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# Investigations on the Role of Acyl Initiators and $CO_2$ in Nylon 4 Polymerization*

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## Summary

The preparation of high molecular weight nylon 4 with alkali metal pyrrolidonate catalysts, acyl initiators, and $CO_2$ was studied. Isolated sodium pyrrolidonate and the appropriate amount of acyl initiator gave unusually high molecular weight nylon 4 ($\bar{M}_w$ >200,000). The molecular weight-initiator concentration relationship indicates that acyl compounds play a dual role in the polymerization, acting both as initiators and scavengers for chain-terminating impurities. One potential chain terminator was identified as 4-aminobutyric acid. The high polymer molecular weights obtained in the presence of $CO_2$ can also be explained by the scavenging of chain terminators by $CO_2$. Determination of the number of growing chains, however, shows that $CO_2$, unlike the acyl compounds, is not an initiator in nylon 4 polymerization.

## Introduction

The slow, base-catalyzed polymerization of 2-pyrrolidone (py) to nylon 4 was first reported by Ney, Nummy, and Barnes.[1,2] A subsequent discovery[3] has shown that by adding an acyl compound such as N-acyl pyrrolidone, acid anhydride, acid chloride, lactame, or ester to the alkaline catalyst, the rate of polymerization can be dramatically increased. The nylon 4 produced with these acyl initiators is relatively low molecular weight and has a very broad molecular weight distribution.[4] The synthesis of high molecular weight nylon 4 with a narrow molecular weight distribution was accomplished by Barnes[5] using a catalyst prepared from potassium pyrrolidonate (py-K) and $CO_2$.

To explain the accelerating effect of N-acyl lactams and other acyl compounds, it was proposed[6] that propagation proceeds rapidly through the attack of py anion on the acyl-substituted lactame carbonyl. In a paper describing the preparation of nylon 4 with $CO_2$, Peters and Gervasi[7] suggested that py anion and $CO_2$ form py-carboxylate which acts as a slow initiator. Roda and co-workers[8] isolated and

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characterized the alkali metal salts of py-carboxylate but the site of $CO_2$ attachment (N or O) remains unresolved. On the basis of kinetic investigations, the same authors[9] concluded that $CO_2$ does not participate directly in the polymerization and speculated that py-carboxylate may influence the basicity of the system may serve as a nucleation center for the polymer or it may act as a drying agent to remove water from the reaction mixture.

In the course of our work on nylon 4 polymerization, we confirmed that acetic anhydride ($Ac_2O$) indeed accelerates the base-catalyzed reaction, but instead of the low molecular weights reported in the literature, we obtained relatively high molecular weight nylon 4. Under certain conditions $Ac_2O$ gave almost as high molecular weight polymer as $CO_2$. To explain this surprising result, a detailed study of the effect of initiator concentration on conversion and molecular weight was undertaken.

## Experimental

Isolated sodium pyrrolidonate (py-Na) was prepared from py and $CH_3ONa$. The methanol, formed in the reaction, was removed by azeotropic distillation. The resulting suspension was filtered to give isolated py-Na or was reacted with $CO_2$ and filtered to give a white solid consisting of isolated sodium pyrrolidonate-carboxylate (py-Na/$CO_2$). The amount of $CO_2$ in the catalyst was varied by the length of $CO_2$ introduction. Details of the catalyst preparation are described in a patent.[10] In situ potassium pyrrolidonate (py-K) and in situ potassium pyrrolidone-carboxylate (py-K/$CO_2$) were prepared from py, KOH, and $CO_2$ by the method of Barnes. Experimental details are given in Reference 11.

Polymerizations were carried out in dry polyethylene bottles, under nitrogen, by mixing and heating py with a preweighed amount of catalyst, initiator, or other additive. Concentrations are reported as mole percent based on monomer. The polymer was isolated by breaking up the hardened polymer mass into granules, washing it with distilled water, and drying it in vacuum at 70°C. Weight average molecular weights were calculated from the intrinsic viscosity determined in m-cresol.[12]

## Results and Discussion

### High Molecular Weight nylon 4 With N-acyl Initiators

Polymerization reactions carried out with isolated py-Na catalyst and various initiators are summarized in Figures 1-3. The initiator in these reactions is N-acyl pyrrolidone or a compound which forms an N-acyl pyrrolidone in situ. For $Ac_2O$ and py-Na, the initiator forming reaction can be formulated as:

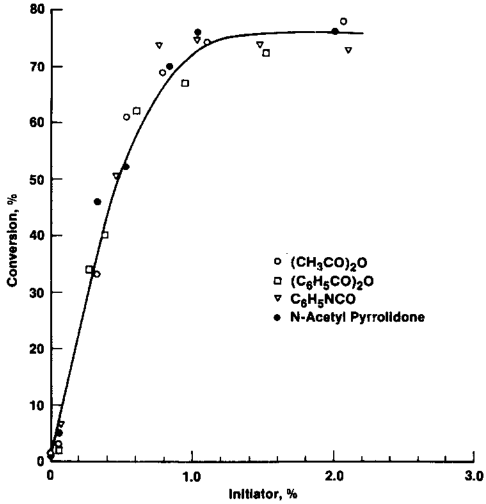


**Figure 1 - Effect of Initiator Concentration on Nylon 4 Conversion - 5% Isolated py-Na, 50°C, 22 Hr**

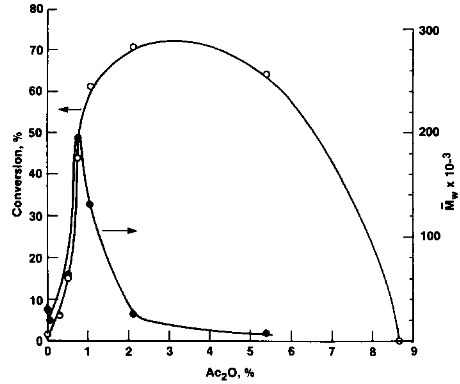


**Figure 2 - Effect of Acetic Anhydride Concentration on Nylon 4 Conversion and Molecular Weight - 10% Isolated py-Na, 50°C, 22 Hr**

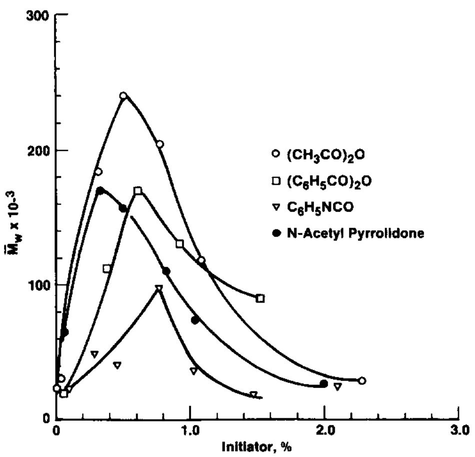


**Figure 3 - Effect of Initiator Concentration on Nylon 4 Molecular Weight -5% Isolated py-Na, 50°C, 22Hr**

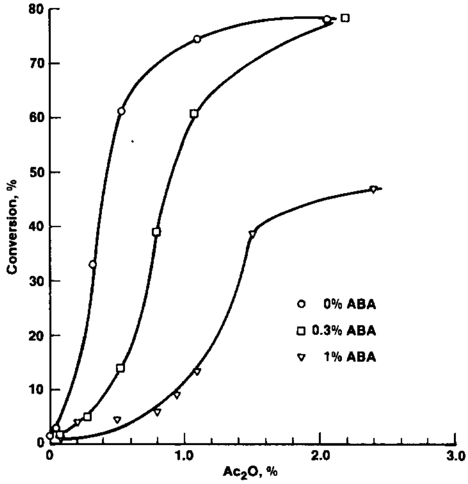
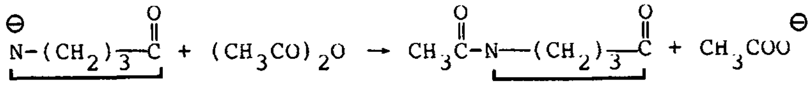


**Figure 4 - Effect of Acetic Anhydride and 4-Aminobutyric Acid Concentration on Nylon 4 Conversion - 5% Isolated py-Na, 50°C, 22 Hr**



$$\underbrace{\overset{\ominus}{N}-(CH_2)_3-\overset{O}{\overset{\|}{C}}} + (CH_3CO)_2O \rightarrow CH_3\overset{O}{\overset{\|}{C}}-\underbrace{N-(CH_2)_3-\overset{O}{\overset{\|}{C}}} + CH_3COO^{\ominus} \qquad (1)$$

Similar reactions, leading to N-acyl pyrrolidone formation, can also be postulated between benzoic anhydride and py-Na or phenylisocyanate and py-Na.

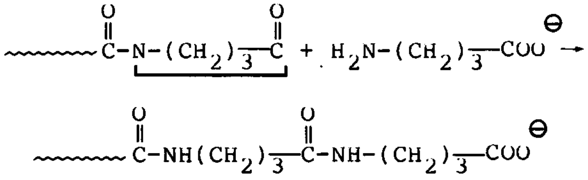
Figure 1 shows the expected increase in polymer conversion as the concentration of the initiator is increased. It can be seen that all of the compounds tested are about equally effective, indicating that Reaction (1) is fast and quantitative. The effect of $Ac_2O$ concentration on conversion, using 10% isolated py-Na catalyst, is shown in Figure 2. After an initial rise, the conversion at about 3% $Ac_2O$ goes through a maximum and then it declines as the $Ac_2O$ concentration is increased. We believe that this decline in conversion, at high $Ac_2O$ concentrations, is also caused by Reaction (1), as excessive acylation removes the py-Na catalyst from the system. As expected, the position of the maximum depends on the amount of py-Na catalyst present in the reaction mixture; with 2% isolated py-Na the maximum occurs at about 1% $Ac_2O$.

The effect of initiator concentration on molecular weight in py-Na catalyzed polymerizations is shown in Figures 2 and 3. Unexpectedly, it was found that the molecular weight, plotted against initiator concentration, passes through a maximum, and that within a narrow range of initiator concentration, very high molecular weight polymer is formed. All of the initiators tried showed this effect, but $Ac_2O$ produced the highest molecular weight polymer. The phenomenon appears to be general, and distinct molecular weight maxima were also obtained in polymerizations carried out with in situ and isolated py-K catalysts. By judicious selection of the amount of $Ac_2O$ added, nylon 4 with a molecular weight of 340,000 was prepared. This is much higher than that reported before for N-acyl lactam-initiated polymerizations and it approximates the molecular weights achieved with $CO_2$.

## The Role of N-acyl Initiators in nylon 4 Polymerization

The observation that, within a relatively narrow range of initiator concentration the molecular weight goes through a maximum, suggests that these initiators play a dual role in nylon 4 polymerization. We believe that in Figures 2 and 3 the initial rise in molecular weight at low acyl compound concentrations is caused by the scavenging of chain-terminating impurities by the initiator. As the concentration of acyl compound is increased, the rate of initiation will also increase, resulting in a decrease of the molecular weight. [This decrease in molecular weight is not caused by the depletion of py-Na catalyst, according to Reaction (1), because it occurs at initiator concentrations where the conversion still rises.] The opposing effects of scavenging and initiation thus provide a qualitative explanation for the maxima in the molecular weight curves. Based on these results, we propose that chain-terminating impurities are also responsible for the low rates and molecular weights observed in "initiator-free" polymerizations.

In theses reactions one potential terminator is 4-aminobutyric acid (ABA), or a derivative of it, formed during catalyst preparation.[9] We have confirmed the presence of ABA in an aqueous solution of in situ py-K by thin layer chromatography (2,4-dinitrofluorobenzene derivative). The ABA may react with the growing chain ends, believed to be imide groups,[6] thereby terminating chain growth:



$$\sim\sim\overset{O}{\overset{\|}{C}}-N-(CH_2)_3-\overset{O}{\overset{\|}{C}} + H_2N-(CH_2)_3-COO^{\ominus} \rightarrow \sim\sim\overset{O}{\overset{\|}{C}}-NH(CH_2)_3-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_3-COO^{\ominus} \qquad (2)$$

Addition of an N-acyl initiator may remove the chain terminator by forming N-acyl-ABA.

Inhibition and scavenging by ABA and $Ac_2O$, respectively, was confirmed in experiments where ABA was deliberately added to the reaction mixture. The addition of ABA reduces the rate of polymer formation (Figure 4) which can, however, be offset by increasing the $Ac_2O$ concentration. As observed before, the molecular weight as a function of $Ac_2O$ concentration goes through a maximum (Figure 5) whose position is displaced to the right as the concentration of ABA is increased. These results are consistent with the scavenging of ABA by $Ac_2O$. The data also indicate that scavenging becomes less efficient at high ABA concentration, which limits the ultimate conversion and maximum molecular weight that can be attained. The formation of variable amounts of ABA, in different batches of catalyst preparations, may explain the range of molecular weight maxima shown in Figure 3.

### The Role of $CO_2$ in nylon 4 Polymerization

Base-catalyzed py polymerization, carried out in the presence of $CO_2$-containing catalysts, shows many similarities to the N-acyl compound-initiated reaction. Polymer yields and molecular weight pass through a maximum as the amount of $CO_2$ in the catalyst is increased. This is shown for a series of polymerizations carried out with isolated py-Na/$CO_2$ catalyst (Figure 6).

We suggest that in these reactions the increase of conversion and molecular weight with $CO_2$ concentration is also

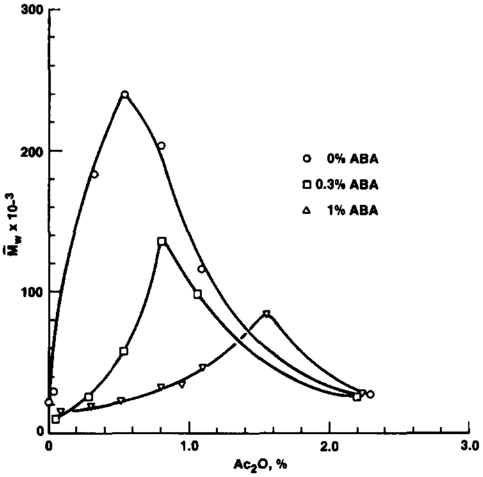


**Figure 5 - Effect of Acetic Anhydride and 4-Aminobutyric Acid Concentration on Nylon 4 Molecular Weight - 5% Isolated py-Na, 50°C, 22 Hr**

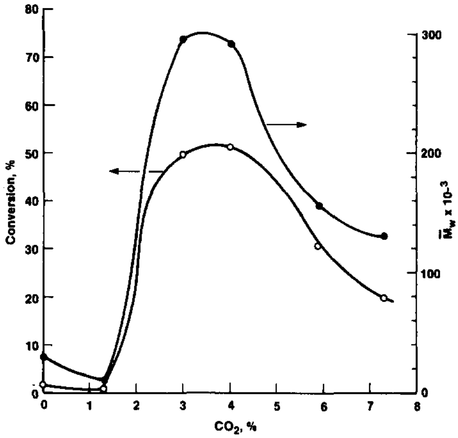


**Figure 6 - Effect of $CO_2$ Concentration on Nylon 4 Conversion and Molecular Weight - 10% Isolated py-Na, 50°C, 22 Hr**

## TABLE I

## APPARENT NUMBER OF CHAINS IN NYLON 4 POLYMERIZATIONS

| Catalyst | Conv., %[1] | $\bar{M}_w$ x $10^{-3}$ | Apparent No. of Chains,[2] n x $10^{-5}$ |
|---|---|---|---|
| 10% In-Situ py-K | 4 | 35 | 11 |
| 10% In-Situ py-K/$CO_2$ (3% $CO_2$) | 48 | 500 | 10 |
| 10% In-Situ py-K + 0.8% NAP | 55 | 28 | 196 |
| 10% Isolated py-Na | 1.5 | 30 | 5 |
| 10% Isolated py-Na/$CO_2$ (1.3% $CO_2$) | 0.5 | 10 | 5 |
| 10% Isolated py-Na/$CO_2$ (3% $CO_2$) | 50 | 296 | 17 |
| 10% Isolated py-Na/$CO_2$ (4% $CO_2$) | 52 | 290 | 18 |
| 10% Isolated py-Na/$CO_2$ (5.9% $CO_2$) | 31 | 156 | 20 |
| 10% Isolated py-Na/$CO_2$ (7.3% $CO_2$) | 20 | 130 | 15 |
| 10% Isolated py-Na + 2.1% $Ac_2O$ | 71 | 26 | 270 |
| 10% In-Situ py-K/$CO_2$ (3% $CO_2$) + 10% $(CH_3)_4$ NCl | 59 | 820 | 7 |
| 2% In-Situ py-K/$CO_2$ (0.6% $CO_2$) + 1.4% 18-Crown-6 | 63 | 610 | 10 |

[1] 50°C, 22 Hours

[2] Conversion/$\bar{M}_w$

caused by the scavenging of chain-terminating impurities. For example, the suspected impurity (ABA) may react with py-Na/$CO_2$ or with the free $CO_2$ in equilibrium with py-carboxylate to give a carbamate salt. For example:

$$2\ {}^{\ominus}OOC\text{-}(CH_2)_3\text{-}NH_2 + \text{py-Na}/CO_2 \rightarrow$$
$${}^{\ominus}OOC\text{-}(CH_2)_3\text{-}NH\text{-}COO^{\ominus} \cdot H_3\overset{\oplus}{N}\text{-}(CH_2)_3\text{-}CO\overset{\ominus}{O} + \text{py-Na} \qquad (3)$$

Analogous reactions between primary amines and $CO_2$ are well known.[13] However, py-Na/$CO_2$ or $CO_2$, unlike $Ac_2O$, is not an initiator. From Figure 6 it can be seen that in contrast to the analogous py-Na/$Ac_2O$ system (Figure 2), there is no decrease in molecular weight at high conversions. The decline in conversion and molecular weight occurs simultaneously at high py-Na/$CO_2$ concentrations where the reaction mixture is low in py-Na.

The absence of initiation by $CO_2$ in nylon 4 polymerization becomes also evident when the apparent number of chains, n, are considered. The results, summarized in Table I, show that n is approximately the same for polymerizations carried out with in situ py-K and py-K/$CO_2$. If py-K/$CO_2$ or $CO_2$ were initiators, a significant increase in n would be expected. A comparison of isolated py-Na and py-Na/$CO_2$ polymerizations shows a small increase of n for the latter, but no further change of n as the concentration of $CO_2$ is increased. The validity of this analysis is confirmed by the fact that N-acetyl pyrrolidone (NAP) or $Ac_2O$, both of them true initiators, increase the value of n by a factor of about 20 to 50.

In a previous study it was shown that in situ py-K/$CO_2$ plus an onium salt or crown ether produces high rates and molecular weights in nylon 4 polymerization.[14] The number of growing chains calculated for these reactions are approximately the same as that found for the py-K catalyzed reaction (Table I) indicating that these additives are not initiators for nylon 4 polymerization. Based on the present results, it is postulated that the high conversions and molecular weights obtained with the onium salts or crown ethers are caused by the combined effect of "freer" (more reactive) py-anions and $CO_2$ scavenger.

An earlier report claimed that in nylon 4 polymerization, py-carboxylate is the initiator leading to growing chains with carbamate end groups.[7] This initiation mechanism is contradicted by the results of the present investigation and also by our previous finding, which showed the absence of $CO_2$ in nylon 4 prepared with radioactive $CO_2$.[11] The recent kinetic analysis of Brozek and co-workers,[9] demonstrating that $CO_2$ does not participate directly in nylon 4 polymerization, is consistent with the conclusions of the present work.

## Acknowledgment

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