

Synthesis of Nylon 4 through the Use of the Carbon Dioxide / Potassium Pyrrolydonate Catalyst System with and without Added 18-Crown-6 Ether Activator

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Synopsis

The anionic polymerization of 2-pyrrolidone at 40°C via CO₂/KOH and CO₂/KOH/18-Crown ether catalyst for membrane separation purposes was investigated in detail. The effects of reaction time, CO₂ quantity, and potassium hydroxide concentration including crown ether on yield and intrinsic viscosity were also studied. Under the reaction conditions of reaction temperature 40°C, reaction time 24 h, CO₂ quantity of 60 s at a constant flow rate of 3.5 L/min and 1.98 mol % Crown ether a maximum yield of 95.36% of nylon 4 polymer with intrinsic viscosity of 3.28 was obtained.

INTRODUCTION

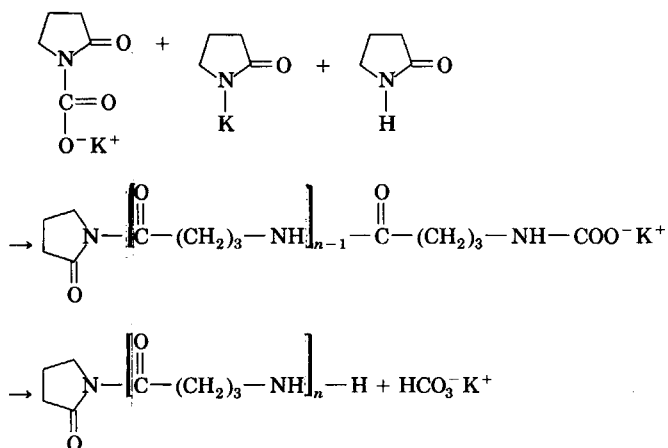
The transport properties of nylon 4 [poly(2-pyrrolidone)] membranes have not been extensively studied until now, although they have very interesting hydrophilic properties and excellent strength. Lonsdale et al.¹ and Orofino² first investigated their transport fluxes; however, they found that nylon 4 membranes behaved erratically in terms of their transport properties. Huang et al.³ showed that nylon 4 membranes had reverse osmosis, dialysis, and ultrafiltration properties, when they were prepared from casting solutions containing suitable amounts of organic or inorganic additives. In general, in order to prepare the polyamide membrane which has the properties of high ultimate tensile strength, low elongation-to-break, and high moduli in the wet state, reasonably high molecular weight, i.e., an intrinsic viscosity of more than 1.5 is needed.⁴

Nylon 4 polymerization in the presence of alkaline salts at low temperatures was first reported by Ney et al.^{5,6} and subsequently studied by Hall.⁷ In the past decade, a number of investigators attempted to increase the product yield and intrinsic viscosity in nylon 4 polymerization using various catalyst systems.⁸⁻¹³ Although most of them produced reasonably high product yields, the intrinsic viscosities obtained were not high enough in most of these studies.

The first study of CO₂/KOH catalyst system for the polymerization of 2-pyrrolidone was done by Ney et al.,^{5,6} and has been reported in detail by

Peters and Gervasi,¹⁴ Schrawski,¹⁵ Barnes,¹⁶ and Huang et al.¹⁷ More recently, the polymerization of 2-pyrrolidone in the presence of CO_2/KOH catalyst system was investigated in depth by Kralicek and co-workers.¹⁸⁻²⁰ Peters and Gervasi¹⁴ claimed that 2-pyrrolidone-carboxylate is the initiator leading to growing chains with carbamate and groups in nylon 4 polymerization. This polymerization mechanism is contradicted by the following recent investigations. Roda et al.²¹ isolated and characterized two alkali carboxylates of 2-pyrrolidone, 2-pyrrolidone-1-carboxylate, and 1-pyrrolin-2-yl carbonate, formed by CO_2 introduction, but the site of CO_2 attachment on the alkali salt of 2-pyrrolidone remains unresolved. On the basis of kinetic studies, Brozek et al.¹⁹ concluded that CO_2 probably does not take part in the polymerization directly as an activator and speculated that the carboxylate may influence the basicity of the system and may be a suitable nucleation center for the polymer and may eventually act in the system as a sufficient drying agent to remove water in the polymerization batch after preparation of alkali metal pyrrolidionate in situ. Also the absence of CO_2 in the resulting nylon 4 polymers was proved using radioactive CO_2 catalyst by Bacskai and Fries.²² It was reported by Bacskai²³ that CO_2 is not an initiator in nylon 4 polymerization using the determination of the number of growing chains.

Therefore, the mechanism of nylon 4 polymerization in the presence of CO_2 activator was presented as follows¹⁹:



In this investigation, in order to synthesize a polymer with both high intrinsic viscosity and high yield for the preparation of membranes for separation purposes, the modified anionic polymerization method of 2-pyrrolidone using CO_2/KOH and $\text{CO}_2/\text{KOH}/18\text{-Crown-6}$ ether catalyst system was studied in detail by varying the polymerization conditions.

EXPERIMENTAL

Polymerization

Into a dry 500-mL four-necked jar equipped with a descending condenser connected to a vacuum pump, thermometer, inlet tube connected to nitrogen

cylinder, and addition funnel, 65 g 2-pyrrolidone were added. The jar in the heating mantle was heated to 110°C under nitrogen and reduced pressure atmosphere; then 3 g potassium hydroxide were added through the addition funnel, and the water from the resulting monohydrate of 2-pyrrolidone was removed by distillation under the same reduced atmosphere followed by 12.5 g of monomer. The hot solution was rapidly transferred to a 250-mL polyethylene bottle which was already purged with nitrogen gas (in order to avoid contacting carbon dioxide gas in the air); then CO₂ dried with silica gel was introduced at a constant flow rate of 3.5 L/min for all experiments for a desired period of time. In the experiments using Crown ether, the given quantity of Crown ether was first placed in a polyethylene bottle before transferring the hot solution from the jar. The bottle was then capped, and the reaction was carried out in a thermostated oven at 40°C. After the desired reaction time, the resulting polymer was dissolved in formic acid and precipitated by adding an excess of deionized water. The precipitated polymer was washed with deionized water at least five times; then the polymer was suspended in acetone, so that the residual water can be evaporated, and vacuum dried at 50°C. The polymer conversion was calculated from the ratio of the yield to the weight of the monomer charged (see Fig. 1).

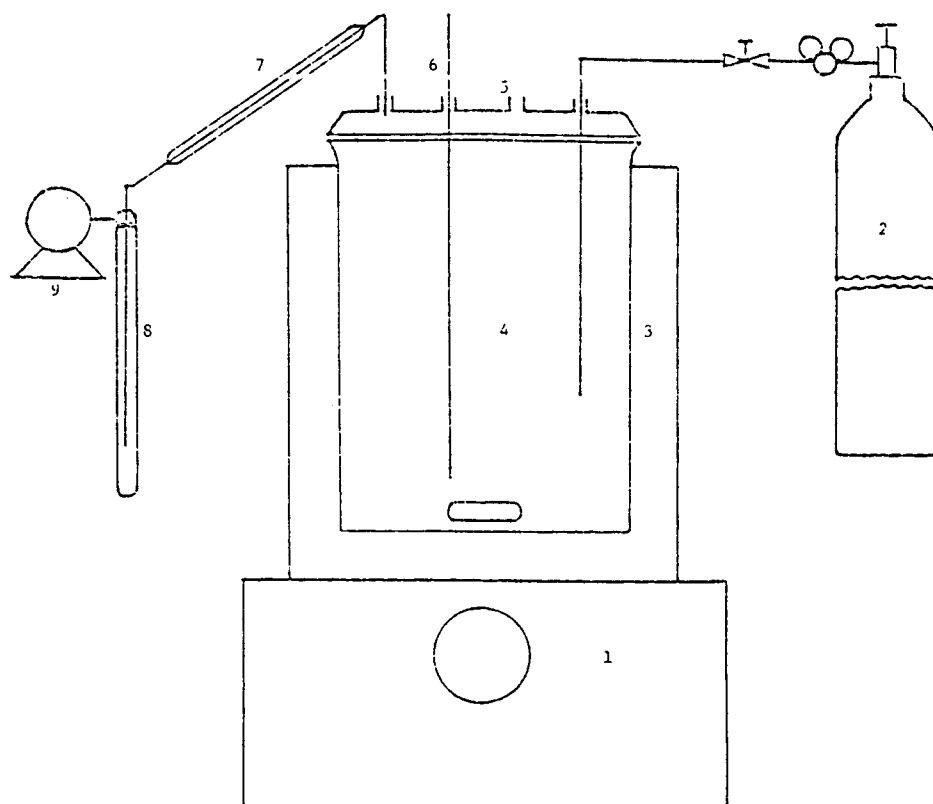


Fig. 1. Experimental assembly of polymerization: (1) magnetic stirrer; (2) nitrogen cylinder; (3) heater; (4) reactor; (5) additional funnel; (6) thermometer; (7) condenser; (8) trap; (9) vacuum pump.

Intrinsic Viscosity Measurement

Intrinsic viscosities of synthesized polymers were calculated from the *single point intrinsic viscosity equation* proposed by Solomon and co-workers.^{24,25} The single point value was measured from a Ubbelodhe viscometer at 25°C in the concentration range of 0.1665–0.5035 g/100 mL formic acid. The calculated intrinsic viscosities were slightly lower than those measured by double extrapolation graphic method.

RESULTS AND DISCUSSION

Potassium 2-pyrrolidionate was prepared by adding KOH directly to the reactor. The reaction between the base and the monomer is stoichiometric and hydration water must be removed by drying the base at 110°C under vacuum conditions. The inhibition effect of water in the course of the anionic polymerization of lactams is ascribed both to the hydrolysis of imide groups and to the decrease of the concentration of lactam anions.

In the experiments using the CO₂/KOH/18-Crown-6 ether catalyst system, this crown compound (macrocyclic polyether)^{26,27} has the most important and unique property in the tendency to form complexes with alkali metal salts. The 18-Crown-6 ether forms 1 : 1 salt-polyether complex in which the cation is encircled by the oxygen atoms of the polyether ring, being held there by the electrostatic attraction between the negatively charged oxygens of the C—O dipoles and the cation. The stability of the formed 18-Crown-6 ether complex depends primarily upon how well the cation fits into it.^{26–28} It was reported that the ring size of the 18-Crown-6 ether is 2.6–3.2 Å and the ionic diameter of potassium is 2.66 Å.^{26,27} The stability constants for the 18-Crown-6 ether with the alkali metal cations go through a maximum at K⁺ as the cation size increases. As a result, the Crown ether forms a highly stable complex with potassium cation and greatly increases the dissociation of the carbonate ion pairs.^{29,30} The carbonate anions, both in potassium carbonate and the growing polymer chain ends are highly unsolvated and very reactive.²⁹ Therefore, the polymerization rates and weights of polymers are low in the absence of the Crown ether.³¹

In order to investigate the optimum reaction conditions to obtain high molecular weight and intrinsic viscosity polymers, the following reaction conditions were obtained: (1) reaction time; (2) CO₂; and (3) the catalyst

TABLE I
Influence of Reaction Time on Yield and Viscosity^a

Sample no.	Time (h)	Intrinsic viscosity [η]	Yield (%)
S-164	24	2.23	10.94
S-140	48	2.58	15.87
S-125	72	3.14	30.94
S-165	120	5.07	31.95
S-126	150	3.36	42.34

^aCO₂ quantity 60 s/constant flow rate of 3.5 L/min., reaction temperature 40°C, KOH quantity 3 g (85.8% KOH).

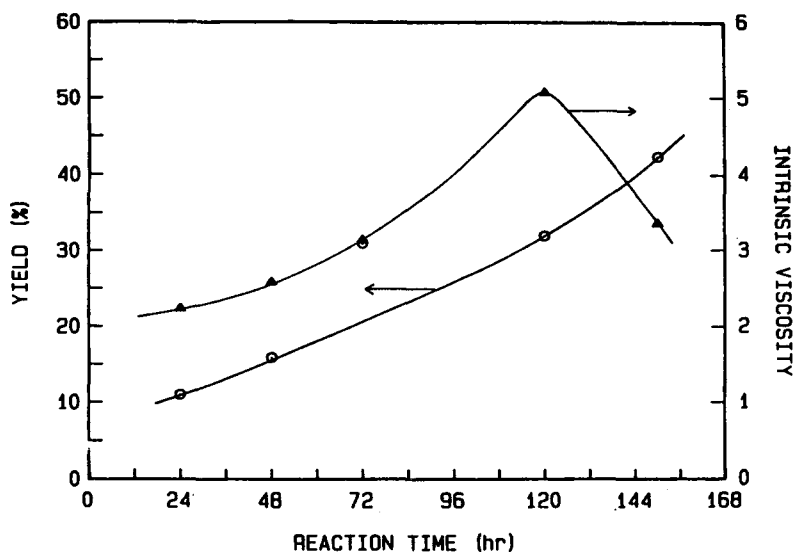


Fig. 2. Influence of reaction time on yield and viscosity on the polymerization of 2-pyrrolidone to form nylon 4. (Reaction conditions, see Table I.)

concentration including Crown ether. In general, 2-pyrrolidone may be polymerized at a temperature from 15°C to about 100°C, preferably 25–70°C.^{31,32} The most efficient and optimal temperature ranges between 40 and 55°C for nylon 4 polymerization.^{17,33} In this study, the reaction temperature, 40°C, was used for all experiments.

Table I and Figure 2 show that the yield and the viscosity of the polymer increased with reaction time. Our present results are higher than those previously reported by Huang et al.¹⁷ at 45°C and lower than their data 50°C. However, the intrinsic viscosities are higher than those published by them.

The influence of the CO₂ quantity on the viscosity and yield is shown in Table II and Figure 3. The intrinsic viscosity and yield of the nylon 4 polymer increased with increasing CO₂ quantity up to 30 s at a constant flow rate of 3.5 L/min. But above CO₂ quantity of 30 s, the product yield decreased with increasing CO₂ quantity.

TABLE II
Influence of CO₂ Quantity on Yield and Viscosity^a

Sample no.	CO ₂ quantity ^b (h)	Intrinsic viscosity [η]	Yield (%)
S-158	10	3.58	35.93
S-155	30	4.00	43.66
S-173	40	4.15	36.81
S-161	50	4.37	34.42
S-165	60	5.07	31.95
S-156	90	3.24	12.21

^aReaction temperature 40°C, KOH quantity 3 g (85.8% KOH), reaction time 120 h.

^bCO₂ quantity in s/constant flow rate of 3.5 L/min.

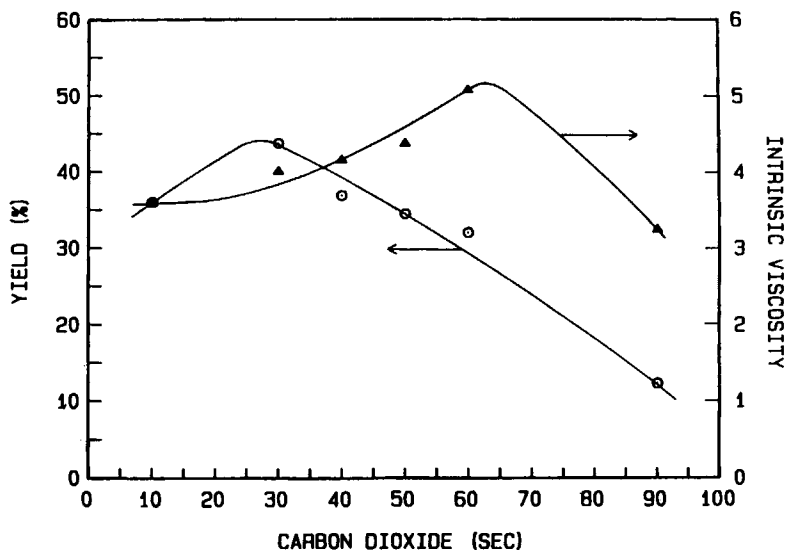


Fig. 3. Influence of carbon dioxide quantity on yield and viscosity on the polymerization of 2-pyrrolidone to form nylon 4. (Reaction conditions, see Table II.)

Table III and Figure 4 show the influence of KOH concentration on yield and viscosity. The yield increased with increasing KOH concentration in the range of 0.04–0.12 mol potassium pyrrolidonate/mol 2-pyrrolidone. From the above results, it was found that the maximum conversion 57.85% with the intrinsic viscosity of 4.87 was obtained. When we compare these results with data in the literature,^{18–20,23,34} our maximum conversion is slightly low. However, the intrinsic viscosity data is higher than those reported by Jung et al.³⁴

Tables IVA, IVB, and Figures 5(a) and 5(b) show the influence of 18-Crown-6 ether concentration on yield and viscosity when the CO quantities are 60 and 30 s, respectively. The yield increased exponentially with increasing Crown ether concentration in both cases. Also the intrinsic viscosity increased with increasing Crown ether concentration. The maximum product yield of nylon 4 of 95.36% was obtained. In the experiments using the CO₂/KOH/18-Crown-6 ether catalyst system, as mentioned earlier, because of the unique property of

TABLE III
Influence of KOH Concentration on Yield and Viscosity^a

Sample no.	Mole potassium pyrrolidonate/ mol 2-pyrrolidone	Intrinsic viscosity [η]	Yield (%)
S-154	0.04	3.76	18.33
S-165	0.06	5.07	31.95
S-159	0.08	5.04	47.42
S-152	0.10	4.87	57.85
S-153	0.12	5.68	57.67

^aReaction temperature 40°C, reaction time 120 h, CO₂ quantity 60 s/constant flow rate of 3.5 L/min.

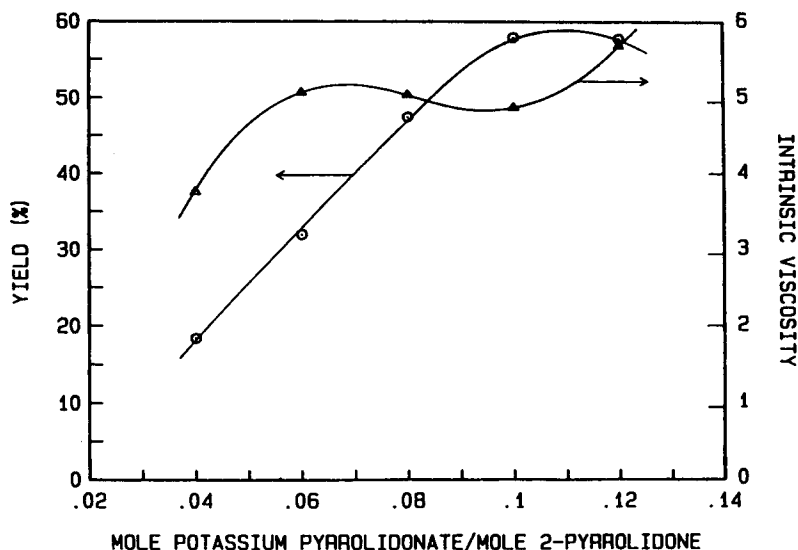


Fig. 4. Influence of KOH concentration on yield and viscosity on the polymerization of 2-pyrrolidone to form nylon 4. (Reaction conditions, see Table III.)

TABLE IVA
Influence of Crown Ether Concentration on Yield and Viscosity^a

Sample no.	Crown ether (mol %)	Mole ratio K and crown	Intrinsic viscosity [η]	Yield (%)
S-164	—	—	0.23	10.94
S-116	0.49	1:0.08	4.51	16.27
S-162	1.04	1:0.17	4.0	17.57
S-166	1.30	1:0.22	5.53	19.53
S-163	1.61	1:0.27	6.07	37.47
S-172	1.86	1:0.31	4.32	59.23
S-118	1.98	1:0.33	3.28	95.36

^aReaction temperature 40°C, reaction time 24 h, CO₂ quantity 60 s/constant flow rate of 3.5 L/min.

TABLE IVB
Influence of Crown Ether Concentration on Yield and Viscosity^a

Sample no.	Crown ether (mol %)	Mole ratio K and crown	Intrinsic viscosity [η]	Yield (%)
S-171	—	—	2.35	13.03
S-167	0.51	1:0.08	4.28	13.88
S-168	1.13	1:0.19	5.63	24.78
S-170	1.69	1:0.28	6.09	31.56
S-169	2.15	1:0.36	6.39	58.05

^aReaction temperature 40°C, reaction time 24 h, CO₂ quantity 30 s/constant flow rate of 3.5 L/min.

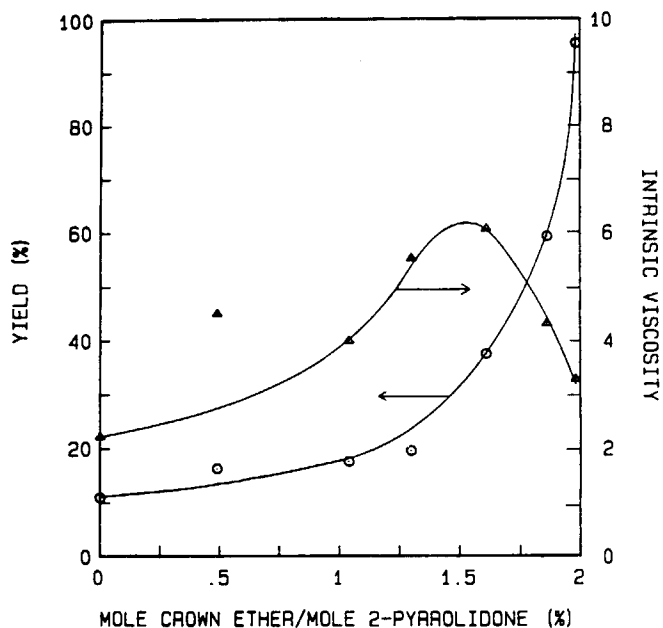


Fig. 5(a). Influence of Crown ether concentration on yield and viscosity on the polymerization of 2-pyrrolidone to form nylon 4. (Reaction conditions, see Table IVA.)

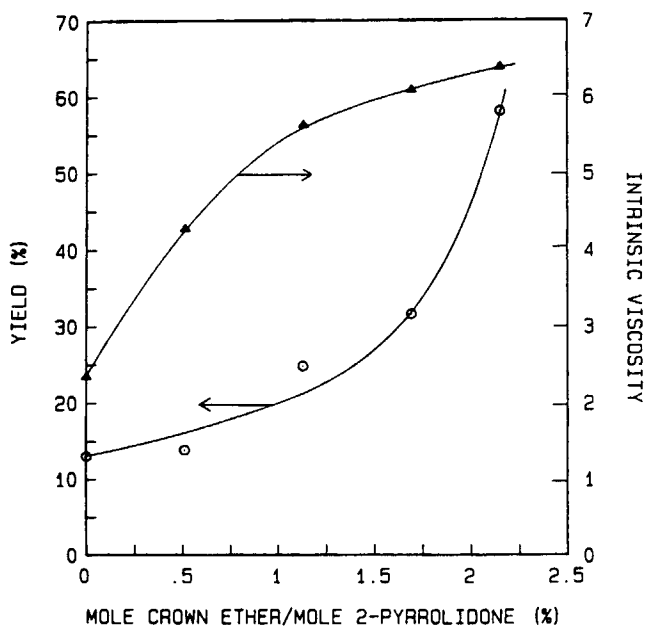


Fig. 5(b). Influence of Crown ether concentration on yield and viscosity on polymerization of 2-pyrrolidone to form nylon 4. (Reaction conditions, see Table IVB.)

Crown ether, both intrinsic viscosity and yield were much higher than those obtained without Crown ether catalyst.

CONCLUSIONS

In the case of using the CO₂/KOH catalyst system, the product yield increased with increasing reaction time, the mole ratio between the potassium pyrrolidonate and the monomer up to 0.10, and CO₂ quantity up to 60 s (because there was no significant difference in product yield up to 60 s); thus high intrinsic viscosities can be obtained for the making of membranes for the separation purposes. By using the CO₂/KOH/18-Crown-6 ether catalyst system, this system produces nylon 4 polymer which has higher intrinsic viscosities and product yields than those previously reported in the literature. The highest conversion was obtained when the reaction conditions were CO₂ quantity of 60 s, and Crown ether mol % of 1.98.

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