Some Effects of Cocatalyst Structure on the Anionic Polymerization of ε-Caprolactam
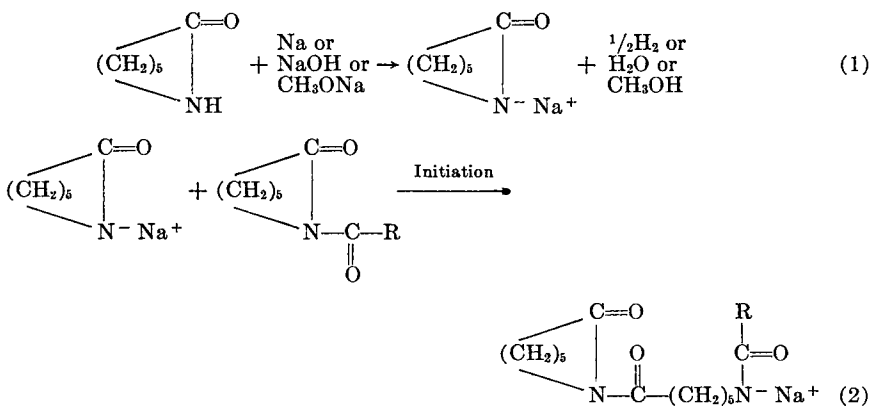
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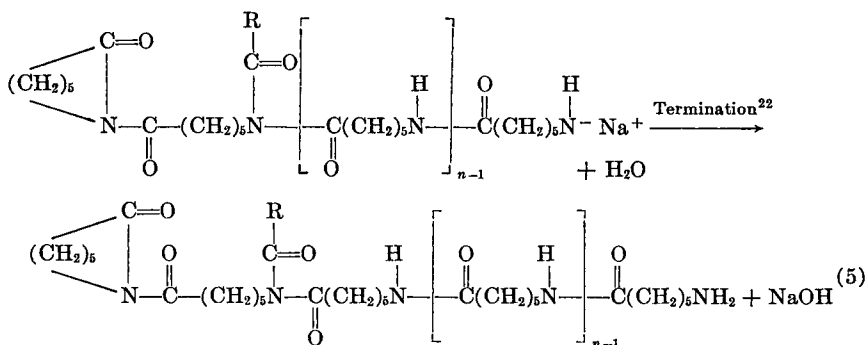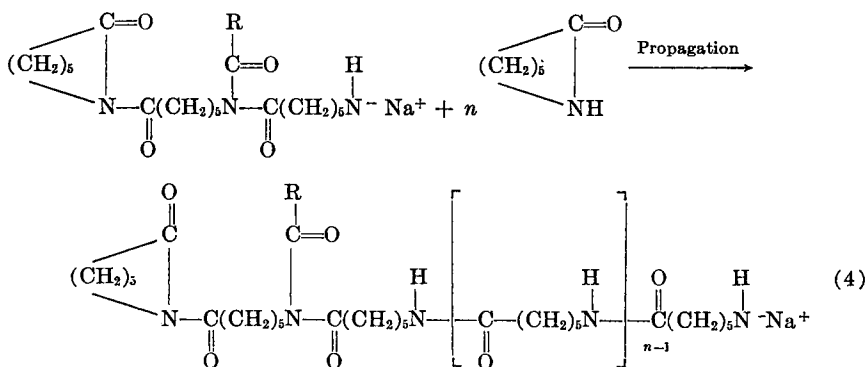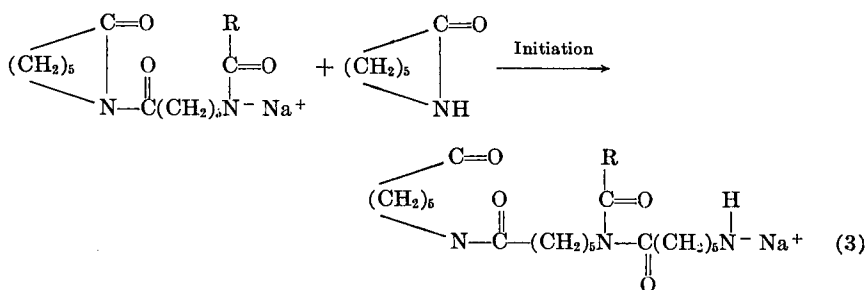
Synopsis

N-Acetyl, N-butyryl, N-stearyl, N-benzoyl, N-4-methoxybenzoyl, and N-4-nitrobenzoyl caprolactams were prepared and used as cocatalysts for the anionic polymerization of caprolactam. The results of these studies indicate that all of the cocatalysts used, except N-acetylcaprolactam, exert a steric effect which lowers both the rate and degree of polymerization. The N-benzoyl derivative appeared to be a slightly better cocatalyst than the N-4-methoxybenzoyl derivative. This may be due to the fact that the N-benzoyl group is the more electron-attracting group. N-4-Nitrobenzoylcaprolactam was unstable under the reaction conditions employed.

INTRODUCTION

The anionic polymerization of caprolactam and other lactams has been studied by several investigators.[1-22] In order to make the polymerization go fast, the addition of a cocatalyst is necessary.[5-22] Among the better cocatalysts for this reaction are acyl compounds[15,19,22] and isocyanates.[12,17,18] Usually, N-acetylcaprolactam or phenylisocyanate are the specific specie used in polymerizations of this nature.[12,15,17-19,22] The generally accepted mechanism for this process is as given in eqs. (1)–(5):

$$(CH_2)_5 \begin{matrix} C=O \\ | \\ NH \end{matrix} + \begin{matrix} Na \text{ or} \\ NaOH \text{ or} \\ CH_3ONa \end{matrix} \rightarrow (CH_2)_5 \begin{matrix} C=O \\ | \\ N^- Na^+ \end{matrix} + \begin{matrix} {}^1\!/_2H_2 \text{ or} \\ H_2O \text{ or} \\ CH_3OH \end{matrix} \quad (1)$$

$$(CH_2)_5 \begin{matrix} C=O \\ | \\ N^- Na^+ \end{matrix} + (CH_2)_5 \begin{matrix} C=O \\ | \\ N-C-R \\ \| \\ O \end{matrix} \xrightarrow{\text{Initiation}}$$

$$(CH_2)_5 \begin{matrix} C=O \\ | \quad O \\ N-C-(CH_2)_5N^- Na^+ \end{matrix} \begin{matrix} R \\ | \\ C=O \end{matrix} \quad (2)$$

where R = CH₃ or NHC₆H₅.

$$\text{(structure)} + \text{(CH}_2\text{)}_5 \xrightarrow{\text{Initiation}}$$

$$\xrightarrow{\text{(3)}}$$

$$\text{(structure)} + n \text{ (CH}_2\text{)}_5 \xrightarrow{\text{Propagation}}$$

$$\xrightarrow{\text{(4)}}$$

$$\xrightarrow{\text{Termination}^{22}}$$

$$+ \text{H}_2\text{O}$$

$$\text{(structure)} \cdots \text{C(CH}_2\text{)}_5\text{NH}_2 + \text{NaOH} \quad \text{(5)}$$
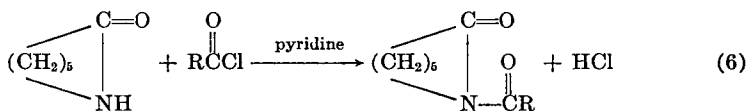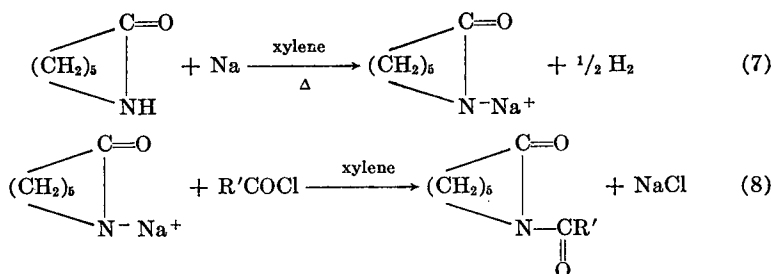
While some work has been done concerning what types of materials exhibit the cocatalysis effect,[1-22] no work has been done which attempts to define what structural features are important within a given class of co-catalysts. In this paper, the results of work done with a variety of N-acyl-caprolactams of differing steric and electronic natures will be described.

A series of N-acylcaprolactams having different acyl groups on the lactam nitrogen atom were prepared by one of two methods.

$$\text{(CH}_2\text{)}_5 \text{(lactam)} + \text{RCCl} \xrightarrow{\text{pyridine}} \text{(CH}_2\text{)}_5 \text{(product)} + \text{HCl} \quad \text{(6)}$$

where $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5, p\text{-O}_2\text{NC}_6\text{H}_4, p\text{-CH}_3\text{OC}_6\text{H}_4$.

$$(CH_2)_5 \underset{NH}{\overset{C=O}{\Big|}} + Na \xrightarrow[\Delta]{xylene} (CH_2)_5 \underset{N^-Na^+}{\overset{C=O}{\Big|}} + {}^{1}/_{2}\,H_2 \qquad (7)$$

$$(CH_2)_5 \underset{N^-Na^+}{\overset{C=O}{\Big|}} + R'COCl \xrightarrow{xylene} (CH_2)_5 \underset{N-CR'}{\overset{C=O}{\Big|}} + NaCl \qquad (8)$$
$$\underset{\overset{\|}{O}}{}$$

where $R' = n\text{-}C_4H_9,\ n\text{-}C_{17}H_{35}$.

The pyridine method[23] worked well for all acyl halides except n-butyryl and stearyl chlorides. To prepare these compounds, it was necessary to use the sodium salt method.[24] With the exception of the N-acetyl[15] and N-benzoyl[24] caprolactams, all the cocatalysts are new compounds.

EXPERIMENTAL

Pyridine Method

Benzene (200 ml.), pyridine (90 ml.), caprolactam (0.1 mole), and 0.1 mole of the acyl chloride were mixed and heated at 90–100°C. for 30 min. The mixture was then poured into 500 ml. of water and the benzene layer washed with 5% sodium carbonate solution. The benzene solution was dried and the solvent removed. The crude product was recrystallized from ligroin or distilled at reduced pressure.

Sodium Salt Method

Xylene (200 ml.) with 0.1 mole of sodium suspended within as chunks was heated to reflux with fast stirring. When the sodium was powdered, the slurry was cooled rapidly to room temperature while the initial stirring rate was maintained. To the suspension of sodium powder was added 0.1 mole of caprolactam. This mixture was stirred at 100°C. until the sodium had disappeared. The acyl chloride was then added and the mixture stirred until the voluminous lactam salt was replaced in suspension, by a sodium chloride precipitate. The mixture was cooled, filtered, and the solvent allowed to evaporate at room temperature. The residue was recrystallized from ligroin or distilled at reduced pressure.

Infrared spectra of liquids were taken in chloroform. Solid samples were handled in potassium bromide wafers.

Table I summarizes the results obtained from the procedures used to prepare the cocatalysts.

Polymerizations

The polymerization reactions were carried out in a cyclohexanone vapor bath (b.p. = 155°C.). A 0.1 mole portion (11.3 g.) of caprolactam was melted in a test tube in the bath and was sparged with nitrogen for 30

TABLE I

Physical Properties of *N*-Acylcaprolactams

| *N*-Acyl group and yield, % | Physical constants | | | | | | Infrared data, cm.$^{-1a}$ |
| | b.p., °C./mm. Hg | m.p., °C. | C, % | | H, % | | |
			Calcd.	Found	Calcd.	Found	
Acetyl, 30%	126/14[b]		.61.90	61.73	8.38	8.26	740s, 855w, 885w, 970m, 1090w, 1130w, 1165w, 1190m, 1265m, 1335m, 1360w, 1375m, 1390w, 1465w, 1695s, 2850w, 2935w, 3010w
Butyryl, 20%	100/0.1[c]		65.50	65.29	9.35	9.33	845w, 880w, 915w, 965s, 1155s, 1185s, 1205s, 1245w, 1260m, 1290w, 1315w, 1330m, 1350m, 1370m, 1390s, 1440m, 1460m, 1700s, 1870m, 2890m, 2940s, 2970s
Stearyl, 8%	156/0.1	37–39	74.80	74.63	11.87	11.94	865w, 970w, 1070w, 1090w, 1140s, 1170m, 1245m, 1320m, 1335w, 1370m, 1455m, 1680s, 2860s, 2925s
Benzoyl, 25%		69	71.80	71.77	6.92	6.98	695s, 850w, 875w, 920m, 975s, 1080m, 1150s, 1175s, 1275s, 1330s, 1350s, 1380s, 1450s, 1675s, 2860m, 2940s, 3000m
4-Methoxy-benzoyl, 68%		95	67.9	68.00	6.86	6.46	970s, 1020s, 1160s, 1240s, 1500s, 1590s, 1660s, 1760s, 2930s
4-Nitroben-zoyl, 90%		105	59.40	60.00	5.34	5.42	855m, 975m, 1145m, 1185m, 1285m, 1360s, 1525s, 1690s, 2490s

[a] s = strong intensity; m = medium intensity; w = weak intensity.
[b] n_D^{25} = 1.4868; d^{25} = 1.1335.
[c] n_D^{24} = 1.4818; d^{25} = 1.0845.

min. to remove traces of water. Sodium methoxide (0.225 g.; 0.0042 mole) was added and the mixture sparged and heated for an additional 30 min. to remove methanol. The cocatalysts were added at different concentrations and the mixtures were left in the bath until they solidified or until it was apparent that solidification would not occur.

The samples of nylon 6 were ground up and extracted with chloroform to remove any unreacted caprolactam. The nylon 6 was then vacuum-dried and 0.5 g. of sample was dissolved in concentrated sulfuric acid. These samples were then allowed to run through a No. 75 viscometer and the efflux times compared with that of pure concentrated sulfuric acid.

RESULTS AND DISCUSSION

Table II displays the results obtained from several polymerizations with different cocatalysts at various concentrations.

Table II shows the cocatalysts in order of increasing size of the *N*-acyl groups. As can be seen from the table, as the size of the acyl group in-

TABLE II

Polymerization of ε-Caprolactam in the Presence of N-Acylcaprolactam Cocatalysts

Acyl group	Co-catalyst, mole-%	N-Sodio-capro-lactam, mole-%	Solidification time, sec.	Melting point, °C.	Polymer yield, %	Inherent viscosity
N-Acetyl	0.5	4.2	205	232	81.3	0.97
	1.0	4.2	138	229	100	0.74
	1.5	4.2	70	229	85.5	0.69
N-n-Butyryl	0.5	4.2	5838	232	23.1	0.40
	1.0	4.2	338	230	90.0	0.64
	1.5	4.2	161	230	97.4	0.84
N-Benzoyl	0.5	4.2	No solid	215	8.75	0.11
	1.0	4.2	625	230	81.6	0.65
	1.5	4.2	144	230	100	0.65
N-p-Methoxy-benzoyl	0.5	4.2	No solid	215	7.64	0.04
	1.0	4.2	1520	235	48.3	0.52
	1.5	4.2	325	235	87.9	0.68
N-Stearyl	0.5	4.2	No solid	227	6.0	0.26
	1.0	4.2	No solid	230	4.5	0.25
	1.5	4.2	No solid	228	4.3	0.32

creased, the rate and degree of polymerization decreased and were directly proportional to the cocatalyst concentration. This might be expected because as the size of the acyl group increased it might be more difficult for the N-sodiocaprolactam ion pair to approach the cocatalyst molecule closely enough to break the amide linkage and initiate a polymer chain. Thus, fewer chains would be initiated, the early stages of chain propagation would also be slow, and the slowly growing chain would be terminated before it could attain a high degree of polymerization. As the cocatalyst concentration was increased, the rate and degree of polymerization increased because more cocatalyst was present to migitate the steric effect. When the N-acyl group was small enough (N-acetyl), the cocatalyst concentration was proportional to the rate of polymerization but inversely proportional to the degree of polymerization. This latter behavior is typical of most addition polymerizations and was observed by other investigators in similar type polymerizations.[22] The yields of polymer also agree with these rationalizations.

Three para-substituted N-benzoylcaprolactams were prepared, N-benzoyl, N-p-methoxybenzoyl, and N-p-nitrobenzoyl, to see if the electron withdrawing or releasing power of the N-acyl group effected the polymerization. Unfortunately, the N-nitrobenzoyl derivative was unstable under the polymerization conditions. When added to the reaction mixture, the solution became black and no polymerization occurred. However, the other two derivatives were stable and could be used as cocatalysts without difficulty.

It might be expected that the more electronegative N-acyl group would facilitate cleavage of the cyclic amide linkage by the N-sodiocaprolactam

ion pair and therefore be a better cocatalyst than the less electronegatively substituted cocatalysts.   From Table II, it can be observed that the more electronegative benzoyl derivative was the better catalyst of the two tried. However, neither of the more electron-attracting benzoyl derivatives was as good a catalyst as the N-acetyl or N-butyryl caprolactams.

In summary, it can be said that in these studies, the best cocatalysts of the N-acylcaprolactams employed had the smallest N-acyl groups.   An electronegativity effect was observed.   The steric effect will override the electronegativity effect by a large margin unless the groups in question are of equal or similar size or the steric blocking group is very much larger than the electronegative group.

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Résumé

On a préparé les *N*-acétyle, *N*-butyle, *N*-stéaryle, *N*-benzoyle, *N*-4-méthoxybenzoyle, et *N*-4-nitrobenzoyle-caprolactames, et on les a employés comme catalyseurs pour la polymérisation anionique du caprolactame. Les résultats de ces études indiquent que tous ces cocatalyseurs, sauf le *N*-acétylcaprolactame, exercent un effet stérique, et abaissent ainsi le degré et la vitesse de la polymérisation. Le dérivé *N*-benzoylé semblait être légèrement meilleur que le dérivé *N*-4-méthoxybenzoylé. Ceci est peut-être dû au fait que le groupe *N*-benzoyle est le groupe le plus électrocapteur. Le *N*-4-nitrobenzoyl-caprolactame était instable dans les conditions réactionnelles employées.

Zusammenfassung

N-Acetyl-, *N*-Butyryl-, *N*-Stearyl-, *N*-Benzoyl-, *N*-4-Methoxybenzoyl- und *N*-4-Nitrobenzoylcaprolactam wurden hergestellt und als Cokatalysatoren bei der anionischen Polymerisation von Caprolactam verwendet. Wie aus diesen Untersuchungen hervorgeht, haben alle diese Cokatalysatoren mit Ausnahme von *N*-Acetylcaprolactam eine sterische Wirkung, wodurch sowohl die Geschwindigkeit der Polymerisation als auch der Polymerisationsgrad erniedrigt werden. Das *N*-Benzoyl-Derivat ist anscheinend ein besserer Cokatalysator als das *N*-4-Methoxybenzoyl-Derivat. Dies dürfte auf die stärker elektronenanziehende Natur der *N*-Benzoylgruppe zurückzuführen sein. *N*-4-Nitrobenzoylcaprolactam war unter den gegebenen Reaktionsbedingungen nicht stabil.