.39	0.17											
R = n -C ₁₂ H ₂₄																			
Polymerization time, sec.	300	171	133	115	313	493	>1,000	>1,000											
Yield of polymer, %	74	81	92	89	51	33	14	8											
Inherent viscosity	1.21	1.34	1.23	0.92	0.86	0.21	<0.01	<0.01											
R = n -C ₁₂ H ₂₇																			
Polymerization time, sec.	304	204	139	117	407	>1,000	>1,000	>1,000											
Yield of polymer, %	72	81	92	89	42	9	5	<0.6											
Inherent viscosity	1.22	1.53	1.34	0.93	0.83	<0.01	<0.01	<0.01											

(continued)

TABLE I (continued)

Cocatalyst ^b	Base concentration in mole-% NaH									
	0.29	0.57	1.15	2.29	3.44	4.58	5.73	6.88	>1,000	>1,000
R = <i>n</i> -C ₇ H ₁₅	>1,000	>1,000	>1,000	>1,000	>1,000	>1,000	>1,000	>1,000	>1,000	>1,000
Polymerization time, sec.										
Yield of polymer, %	<0.6	5	7	6	6	4	5	5	<0.6	<0.6
Inherent viscosity	<.01	0.11	0.17	0.23	0.21	<0.01	<0.01	<0.01	<0.01	<0.01
R = phenyl										
Polymerization time, sec.	805	212	156	135	190	>1,000	>1,000	>1,000	>1,000	>1,000
Yield of polymer, %	70	96	95	67	53	27	20	16	16	16
Inherent viscosity	0.67	0.94	1.00	0.71	0.69	0.53	0.28	0.11	0.11	0.11
R = 4-cyanophenyl										
Polymerization time, sec.	385	168	143	139	100	85	349	646	646	646
Yield of polymer, %	59	95	83	88	66	45	40	35	35	35
Inherent viscosity	1.30	1.37	1.33	1.29	1.22	1.11	0.80	0.68	0.80	0.68
R = 4-iodophenyl										
Polymerization time, sec.	805	244	160	109	122	607	>1,000	>1,000	>1,000	>1,000
Yield of polymer, %	60	97	100	69	56	28	18	10	10	10
Inherent viscosity	0.71	1.01	1.13	0.83	0.80	0.54	0.38	0.14	0.38	0.14
R = 4-bromophenyl										
Polymerization time, sec.	838	301	162	95	93	536	>1,000	>1,000	>1,000	>1,000
Yield of polymer, %	54	98	99	70	60	29	14	10	10	10
Inherent viscosity	0.71	1.01	1.16	0.95	0.90	0.59	0.41	0.13	0.41	0.13
R = 4-chlorophenyl										
Polymerization time, sec.	876	445	176	87	91	456	>1,000	>1,000	>1,000	>1,000
Yield of polymer, %	43	100	100	78	67	28	12	6	6	6
Inherent viscosity	0.83	1.04	1.18	1.01	0.95	0.62	0.41	0.41	0.41	0.41

^a Errors in time, % yield, and viscosity are ± 3 , ± 0.6 , ± 0.01 , respectively.

^b Cocatalyst concentration held constant at 0.05 mole-%. Temperature held at $154 \pm 0.5^\circ\text{C}$.

^c All values are averages of duplicate experiments.

At very low base concentrations, the yields of polymer were high. As the concentration of base increased to about 2 mole-%, the maximum yields of polymer were obtained, and as the concentration of base was further increased, the yields of polymer began to decrease.

TABLE II
Degradation of 6-Nylon with *N*-Sodiocaprolactam^a

Base concentration, mole-%	Reaction time, sec.	Inherent viscosity before reaction	Inherent viscosity after reaction
4.32	98	0.93	0.90
3.91	45	0.53	0.53
2.56	170	1.07	0.92
0.98	70	0.50	0.49
0.79	211	1.28	1.13
0.79	3600	1.28	0.92
0.56	217	1.08	0.90
0.56	3600	1.08	0.81

^a All experiments employed 3-g. samples of 6-nylon and were carried out at 230–240°C.

According to either mechanism shown earlier, the anion concentration determined the concentration of initiator species present to start polymer chains, however, it probably was not 100% efficient in forming initiator species. Also, there probably was a certain amount of residual water present in the monomer and this water was capable of reacting with and destroying a certain number of initiator species.

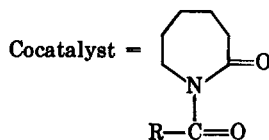
Low Base Concentration

At low base concentrations, 0.29–0.57 mole-%, few initiator species were formed and some of these may have been destroyed by the residual water present. Fewer polymer chains were initiated. Each polymer sample had a moderately high inherent viscosity as can be seen in Table I. These polymers solidified slowly since there were too few chains present to use up all of the monomer present before termination occurred. The yields of polymer were moderately high at the low base concentrations.

Medium Base Concentration

As the base concentration increased to about 0.57–1.15 mole-%, the time necessary to produce solid polymer decreased because there were many initiator species present. Many polymer chains were formed and most of the monomer present was consumed before termination occurred. The inherent viscosities of the samples in most cases, reached their maximum values at these base concentrations since most of the available monomer was incorporated into polymer molecules before termination occurred.

TABLE III
Data Concerning the Effect of Temperature on the
Fast Anionic Polymerization of Caprolactam^a



Cocatalyst	Polymeri- zation tempera- ture, °C. ^b	Polymerization time, sec.	Yield of polymer, %	Inherent viscosity
R = CH ₃	142	116	100	0.58
	154	74	100	0.80
	175	20	100	1.02
R = C ₂ H ₅	142	116	98	0.81
	154	98	98	1.02
	175	35	100	1.17
R = <i>n</i> -C ₃ H ₇	142	117	97	0.81
	154	83	96	1.03
	175	27	100	1.19
R = <i>n</i> -C ₄ H ₉	142	125	96	0.84
	154	56	100	1.03
	175	30	100	1.16
R = <i>n</i> -C ₅ H ₁₁	142	151	98	0.84
	154	60	97	1.03
	175	32	100	1.18
R = <i>n</i> -C ₆ H ₁₃	142	169	98	0.88
	154	72	100	1.05
	175	36	100	1.23
R = <i>n</i> -C ₇ H ₁₅	142	175	98	0.91
	154	80	100	1.10
	175	36	97	1.24
R = <i>n</i> -C ₈ H ₁₇	142	181	94	0.93
	154	82	100	1.14
	175	35	97	1.25
R = <i>n</i> -C ₉ H ₁₉	142	186	93	0.98
	154	86	99	1.19
	175	35	96	1.27

(continued)

High Base Concentration

As the base concentration further increased, it was expected that the inherent viscosities of the samples might steadily increase. However, it was found that this was not the case as Table I shows. At about 2 mole-% of base, the inherent viscosity started to decrease gradually and at about 5 mole-% of base, the inherent viscosity was decreasing very rapidly. One possible explanation for these results was that at these high base concentrations there were a large number of initiators formed so that many polymer chains were started. Since there were so many polymer

TABLE III. (continued)

Cocatalyst	Polymerization temperature, °C. ^b	Polymerization time, sec.	Yield of polymer, %	Inherent viscosity
R = <i>n</i> -C ₁₀ H ₂₁	142	186	86	1.00
	154	87	97	1.20
	175	35	96	1.27
R = <i>n</i> -C ₁₁ H ₂₃	142	190	93	0.88
	154	89	97	0.94
	175	39	98	1.23
R = <i>n</i> -C ₁₂ H ₂₅	142	285	86	0.84
	154	115	89	0.92
	175	55	98	1.24
R = <i>n</i> -C ₁₃ H ₂₇	142	286	84	0.84
	154	117	88	0.92
	175	56	90	1.23
R = <i>n</i> -C ₁₇ H ₃₅	142	>1,000	0	<0.01
	154	>1,000	6	0.23
	175	>1,000	2	0.01
R = Phenyl	142	212	57	0.46
	154	135	68	0.72
	175	29	76	1.33
R = 4-Cyanophenyl	142	286	83	1.01
	154	139	90	1.29
	175	70	95	1.36
R = 4-Iodophenyl	142	170	55	0.51
	154	100	70	0.81
	175	30	81	1.33
R = 4-Bromophenyl	142	153	50	0.55
	154	95	70	0.95
	175	31	85	1.33
R = 4-Chlorophenyl	142	151	60	0.63
	154	87	78	1.01
	175	26	90	1.35

^a Cocatalyst concentration constant at 0.05 mole-%. Base concentration constant at 2.29 mole-%.

^b Actual temperature readings were 141.9 ± 0.1°C., 154 ± 0.5°C., and 175 ± 0.4°C.

chains growing, each one might have been of lower molecular weight, that is, lower inherent viscosity because there was only a limited amount of monomer available for polymerization. Many of the very low molecular weight chains were extracted along with the unreacted monomer so that lower yields resulted at these high base concentrations. These low molecular weight polymers might also keep the whole polymer melt from turning solid until enough longer chains could form. Therefore, the time necessary to produce solid polymer increased.

The data in Table I also show that as the size of the acyl group on the cocatalyst increased, the rate of polymerization decreased, the yield of polymer decreased, and the degree of polymerization increased slightly. These

are general trends only for it can be seen that the statements are not quite accurate in detail where the *N*-acyl group is propionyl, butyryl, or pentanoyl. This aberration does not appear to be an artifact and is quite reproducible under the reaction conditions employed. As Table III indicates, temperature is not an important factor, and the order of cocatalyst efficacy remained essentially the same at the three reaction temperatures employed.

Polymerizations of caprolactam were carried out at a constant base concentration while the type of straight chain cocatalyst was varied at a constant concentration. The results shown in Tables I and III indicated that the times and yields of polymerization, along with the inherent viscosities of the polymers produced, in general, were dependent upon the size of the *N*-acylcaprolactam cocatalyst used.

Table I shows the effect of cocatalyst size on the time necessary to produce solid polymer holding the concentration of catalyst and cocatalyst constant. The *N*-acetyl cocatalyst produced polymer rapidly. The time necessary to produce solid polymer then increased as the size of the cocatalyst increased. Up to the *N*-butyryl derivative, the longest times were noted and then the times began to decrease. They continued to decrease as the size of the cocatalyst increased up to the *N*-heptanoyl derivative. From this derivative on, the time necessary to produce solid polymer increased steadily up to the tridecyl derivative. *N*-stearylcaprolactam did not produce any solid polymer in 1000 sec.

The effect of cocatalyst size on the per cent yield of polymer produced at a constant catalyst and cocatalyst concentration also is displayed in Table I. The *N*-acetyl cocatalyst produced high yields of polymer. The *N*-propionyl and *N*-butyryl cocatalysts produced lower yields of polymer than the *N*-acetyl derivative. The yields of polymer then increased with increasing cocatalyst size. The *N*-heptanoylcaprolactam gave the highest yields of polymer. As the size of the cocatalysts got larger still, the yields of polymer decreased steadily and at *N*-stearyl-caprolactam only small amounts of polymer were produced.

Table I also notes the effect of cocatalyst size on the inherent viscosity of the polymers produced at a constant catalyst and cocatalyst concentration. The *N*-acetyl cocatalyst gave moderately high inherent viscosities. The inherent viscosity then dropped off when the *N*-propionyl derivative was used. As the size of the cocatalyst was further increased, there was a steady increase in the inherent viscosities noted, however, when *N*-stearylcaprolactam was used as the cocatalyst, the inherent viscosity was so low that it was difficult to measure.

In general, the initial expectations were fulfilled with the exception of the three and four carbon chain derivatives which gave totally unexpected results. Since the concentration of initiator species is the only variable in the polymerization, all of the results obtained are explained in terms of the initiator concentration. Molecular models were constructed and used to rationalize many of the results.

The size of the *N*-acyl group on the cocatalyst may determine the ease of formation of an initiator species. The acetyl group was too small to block the attack of an anion on the cocatalyst, so quite a few initiator species could form and almost all of the monomer was used to produce relatively high molecular weight polymer. The propionyl and butyryl groups were slightly larger and molecular models showed that they both were just big enough to offer steric blocking to the ring amide site. These smaller cocatalysts could not easily interact with any of the other atoms in the lactam ring. Therefore, fewer initiator species could be formed and it took longer to produce solid polymer. Fewer chains were started and they could not use up all of the monomer present before termination occurred, and therefore, each chain had a lower molecular weight.

The *N*-valeroyl, *N*-hexanoyl, and *N*-heptanoyl derivatives, being larger than the *N*-butyryl derivative, still blocked attack of the amide site. However, models indicated that these derivatives might interact sterically with other atoms in the lactam ring in such a fashion that the lactam ring's carbonyl site could be more open to attack by an anion. More initiator species were formed and more polymer chains were started. Since there were many growing polymer chains, most of the available monomer was consumed before chain termination could occur. Therefore, each polymer chain was able to grow to a high molecular weight.

The cocatalysts larger than the *N*-heptanoyl offered progressively larger amounts of blocking to an attacking caprolactam anion. Models showed that in most conformations, these long chain cocatalysts might grossly interfere with the attack of an anion on the lactam ring carbonyl group because of their large bulk regardless of other factors. Fewer initiator species formed and there were fewer polymer chains growing. Each chain was able to grow to a higher molecular weight, but the rate at which solid polymer formed decreased because there were not enough growing chains to use up all of the monomer quickly, and therefore, the polymer to monomer ratio got large slowly. Also, since larger amounts of chain termination could occur at this slower rate, lower yields of polymer resulted.

When the very highly sterically blocked *N*-stearylcaprolactam was used, extremely few initiator species were formed. Therefore, in 1000 sec. no solid matter had formed and the polymers that were present were of extremely low molecular weight. Very little of the monomer had been incorporated into these polymers so that the yield of polymer was very low. This unreacted monomer was recovered after extraction of the polymer.

The polymerization times and yields along with the inherent viscosities of the polymers produced stayed in the same relative order regardless of the concentration of catalyst and cocatalyst employed.

If molecular models of the various cocatalyst employed in this work are constructed, it can readily be noted that as the size of the *N*-acyl group increases, the blocking ability of the *N*-acyl group for the ring carbonyl group increases, and therefore, the facility of ring cleavage by the caprolactam anion would decrease, and fewer initiator species would be formed.

Further examination of the molecular models for the homologous series of cocatalysts employed also indicates that the anomaly in the series of cocatalysts, where the acyl groups are propionyl through pentanoyl might be justified by saying that these *N*-acyl groups block the approach to the ring carbonyl carbon atom more effectively than some of the larger *N*-acyl groups employed, perhaps due to the interaction of the slightly larger *N*-acyl chains with the ring hydrogen atoms. Furthermore, these effects seem to be operative mainly at the two higher reaction temperatures used. Perhaps this is due to different conformer populations being present at the higher temperatures.

Tables I and III also show data for various substituted *N*-benzoylcaprolactam cocatalysts. However, the data here are not as clear-cut as the data for the simple *N*-acyl cocatalysts. It appears that in general 4-cyanobenzoylcaprolactam is the best cocatalyst under all the experimental conditions attempted. This may be due to the fact that the highly electronegative cyano group weakened the ring amide linkage in the cocatalyst enabling the 4-cyanobenzoylcaprolactam to function more effectively in the initiation steps. At the lowest base concentrations, except for the cyano derivative, all of the cocatalysts seemed to have about the same effect on the polymerization. However, as the base concentration was increased, the other cocatalysts appeared to become more effective, and the three 4-halobenzoyl derivatives actually became more effective with regard to rate than the cyano derivative. At the highest base concentrations, their cocatalytic properties dropped off while those of the cyano compound remained somewhat better.

In summary, it might be said that the rate, degree of polymerization, and the yield of product are markedly affected by both the base concentration and the steric nature of the cocatalyst. A possible electronic effect employing substituted *N*-benzoylcaprolactams was also noted. The steric effect appears to be uniform over a wide range of catalyst (base) concentration.

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Résumé

Une étude de l'effet de la concentration en catalyseur (base), de la grandeur et de la substitution du cocatalyseur *N*-acylcaprolactame sur la polymérisation anionique rapide du caprolactame indiquait que l'effet stérique dû à la grandeur dû cocatalyseur existe et peut être un effet électronique dû à la substitution du cocatalyseur pouvait être noté. La vitesse de polymérisation, le degré de polymérisation et le rendement en polymère étaient directement reliés à ces effets. On notait également que à concentration en base élevée, la vitesse et le degré de polymérisation décroissaient tous les deux. Cette dernière observation suggérerait que la réinterprétation de certains résultats de mécanismes de réaction peut être importante si la dégradation du polymère n'est pas un facteur appréciable au cours de la réaction.

Zusammenfassung

Eine Untersuchung des Einflusses der Katalysator-(Basen)-konzentration und der Grösse und Substitution des Cokatalysators *N*-Acylcaprolactam auf die schnelle anionische Polymerisation von Caprolactam zeigte, dass ein durch die Grösse des Cokatalysators bedingter sterischer Effekt besteht; ein durch die Cokatalysatorsubstitution ausgeübter elektronischer Effekt ist vielleicht auch vorhanden. Polymerisationsgeschwindigkeit, Polymerisationsgrad und Ausbeute an Polymerem stehen zu diesen Effekten in Beziehung. Weiters wurde festgestellt, dass bei hohen Basenkonzentrationen Polymerisationsgeschwindigkeit, Polymerisationsgrad und Polymerisationsausbeute abnehmen. Diese Beobachtungen lassen erkennen, dass eine Neuinterpretation mancher Daten bezüglich des Reaktionsmechanismus von Bedeutung sein kann, wenn der Polymerabbau nicht ein beträchtliches Ausmass während der Reaktion hat.

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