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# *Polymerization Mechanisms*

## Polymerization of Lactams.

### 70. Anionic Polymerization of 2-Pyrrolidone Accelerated with N-Iminolactams

**Jiří Brožek, Petr Řehák, *Jan Roda* and Jaroslav Králíček**

Department of Polymers, Prague Institute of Chemical Technology,
166 28 Prague 6, Czechoslovakia

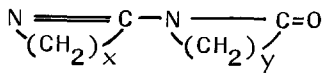
Summary

A pronounced acceleration of the anionic polymerization of 2-pyrrolidone (PD) occurs with the following N-iminolactams: 1-(1-pyrrolin-2-yl)-2-pyrrolidone (PDPD), 1-(1-azacyclohept-1-en-2-yl)-2-pyrrolidone (CLPD), and 1-(1-azacyclohept-1-en-2-yl)-1-aza-2-oxocycloheptane (CLCL). This acceleration effect on the anionic polymerization of PD initiated with 2-oxo-1-pyrrolidinylpotassium decreases in the sequence CLPD > PDPD > CLCL. The possible role of N-iminolactams in the system is discussed.

Introduction

The fibre-forming poly(2-pyrrolidone) - Nylon 4 - is obtained by the anionic polymerization of the lactam with the five-membered ring, 2-pyrrolidone (PD). The nonactivated polymerization, which is initiated only with salts of PD (preferably with 2-oxo-1-pyrrolidinylpotassium - KPD), has a heterogeneous character and exhibits the formal kinetics of zero order (1). Although the yields of practical importance are attained first after several tens of hours, the polymer can be spun from melt. This fails in the case of so called activated polymerization, where compounds comprising or forming a diacylalkylamine (N-acyllactam) structure in the system are used to accelerate the polymerization. However, some special compounds accelerate the nonactivated polymerization, retain its kinetic features (a linear increase of conversion with polymerization time in the heterogeneous system), and provide a heat stable polymer. The best known of these compounds is $CO_2$ (2,3), but a more pronounced acceleration of the PD polymerization was obtained with some N-iminolactams. The effect of 1-(1-pyrrolin-2-yl)-2-pyrrolidone (PDPD) was studied in details (1,4), whereas only fundamental kinetic data about the structural analogue of PDPD derived from 6-caprolactam - 1-(1-azacyclohept-1-en-2-yl)-1-aza-2-oxocycloheptane (CLCL) are given in the patent of BOUR (5).

This paper presents a comparison of activities of PDPD, CLCL, and 1-(1-azacyclohept-1-en-2-yl)-2-pyrrolidone (CLPD), which has been also mentioned in another patent report (6).



x = 3, y = 3 ⟶ PDPD
x = 5, y = 3 ⟶ CLPD
x = 5, y = 5 ⟶ CLCL

Results and Discussion

The polymerization were carried out at 30-45°C with 1.5 mol% 2-oxo-1-pyrrolidinylpotassium (KPD) prepared in situ and 0.5 mol% of N-iminolactam. The effect of N-iminolactams was evaluated from a conversion determined gravimetrically ($C_W$), on the one hand, and by the chromatographic analysis of extract ($C_G$), on the other, and also from the intrinsic viscosity of extracted polymers [η].

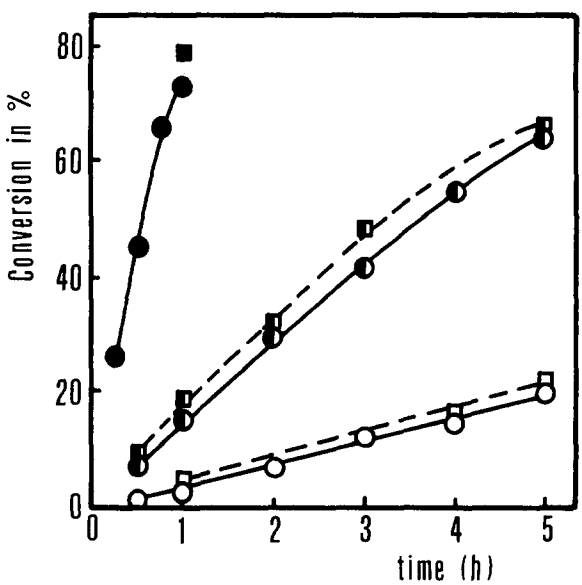



Fig.1 Dependence of conversion determined gravimetrically (○, ——) and by chromatography (□, - - -) on time for the polymerization of PD initiated with 1.5 mol% 2-oxo-1-pyrrolidinylpotassium and 0.5 mol% N-iminolactam at 40°C: ● ■ -CLPD, ◐ ◧ -PDPD, ○ □ -CLCL.

The conversion plots (Fig.1 shows the plot for 40°C) are characterised in all cases by the linear increase of $C_W$ and $C_G$ with polymerization time, similarly as it is in the nonactivated polymerization and the "related" polymerization accelerated with $CO_2$ (3). This linearity reaches up to the conversion of 60-70%. The polymerization thus exhibits formally the kinetics of zero order.

The differences between activities of the individual N-iminolactams are distinct; their efficiency increases in the sequence CLCL < PDPD < CLPD. This can be seen also in Table 1, where the apparent rate constants are given for all three accelerated polymerizations and temperatures 30-45°C. Activation energies were calculated for this temperature range (see Table 1) from the apparent rate constants determined from $C_W$ and from the kinetically more correct $C_G$, which is however determined with higher experimental errors. The Arrhenius parameters were optimized by the non-linear least-square method.

Strikingly, the replacement of the five-membered ring

TABLE 1

Apparent rate constants $k_{ax}$ ($10^2$.mol.kg$^{-1}$.min$^{-1}$) and activation energies $E_{ax}$ (kJ.mol$^{-1}$) determined from the gravimetric (x=w) and chromatographic (x=g) conversions for the polymerization of 2-pyrrolidone initiated with 1.5 mol% 2-oxo-1-pyrrolidinylpotassium and 0.5 mol% N-iminolactam (A).
(A): 1-(1-Pyrrolin-2-yl)-2-pyrrolidone ~ PDPD; 1-(1-azacyclohept-1-en-2-yl)-2-pyrrolidone ~ CLPD; 1-(1-azacyclohept-1-en--2-yl)-1-aza-2-oxocycloheptane ~ CLCL.

| A | CLPD | | PDPD | | CLCL | |
|---|---|---|---|---|---|---|
| Temp. °C | $k_{aw}$ | $k_{ag}$ | $k_{aw}$ | $k_{ag}$ | $k_{aw}$ | $k_{ag}$ |
| 30 | 10.5 | 10.9 | 1.68 | 1.88 | 0.441 | 0.580 |
| 35 | 13.7 | 13.3 | 2.19 | 2.25 | 0.661 | 0.631 |
| 40 | 15.4 | - | 2.71 | 3.11 | 0.806 | 0.824 |
| 45 | - | - | 3.38 | 3.29 | 1.09 | 1.03 |
| $E_{ax}$ | 29 | ≈31 | 36 | 31 | 46 | 31 |

with a double bond in PDPD by a seven-membered ring increased the activity more than fivetimes. Such extreme acceleration, which is the highest found in the anionic PD polymerization, has not yet been reported, though CLPD was mentioned in patent (6). Suitable conditions (45 °C) allow to achieve the 80% conversion with CLPD within 2 hours. On the contrary, application of the structural analogue derived from 6-caprolactam (CLCL) slowed down the polymerization about fourtimes in comparison to PDPD.

In all cases, [η] increased, after an initial abrupt growth, gradually with the polymerization time and only little exceeds 100 cm$^3$.g$^{-1}$ at the limit conversion (≈80%) after 5 hours of polymerization at utmost. Only acceleration with CLCL gave higher [η] by about 50%. The molecular weights are just little above the processing limit.

The course of polymerization at the optimum temperature 45 °C (4) is illustrated in Fig. 2 for all three N-iminolactams used up to 30 hours of polymerization. The limit conversion was attained during this time also with CLCL for the given concentration of initiation system. The figure perfectly illustrates the difference between acceleration activities of N-iminolactams and makes the extreme efficiency of CLPD more marked. The dependences of [η] on time are not so unambiguous (cf. Fig. 3). The highest values are attained with CLCL, where [η] approaches 200 cm$^3$.g$^{-1}$, whereas with CLPD and PDPD the values [η] oscillate around ≈ 100 cm$^3$.g$^{-1}$ after the initial rapid increase.

Explanation of the differences in activities of the used accelerating compounds is complex. In our previous paper concerning the effect of PDPD (1), we concluded that the character of polymerization is similar to the nonactivated polymerization. The linear increase of conversion with polymerization time, which is the most typical feature of the nonactivated polymerization, is explained by a continuous formation of growth centres in the reaction of lactam with its anion(7).

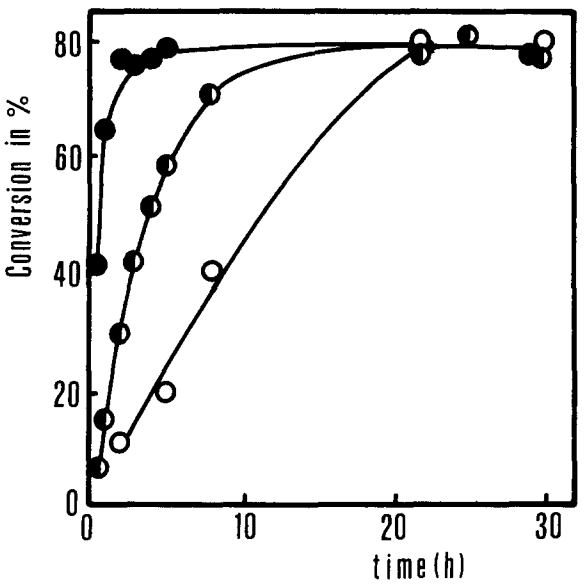



Fig.2 Dependence of conversion determined gravimetrically on time for the polymerization of PD initiated with 1.5 mol% 2-oxo-1-pyrrolidinylpotassium and 0.5 mol% PDPD (◐), CLPD (●), and CLCL (○) at 45°C.

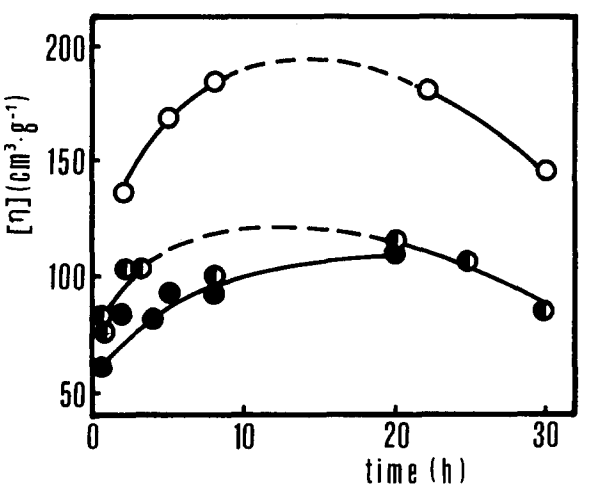
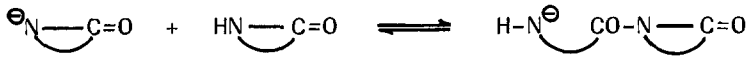
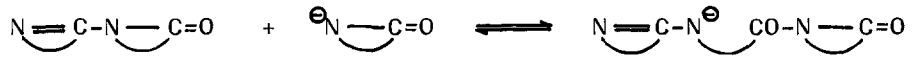



Fig.3 Dependence of intrinsic viscosity [η] on time for the polymerization of PD; for conditions and symbols see Fig.2.

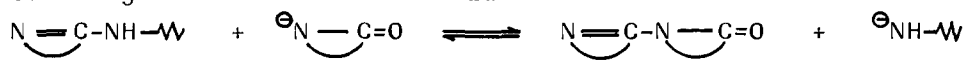


The acceleration of polyreaction in the presence of N-iminolactams may be then explained by an enhanced production of growth centres caused by affecting the dissociation of the lactam salt (more lactam anions take part in the initiation reaction). This may be evoked by a positive influence of N-iminolactams on acidobasic equilibria in the system. However, we are not able to explain the difference in their activities. Small differences of the structure surprisingly influence their activity. Let us admit that the counterion of the lactam anion in the alkaline salt of 2-pyrrolidone may be bound in a complex with N-iminolactams, which have a favourable steric disposition for such bonding and also a favourable distribution of free electron pairs, as it has been proposed in our previous paper (4). In this case, it cannot be excluded that the different tendency to form such complexes may be a consequence of fine differences in the structure of individual N-iminolactams. The different concentrations of active lactam anions and, consequently, the difference in polymerization rate can ensue from this fact.

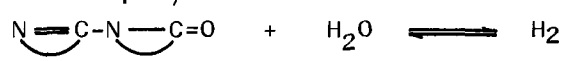
This assumed feature can be combined with the direct participation of N-iminolactams as growth centres of polyreaction:



N-Iminolactams can be regenerated in the subsequent reaction of the growth centres with a lactam anion:



In addition to this, N-iminolactams may bind residual water in the polymerization mixture:



so that the final drying and formation of N-(ω-aminoacyl)-lactam can also cause acceleration of the polymerization process.

## Experimental

1-(1-Pyrrolin-2-yl)-2-pyrrolidone was prepared according to GLICKMANN and MILLER (6) by the reaction of PD with 2,3-dihydro-5-methoxy-1H-pyrrole (butyrolactim methyl ether), which was prepared from PD and dimethyl sulfate according to PETERSEN and TITZE (8); m.p. of PDPD 61°C (DSC).

1-(1-Azacyclohept-1-en-2-yl)-2-pyrrolidone was prepared analogously by the reaction of PD with 3,4,5,6-tetrahydro-7--methoxy-2H-azepine (caprolactim methyl ether), which was prepared from 6-caprolactam and dimethyl sulfate (9); m.p.of CLPD 58°C (DSC).

1-(1-Azacyclohept-1-en-2-yl)-1-aza-2-oxocycloheptane was synthesized by an acid dehydration of 6-caprolactam in dry benzene with $POCl_3$ (10); m.p. 37°C (DSC); the sample repeatedly crystallized from n-heptane contained 0.2 mol% chlorine.

The purity and identity of the above mentioned compounds were checked by GLC, elemental analysis and IR spectroscopy.

The solution of 2-oxo-1-pyrrolidinylpotassium in 2-pyrrolidone was prepared in situ from a methanolic solution of KOH and PD (1).

For purification of PD, the polymerization procedure in mixing ampoules, and the determination of intrinsic viscosity [η] in cresol see (11); for the determination of conversion, both gravimetrically and by GLC, see (3).

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