

Investigations on Nylon 4 Membranes. Synthesis and Transport Properties. I. Synthesis of Nylon 4 Polymer*

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Synopsis

The synthesis of nylon 4 (polypyrrolidone) by the anionic polymerization of 2-pyrrolidone through the use of the CO₂/potassium pyrrolidonate catalyst system for use in preparing polymer membranes for separation purposes was investigated in detail. The effects of the quantity of CO₂, the potassium pyrrolidonate catalyst, and the reaction temperature on the yield and molecular weights of the nylon 4 were studied. At reaction temperatures of 50°C and a reaction time of 120 hr, a yield of 50.9% with intrinsic viscosity of 4.42 (corresponding to M_n of 108,200 and M_w of 135,850) was obtained. The molecular weight distributions of the nylon 4 were determined by gel permeation chromatography (GPC) using *m*-cresol as the eluting solvent and were found to have a relatively narrow distribution.

INTRODUCTION

Nylon 4 (polypyrrolidone) is a unique polymer with interesting hydrophilic properties. The only previous works on the transport and separation properties of nylon 4 membranes were carried out by Lonsdale et al.¹ and Orofino,² but they were found to exhibit erratic transport fluxes. It was therefore considered worthwhile to reinvestigate the preparation of nylon 4 membranes through improvements in the synthesis of the polymer and in the method of preparation of the membranes. In this article, the synthesis of nylon 4 via the CO₂-activated mechanism is described in detail, and in the second part of this series the preparation and transport properties of the membranes will be reported.

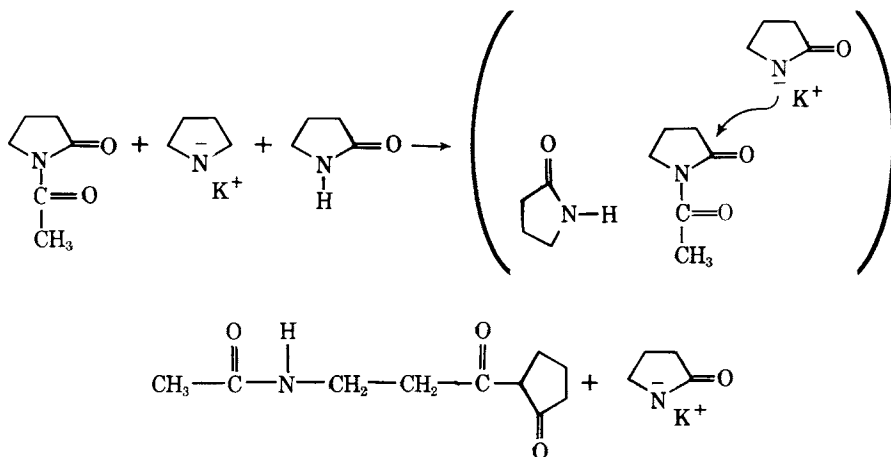
The property of 2-pyrrolidone to polymerize in the presence of alkaline salts at low temperatures was first reported by Ney et al.³⁻⁵ and has subsequently been studied by Hall.⁶ In a number of publications in the open literature in the past decade, it was attempted to improve the thermal stability of the polymer formed by variations in the catalyst system used. Typical examples are the use of *N*-acetylpyrrolidone/MA1Et₄ (where M is Li, Na, or K), diphenyl ketene/MA1Et₄, and diphenyl ketene/K by Tani and Konomi,⁷ of *N*-acetylpyrrolidone/tetramethylammonium pyrrolidonate by Sekiguchi et al.^{8,9} and of γ -butyrolactone/potassium tertiary butanolate by Roda et al.,^{10,11} at temperatures between 30 and 78°C; but the intrinsic viscosities of the polymers obtained in all these cases

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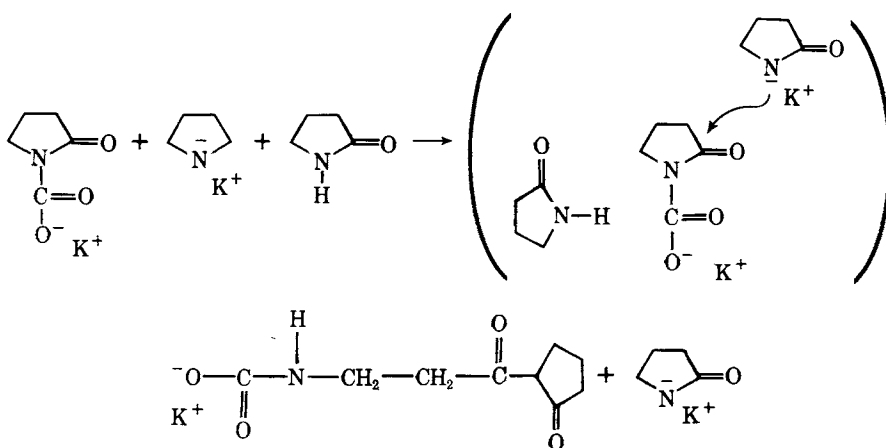
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were not very high. For the polymerization reaction involving the *N*-acetylpyrrolidone/potassium pyrrolidonate catalyst system, the following reaction mechanism has been proposed¹²:



Owing to the attack of the 2-pyrrolidone salt on the CO of the acetyl group which regenerates the initiator, new polymer molecules are formed constantly, so that a low molecular weight polymer having a wide molecular weight distribution results. This method of using *N*-acetylpyrrolidone as the initiator has been described by Peters and Gervasi.¹² The CO₂-activated potassium pyrrolidonate catalyst system to polymerize 2-pyrrolidone by an anionic mechanism was first reported in patents by Ney et al.^{3,4} and has been investigated more recently by Peters and Gervasi,¹² Schirawski,¹³ and Barnes.¹⁴ In this system, the carbamate grouping forms via the CO₂ adducts in the negative charge that reduces the rate of initiation and virtually eliminates the possibility of trans initiation, so that higher molecular weight polymer can be obtained. Although the mechanism is not fully understood the following reaction scheme has been postulated¹²:



Here, in order to obtain a polymer of a higher molecular weight with high yield suitable for the preparation of membranes for separation purposes, the anionic

polymerization of 2-pyrrolidone through the use of the CO₂-activated potassium pyrrolidonate catalyst system was investigated in detail by varying the polymerization conditions.

EXPERIMENTAL

Polymerization

To a 150-ml flask fitted with a magnetic stirrer, descending condenser, and inlet tube which was connected to vacuum and nitrogen, 65 g fractionally distilled 2-pyrrolidone was added. The flask was heated under nitrogen to 80°C; then 3 g potassium hydroxide was added and the water was distilled off under reduced pressure followed by 12.5 g potassium pyrrolidonate. The hot solution was rapidly transferred to a 125-ml polyethylene bottle which had previously been purged with nitrogen. While the solution was still hot, it was rapidly mixed with 50 g fractionally distilled 2-pyrrolidone; then, CO₂ which had been dried over silica gel was introduced at a constant flow rate of 2.5 on a Matheson Rotameter Model R-6-15 for all the experiments for a given period of time. The bottle was then capped, and the reaction was carried out in a thermostatted oven at 50°C. After the predetermined reaction time, the polymerization product was dissolved in formic acid and precipitated by adding an excess of water. The precipitated polymer was washed with deionized water, suspended in acetone, and then vacuum dried at 70°C. The polymer conversion was calculated from the ratio of the yield to the weight of the monomer charged.

Measurement of Intrinsic Viscosity

Intrinsic viscosity measurement was carried out in a dilution-type Ubbelohde viscometer at 25 ± 0.02°C in the concentration range of 0.0624–0.5000 g per 100 ml *m*-cresol. The intrinsic viscosity $[\eta]$ was determined by graphic extrapolation of the reduced viscosity η_{red} to zero concentration.

Measurement of Molecular Weight Distributions and Molecular Weights

The molecular weight distributions were kindly determined by the Technical Department of the DuPont Co., Chattanooga, TN, using a Waters GPC unit with *m*-cresol as the eluting solvent at 90°C. The molecular weights were calculated from the GPC curves by computer using a nylon 66 calibration curve.

TABLE I
Influence of Polymerization Temperature on Viscosity and Yield^a

Temperature, °C	Reduced viscosity η_{red} , 0.5 g/100 ml	Yield, %
35	1.85	12.5
40	1.86	15.0
50	1.87	13.2

^a Polymerization time, 24 hr; CO₂ quantity, 20 sec/constant flow rate (2.5).

TABLE II
Reaction Time Dependence on Yield and Viscosity by a Potassium Pyrrolidonate Concentration of 0.06 mole/mole 2-Pyrrolidone

Time, hr	Reduced viscosity η_{red} , 0.5 g/100 ml	Intrinsic viscosity [η]	Yield, %
G-1 ^a			
6	2.76	2.45	50.0
12	2.85	2.51	53.3
50	2.82	2.48	58.3
74	2.74	2.40	59.8
96	2.67	2.32	66.6
120	2.64	2.29	60.2
650	2.18	1.78	68.9
G-2 ^b			
24	1.82	1.33	19.3
48	1.84	1.33	18.8
72	1.93	1.47	21.6
120	2.01	1.57	25.7
240	2.44	2.08	40.8

^a Polymerization temperature 50°C; CO₂ quantity, 90 sec/constant flow rate (2.5). ^b Polymerization temperature 45°C; CO₂ quantity; 60 sec/constant flow rate (2.5).

RESULTS AND DISCUSSION

Polymerization

CO₂ was introduced into the reaction mixture of purified 2-pyrrolidone and anhydrous potassium 2-pyrrolidonate. The polymerization started in a few minutes as was evidenced by the formation of a slight turbidity in the reaction mixture. In order to investigate the optimum conditions to obtain a polymer

TABLE III
Influence of CO₂ Quantity on Viscosity and Yield by a Potassium Pyrrolidonate Concentration of 0.06 mole/mole 2-Pyrrolidone

CO ₂ quantity sec, ^a	Reduced viscosity η_{red} , 0.5 g/100 ml	Intrinsic viscosity [η]	Yield, %
G-1 ^b			
10	1.61	1.03	14.1
20	1.94	1.48	16.5
40	2.03	1.60	19.2
60	2.42	2.06	33.4
90	2.46	2.10	28.1
120	2.97	2.62	36.9
G-2 ^c			
60	2.40	2.10	59.8
90	4.28	4.42	50.9
120	1.87	1.38	37.0
180	2.10	1.68	39.0
240	2.06	1.70	36.3

^a CO₂ quantity in sec/constant flow rate (2.5). ^b Polymerization temperature 45°C; polymerization time 48 hr. ^c Polymerization temperature 50°C; polymerization time 120°C.

TABLE IV
Influence of Catalyst concentration on Yield and Viscosity^a

Mol potassium pyrrolidonate/mole 2-pyrr.	Reduced viscosity η_{red} , 0.5 g/100 ml	Intrinsic viscosity $[\eta]$	Yield, %
0.0328	2.06	1.66	48.4
0.0581	2.25	1.70	57.6
0.0727	2.69	2.20	74.6
0.1014	2.92	2.33	72.5

^a Under conditions of reaction time of 120 hr at 50°C and CO₂ quantity of 90 sec/constant flow rate (2.5)

of high molecular weight coupled with a good yield, the following attempts were made to investigate the effects of (1) the reaction temperature, (2) reaction time, (3) the CO₂ quantity, and (4) the catalyst concentration. The anionic polymerization of 2-pyrrolidone occurs in a heterogeneous system at temperatures of 25–70°C. Sekiguchi et al.⁹ studied the polymerization of 2-pyrrolidone at temperatures of 30, 45, and 78°C for the initiation system of tetramethylammonium pyrrolidonate and *N*-acetylpyrrolidone and reported that the highest yield of polymer was obtained at 30°C.

The effect of reaction temperature at 35, 40, and 50°C is shown in Table I. As can be seen, there was no noticeable difference in the yield under the polymerization conditions indicated in the table. Schirawski¹³ reported that he obtained the highest relative viscosity for the polymer at ambient temperatures for the initiation system of CO₂/potassium pyrrolidonate.

Table II shows that with the reaction temperature at 45°C and the CO₂ quantity of 60 sec at a constant flow rate of 2.5, the viscosity and the yield of the polymer increased with reaction time.

The influence of the CO₂ quantity on the viscosity and yield using a constant potassium pyrrolidonate concentration of 0.06 mole/mole of 2-pyrrolidone is shown in Table III. Under the reaction conditions of temperature at 45°C and a reaction time of 48 hr, the viscosity and yield of the polymer increased with increasing CO₂ quantity. The conditions of CO₂ quantity of 90 sec at a constant flow rate of 2.5, temperature 50°C, and 120 h of reaction time produced a polymer having the highest intrinsic viscosity of 4.42 with yield of 50.9%.

Table IV shows the influence of the catalyst concentration on the viscosity and yield under the reaction conditions of 120 hr at 50°C and CO₂ quantity of 90 sec at a constant flow rate of 2.5. Both viscosity and yield increased with increasing catalyst concentration in the range of 0.03 to 0.1 mole potassium pyrrolidonate/mole 2-pyrrolidone.

Molecular Weight Distributions and Molecular Weights

The molecular weight distributions were measured by GPC using *m*-cresol as the eluting solvent, and the results were calculated on the basis of a nylon 66 calibration curve from the GPC curves. The results are shown in Table V. Sampe S-4-5, with an intrinsic viscosity of 4.42 (the highest viscosity obtained in the present experiments under the polymerization conditions of potassium pyrrolidonate concentration 0.06 mole/mole 2-pyrrolidone, at 50°C, reaction time 120 hr, and the CO₂ quantity of 90 sec at a constant flow rate of 2.5), gave

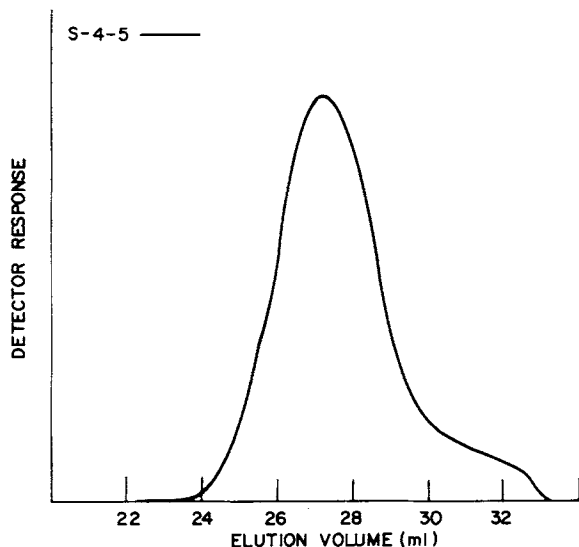


Fig. 1. Differential molecular weight distribution of nylon 4 sample S-4-5.

a M_n value of 108,200 and a M_w value of 135,850 and had a relatively narrow molecular weight distribution of polydispersity 1.26. Figures 1, 2, and 3 show the differential distribution, frequency distribution, and integral molecular weight distribution plots of the nylon 4 sample S-4-5.

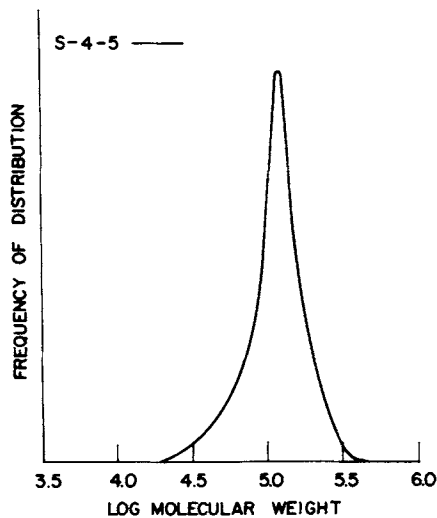


Fig. 2. Frequency molecular weight distribution of nylon 4 sample S-4-5. $\overline{M}_w/\overline{M}_n = 1.256$; $\overline{M}_n = 108,202$; $\overline{M}_w = 135,849$.

TABLE V
Molecular Weight Values of Nylon 4 Obtained from GPC

Sample No.	M_n	M_v	M_w	M_z	$M_{(z+1)}$	M_w/M_n	M_z/M_w
S-4-4	54,100	91,860	98,370	141,750	177,000	1.82	1.44
S-4-5	108,200	132,170	135,850	159,620	181,000	1.26	1.18
S-4-6	42,130	73,600	79,700	122,880	158,690	1.89	1.54

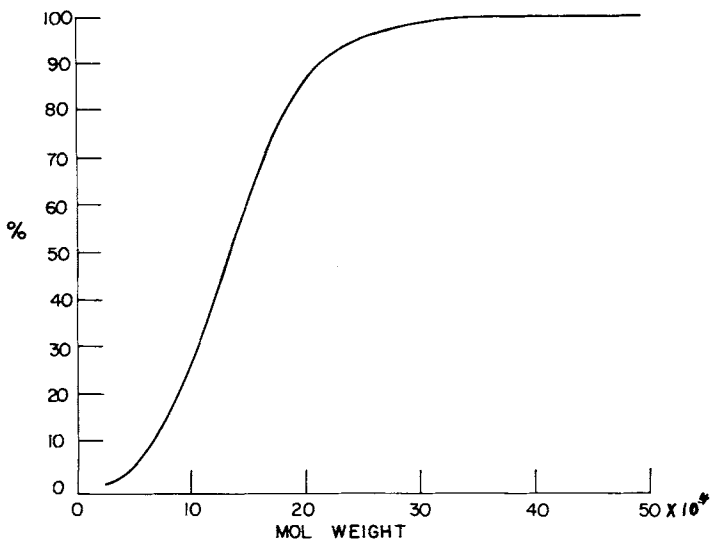


Fig. 3. Integral molecular weight distribution of nylon 4 sample S-4-5. The cumulative amount of nylon 4 polymer, expressed as %, is plotted vs. molecular weight (based on nylon 66)

In conclusion, it has been demonstrated that compared to the other catalyst systems previously reported, the CO_2 /potassium pyrrolidonate catalyst system for the anionic polymerization of 2-pyrrolidone produces, under the optimum conditions that were employed, a nylon 4 polymer with a higher molecular weight and narrow molecular weight distribution at relatively high yields. The exact nature and role of the CO_2 activator is not clearly understood at the present, but work is now underway to determine quantitatively the absorption of CO_2 in the reaction mixture to elucidate its role in the catalyst system and will be published in a separate report.

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