

ANIONIC POLYMERIZATION OF 2-PYRROLIDONE*

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The effect of purity of monomer and of potassium salt of 2-pyrrolidone used as initiator and the effect of reaction conditions on the course of anionic polymerization of 2-pyrrolidone has been investigated. Fundamental differences in the course of activated and nonactivated polymerization have been found. The optimum polymerization rate of the nonactivated polymerization is attained at 50°C and that of the activated one at 40°C. An increase of the particle number in the course of nonactivated polymerization can be ascribed to the formation of new growing centers which are formed due to a simultaneously proceeding disproportionation reaction of pyrrolidone anion with amide group of the monomer or of the polymer. To the contrary, at the N-benzoyl-pyrrolidone activated polymerization of 2-pyrrolidone a decrease of the number of macromolecules with time has been observed; this is evidently due to condensation reactions of chains terminated by N-acyllactam groups.

2-Pyrrolidone is polymerized by basic catalysts only at low temperatures. This type of polymerization is accelerated, as in the case of other lactams of ω -amino acids, by lactams substituted on nitrogen atom by an electrophilic substituent or by the compounds which are able to form such a growing center in the reaction medium. The activation effect of these compounds on the anionic polymerization of lactams has for the first time been proved just in case of 2-pyrrolidone¹. An acid catalyzed pyrrolidone polymerization gives only oligomers².

Besides the effect of monomer purity and the procedure of catalyst preparation, the experimental execution of the polymerization has a dominating effect on a reproducible course of 2-pyrrolidone polymerization. So far, very little attention has been paid to 2-pyrrolidone impurities. The presence of 1-(2-pyrroline-1-yl)-2-pyrrolidone³ and butyramide⁴, besides γ -butyrolactone, in the monomer was proved by GLC chromatography. The evaluation of the content of impurities from the polymerization activity⁵ does not always give a real picture of all impurities present, particularly of those which are insensitive to the anionic polymerization. The monomer may contain compounds with activating and inhibiting effect on the anionic polymerization of lactams at the same time and therefore a sort of compensation has to be anticipated. 2-Pyrrolidone has usually been purified⁵⁻⁹ by the procedure according to Lohr¹²

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which is based on the formation of 2-pyrrolidone monohydrate^{10,11}. Monohydrate of 2-pyrrolidone is stable only at temperatures below its melting point (31°C according to¹³). The water content in 2-pyrrolidone can be reduced by distillation to the minimum value of 0.03 wt. %; an azeotropic distillation with benzene gives 0.01 wt. % (ref.⁵).

In most cases the alkaline salt of 2-pyrrolidone, which is the real polymerization initiator, has been prepared by an unsuitable procedure, *i.e.* by the reaction of monomer with hydroxides or with alkali metals directly in the polymerization medium^{1,5-9,14-17}. To remove water quantitatively which is formed by the equilibrium neutralization reaction is a very difficult process. The preparation of potassium salt by the reaction of potassium with 2-pyrrolidone may give, *via* a reduction of 2-pyrrolidone, compounds (tetramethylene imine and water) with inhibition effect on the anionic polymerization as it is in the case of the reaction of potassium with ϵ -caprolactam^{18,19}. The pyrrolidone polymerization proceeds in a narrow temperature range (25–70°C), *i.e.* well below the melting point of poly(2-pyrrolidone) (265°C) and also below the critical temperature of mixing. Poly(2-pyrrolidone) precipitates from the reaction medium after a short initial homogeneous period. The precipitation is followed by a continuous decrease of the polymerization rate. The polymerization rate decrease in the heterogeneous period of the polymerization is attributed^{8,20-22} to a capture of the growing part of the chain in the crystalline structure of the precipitated polymer and thus decreasing its propagation activity.

In this work we have made an attempt to check the contemporary knowledge about the course of the activated and the nonactivated anionic polymerization of 2-pyrrolidone.

EXPERIMENTAL

Purification of 2-Pyrrolidone

Distilled 2-pyrrolidone (Koch and Light Labor., Ltd.) was allowed to react with water (12 hours) to form the monohydrate in ethyl acetate solution at 5°C according to the procedure described by Lohr¹¹. The crystals formed were washed with cool ethyl acetate, separated, melted and the procedure was repeated. The monohydrate of 2-pyrrolidone thus obtained was melted and water from the mixture was removed by distillation at reduced pressure; the last traces of water were removed by azeotropic distillation with benzene and then dried with molecular sieve Nalsit 4 A (24 h at 35°C). 2-Pyrrolidone was then distilled to a storage vessel with a side arm provided with a three-way stopcock (98°C/1 Torr). By this procedure a chromatographically pure 2-pyrrolidone was obtained (column temperature: 190°C, length 1.6 m, diameter 6 mm, poly(propylene sebacate) on Celit or Carbowax 20M on Chromosorb W-NAW).

Distilled 2-pyrrolidone was rectified on a column packed with Helipak (12 theoretical plates), b.p. 102.5°C/2 Torr. Rectified 2-pyrrolidone contained only one impurity (0.025 wt. %) detected by GLC chromatography as a peak preceding that of 2-pyrrolidone. The successive crystallization from toluene decreased the content of this impurity down to 0.01 wt. %. 2-Pyrrolidone

was after crystallization distilled to a storage vessel as in the preceding case. (The content of γ -butyrolactone can be reduced to 0.08 wt. % only by a repeated fractional melting (4 x) with controlled temperature regime²³ (cooling 6°C/h and heating 3°C/h).)

Potassium Salt of 2-Pyrrolidone

a) To a solution of 8 g (0.09 mol) of purified 2-pyrrolidone in 200 ml of dry xylene was added 3.5 g (0.063 mol) of analytical grade KOH which was finely powdered in dry xylene. After a slow removal of xylene by distillation (for 2 h at 10 Torr) 100 ml of benzene was added to the residue and the solid phase separated. The product was thoroughly washed with dry benzene and diethyl ether while stirring, then freed from solvents at 25°C/10 Torr (2 h) and then at 45°C/1 Torr (2 h); the yield was 90%. The salt was then dried for 2 h at 115°C/1 Torr and prior to polymerization recrystallised from 15% solution of 2-pyrrolidone in pyridine (calculated mol. wt 123.2; determined by acidimetry 123.5).

b) The same procedure was adopted as in the preceding case, but after the removal of prevailing part of xylene by distillation, 150 ml of dry pyridine was added to the distillation residue and the mixture was heated up to 95°C. At this temperature 2-pyrrolidone was stepwise added to the suspension till all the salt get dissolved (about 5 wt. %). After a hot filtration and crystallization (12 h at room temperature) the crystals formed were filtered off, washed with pyridine, benzene and ether; the suspension being filtered was stirred on a sintered glass. The salt hydrate was dried for 3 hours at 25°C/10 Torr and 2 h at 45°C/1 Torr and freed from hydration water by heating for 2 hours at 115°C/1 Torr (mol. wt. determined by acidimetry was 123.0).

All operations described in the preparation procedures were performed in an atmosphere of dry nitrogen which was freed from oxygen. The salt was stored in sealed ampoules under nitrogen. The molecular weight of the salt was determined by conductometric titration (0.1M-HCl).

N-Benzoyl-2-pyrrolidone

The compound was prepared by acylation of 2-pyrrolidone with benzoyl chloride either in the excess of 2-pyrrolidone, (5 mol/mol 2-pyrrolidone) analogously to the preparation of N-benzoyl- ϵ -caprolactam²⁹, or by acylation of 2-pyrrolidone with benzoyl chloride in benzene solution in the presence of triethylamine (cyclohexane-benzene mixture), m.p. 91.5°C.

Polymerisation Procedure

A required amount of 2-pyrrolidone was transferred by nitrogen pressure from a storage vessel through a stainless steel capillary (put through a three-way stopcock) into a distillation flask. After the distillation off of the first fraction of 2-pyrrolidone (1 Torr, 5%) the receiver was quickly replaced by the polymerisation apparatus (Fig. 1). Polymerization apparatus charged by distilled 2-pyrrolidone was thermostated by means of the jacket 9. Polymerization mixture was continuously stirred with a spiral stirrer 1 driven by a rotating magnet 6. Polymerization space was joined through the three-way stopcock to the source of dry nitrogen or to vacuum. Potassium salt of 2-pyrrolidone was poured transferred from an ampoule through the side arm 10 under the flow of nitrogen. After the salt had dissolved a required amount of N-benzoyl-2-pyrrolidone was added and this moment was considered as the start of polymerization. The polymerization mixture was pushed from the transfer channel 11 into the room with rotating stirrer by the pressure of nitrogen (compressing the rubber joint 7); this secured a good homogeneity of the polymerization mixture. Sampling was carried out by producing a slight pressure above the polymerization mixture by

connecting the polymerization room to a low vacuum having the stopcock 12 closed and compressing the rubber joint 7. The time needed for taking a sample was 5 s. The polymerization was stopped by cooling the sampling tube in the ethanol-dry ice mixture. Sampling tube was always replaced under the stream of nitrogen.

Polymerization in Ampoules

The procedure described in²⁴ for the preparation of the reaction mixture and its transfer into ampoules was modified in the way that the solutions of initiator and activator in 2-pyrrolidone were prepared separately and then mixed. The time of whole operation, *i.e.* the time elapsed since the time of mixing of both solutions till filling of polymerization ampoules was shorter than 1.5 min. This is the time interval during which the polymerisation proceeds homogeneously at the concentration of catalytic components of 0.4 mol % of potassium salt of 2-pyrrolidone and 0.4 mol % of N-benzoyl-2-pyrrolidone and when there is no danger of blocking of the capillaries of polymerization ampoules by a precipitating polymer. At lower catalytic system concentrations, or at nonactivated polymerization the filling of ampoules is without difficulties. All ground-joints were finally ground-in and greased with dry 2-pyrrolidone. All operations were performed under an atmosphere of dry and purified nitrogen as mentioned above. Glass parts of the apparatus were prior to polymerization dried for 24 h at 140°C. Assembled apparatus was evacuated, heated with intermittent torch flame-outs and several times purged with nitrogen.

Polymer Characterization

Low-molecular weight parts of polymer were removed by five-time repeated extraction of products (2.5 g) with ethanol (75 ml) under continuous stirring at room temperature. The overall time of extraction of products containing less than 25% of polymer was 24 h, for higher polymer content the time was extended to 36 h; the time stated secures total removal of the monomer.

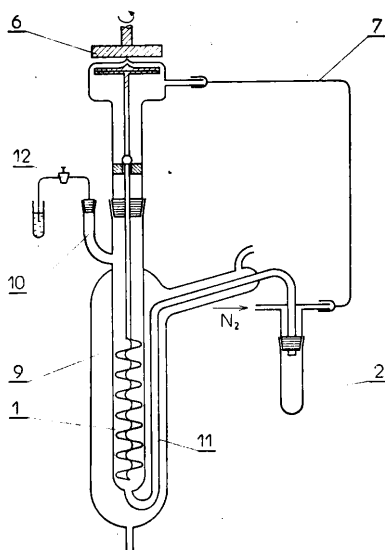


FIG. 1
Polymerization Apparatus

The viscosity of polymer solutions in *m*-cresol (0.4 g/100 ml) was measured in an Ubbelohde viscometer provided with a capillary No 2 at the temperature of 25°C. Intrinsic viscosity was calculated according to Loepelmann's equation²⁵; weight-average molecular weight M_w was calculated from²⁷ $[\mu] = 3.98 \cdot 10^{-4} \overline{M}_w^{0.77}$.

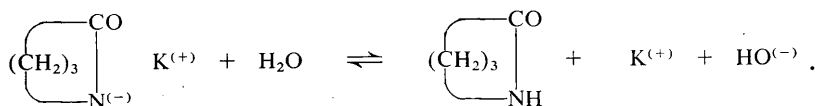
Amino groups were determined by conductometric titration according to the procedure already described²⁸.

RESULTS AND DISCUSSION

The present knowledge about the anionic polymerization of lactams unequivocally determines the approach to this problem. The first condition, which was not in some earlier studies taken in the account, is a high purity of monomer and catalyst components. This was the reason why in this study we have paid so much attention to monomer purity and to the preparation of potassium salt of 2-pyrrolidone. The procedure used enabled us to prepare chromatographically pure 2-pyrrolidone which was free of its main impurity – γ -butyrolactone – which acts as an activator of its anionic polymerisation.

It was proved that the procedure quoted for the preparation of potassium salt of 2-pyrrolidone from potassium hydroxide and 2-pyrrolidone in the presence of xylene, and removing water azeotropically³⁰ at lower pressure does not lead to alkaline hydrolysis of 2-pyrrolidone but to a relatively stable monohydrate of potassium salt; water is removed at temperatures above 100°C. As under these conditions some other reactions can not be excluded, potassium salt of 2-pyrrolidone was additionally recrystallised from pyridine. No difference in the initiation activity of dry potassium salt has been found if the crystallization was performed before drying of the hydrate or after its dehydration.

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. The latter is given by the following equilibrium



Both these effects are temperature dependent; in case of 2-pyrrolidone polymerization, which proceeds at relatively low temperatures, one may assume that the rate of hydrolysis would be lower than the rate of propagation in a homogeneous medium. This can be proved by the course of activated polymerization (Table I) initiated with monohydrate of potassium salt of 2-pyrrolidone. After a fast initial increase of polymer

content the polymerization stopped. The polymer content and the intrinsic viscosity are at the same polymerization times substantially lower than these if potassium salt of 2-pyrrolidone was used for the polymerization (Table I).

A sealed-ampoule polymerization technique was employed when the polymerization proceeded for a longer time period²⁴. But a high rate of polymerization at the beginning of the process brought some difficulties under these experimental conditions. The experimental data thus obtained do not represent the initial stage of polymerization but rather the effect of temperature on the polymerization system which attained a certain content of the polymer before a required temperature was reached. The experiments indicate that the rate of the N-benzoyl-2-pyrrolidone activated and potassium salt of 2-pyrrolidone initiated polymerization proceeding in a heterogeneous region depends upon temperature, the maximum being at around 40°C (Table II). Similar results are quoted in ref.³¹. At higher temperatures the polymerization considerably slows down (60°C), completely stops (70°C) or even the polymer content gradually decreases with time (80°C). These changes are controlled by the polymerization-depolymerization equilibrium in the heterogeneous system containing polymer which was formed just after the addition of the activator and before a selected temperature was attained. In contrast to published data^{7,8} we have obtained a higher polymer content and intrinsic viscosity values at the same temperature, catalyst component concentration and reaction time (Table II). The published data indicate that the optimum conditions of reaction mixture preparation and polymerization were not always observed.

During the activated anionic polymerization the number of polymer molecules decreases with increasing polymer content (Fig. 2). An increase of degree of polymerization and therefore a decrease of polymer molecules number due to condensation re-

TABLE I
Polymerization of 2-Pyrrolidone in the Presence of Potassium Salt of 2-Pyrrolidone or of Its Monohydrate as Initiators (always 0.40 mol %) and N-Benzoyl-2-pyrrolidone (0.40 mol %) at 30°C

Time min	Monohydrate		Anhydrous salt	
	polymer, %	$[\eta]$, dl/g	polymer, %	$[\eta]$, dl/g
2.5	8.6	0.24	12.9	0.40
6	10.9	0.27	14.8	0.42
12	11.8	0.28	15.6	0.43
20	12.2	0.31	16.1	0.43
60	12.6	0.35	17.0	0.47
120	12.7	0.36	17.9	0.51

actions takes place even at 70°C when the polymer content does not change with time. At higher temperature the changes of degree of polymerization are compensated by a simultaneously proceeding depolymerization. On the assumption that no side reactions take place, the number of polymer molecules should be independent of the polymerization time or of the polymer content and should correspond to the concentration of added activator. The simultaneously proceeding disproportionation reaction between lactam and its anion by which new centers of growth are formed should, on the other hand, lead to an increase of number of macromolecules; a part of secondary formed centers of growth can be regarded either as negligible or being compensated by other reactions. The changes of number of macromolecules can be ascribed to base catalysed condensation reactions of N-acyllactam groups or to their aminolysis by amino groups which are formed by disproportionation reaction between 2-pyrrolidone and its anion. In the heterogenous phase of polymerization of 2-pyrrolidone, when poly(2-pyrrolidone) precipitates out of the monomer melt, the growing N-acyllactam end groups being the centers of growth are gradually blocked by the crystalline polymer phase and therefore lose their activity of growth⁸. Those N-acyllactam groups which are present in an amorphous part of precipitated polymer can undergo both to propagation reaction and side reactions.

A substantially higher increase of polymer content is observed at the initial stage of nonactivated (as well as the activated) polymerization of 2-pyrrolidone than at

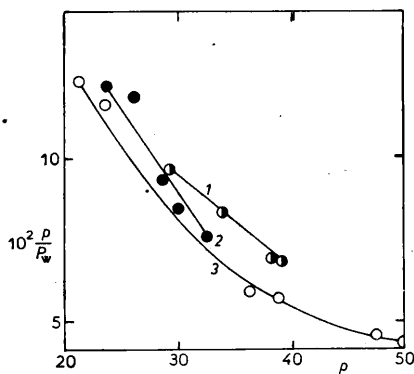


FIG. 2

Polymerization of 2-Pyrrolidone in the Presence of Potassium Salt of 2-Pyrrolidone and N-Benzoyl-2-pyrrolidone (always 0.4 mol %) Particle Number vs Polymer Content, p (%)
Temperatures (°C): 2 30, 3 40, 1 50.

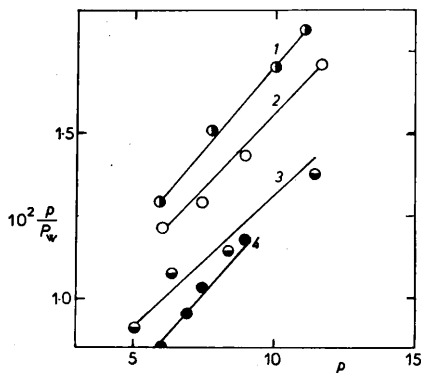


FIG. 3

Nonactivated Anionic Polymerization of 2-Pyrrolidone (Potassium Salt of 2-pyrrolidone 1.2 mol %) Particle Number vs Polymer Content, p (%)
Temperatures (°C): 4 30, 2 40, 3 50, 1 60.

TABLE II
 Polymerization of 2-Pyrrolidone in the Presence of Potassium Salt of 2-Pyrrolidone as Initiator (0.4 mol %) and N-Benzoyl-2-pyrrolidone (0.40 mol %)
B Concentration of amino groups (mol NH₂ per 1 g of polymerization mixture).

Temperature °C	Time h	Polymer %	<i>B</i> · 10 ⁷	[η] dl/g	\bar{P}_w
30	4	18.6	—	0.46	112
	19	23.6	—	0.70	193
	28	26.1	—	0.77	218
	43	27.8	—	0.98	299
	52	28.8	—	1.06	331
	67	30.6	13.0	1.22	396
	73	31.6	—	1.27	418
	75	31.7	—	1.27	418
40	2	21.1	1.3	0.64	172
	5	23.8	1.9	0.73	204
	20	36.5	10.5	1.69	606
	26	38.4	12.0	1.79	653
	42	47.5	10.5	2.53	1 023
	50	50.4	15.6	2.77	1 150
	66	58.5	18.0	3.28	1 430
	68	60.0	18.6	3.38	1 490
50	24	28.7	—	0.98	298
	43	33.7	—	1.23	401
	52	34.5	16.5	1.26	414
	67	38.0	—	1.55	541
	73	38.4	—	1.56	546
60	24	24.6	—	0.84	244
	42	28.4	—	1.00	306
	52	30.1	21.0	1.09	343
	67	32.4	—	1.30	431
	73	32.6	—	1.31	435
70	20	21.9	—	0.63	168
	52	21.8	5.1	0.69	189
	68	21.7	—	0.77	218
	109	22.0	—	0.94	283
80	20	15.3	—	0.42	99
	52	14.8	—	0.40	93
	68	14.0	1.3	0.38	87
	109	11.9	—	0.42	99

TABLE III

Polymerization of 2-Pyrrolidone in the Presence of Potassium Salt of 2-Pyrrolidone as Initiator (1.2 mol %)

B Concentration of amino groups (mol NH₂ per 1 g of polymerization mixture).

Temperature °C	Time h	Polymer %	<i>B</i> · 10 ⁷	[η] dl/g	\bar{P}_w
30	17	2.8	8.5	—	—
	24	3.2	15.0	—	—
	48	5.0	14.0	—	—
	72	5.3	16.0	—	—
	96	6.1	26.5	1.91	710
	120	6.8	27.6	1.92	715
	168	7.4	29.8	1.93	719
	216	9.8	30.2	2.03	769
40	18	3.4	17.0	—	—
	24	3.6	18.5	—	—
	48	4.9	17.4	—	—
	72	6.0	30.7	1.45	496
	96	7.4	36.0	1.62	573
	120	8.9	40.9	1.72	619
	168	11.4	50.6	1.78	648
	216	13.7	70.3	1.81	662
50	18	3.4	19.6	—	—
	24	4.1	20.9	—	—
	48	5.9	33.4	1.36	457
	72	7.8	50.7	1.50	519
	96	10.0	57.6	1.67	596
	120	11.5	65.0	1.75	634
	168	15.8	78.1	1.96	734
	214	21.2	100.0	2.19	848
60	18	1.3	15.0	—	—
	24	1.8	17.3	—	—
	48	2.7	23.3	—	—
	72	3.6	23.4	—	—
	96	4.8	32.0	1.52	528
	120	6.3	47.8	1.04	583
	168	8.6	52.6	2.02	764
	214	11.4	71.5	2.16	833

later stages. The polymer content and the intrinsic viscosity are increasing almost linearly with the time of polymerization; this is contrary to the published results⁵ quoting that the polymerization stops after a certain time. In contrast to the activated polymerization the maximum rate of polymerization is around 50°C. A very similar dependence was found also for the content of basic end groups (Table III).

The disproportionation reaction between lactam and its anion is the only source of centers of growth at the nonactivated polymerization of lactams. The initiation reaction is temperature dependent. The reaction rate increases with temperature as it is indicated by the change of the content of amino groups during polymerization (Table III). The number of centers of growth increases with temperature leading thus to a molecular weight decrease. The fall of the rate of amino group formation at 80°C could be explained by the aminolysis of N-acyllactam groups by primary amino groups. The results quoted in Table III indicate that this reaction would be fast enough even at 60°C. This is also documented by a lower particle number of macromolecules (Fig. 3) and a higher value of intrinsic viscosity at the same polymer content when compared with those at the temperatures of 40 and 50°C. The number of polymer molecules during the activated polymerization of 2-pyrrolidone decreases at all temperatures in the 30–70°C interval. This dependence distinguishes the nonactivated polymerization of 2-pyrrolidone from the activated one (Figs 2 and 3).

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