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Polymerization of Lactams

47. Anionic Polymerization of 2-Pyrrolidone Accelerated by 1-(1-Pyrrolin-2-yl)-2-pyrrolidone

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Summary

The anionic polymerization of 2-pyrrolidone is markedly affected by 1-(1-pyrrolin-2-yl)-2-pyrrolidone which probably influences the propagation reaction. A kinetic analysis of the polymerization process demonstrates its distinct similarity with non-activated polymerization. The polymers thus obtained possess a satisfactory thermal stability.

Introduction

The five-membered lactam, 2-pyrrolidone (PD), yields by heterogeneous anionic polymerization a fibre-forming polyamide (Nylon 4), the main complication involved in its processing is the low thermal stability of the polymer already near its melting point (PETERS and GERVASI,1972).

Poly(2-pyrrolidone) (PPD) is most frequently obtained by means of alkali salts, of which 2-oxo-1-pyrrolidinylpotassium (KPD) is the most efficient, optimally at 40-55°C. In this non-activated polymerization the formation of propagation sites proceeds via a slow disproportionation reaction between the lactam and its anion (ŠEBENDA and KRÁLÍČEK,1958). Probably due to the suitable competition of the initiation, propagation and crystallization of PPD, non-activated polymerization formally obeys the zero-order kinetics. Similar kinetic dependences are obtained in the quicker polymerization of PD in the presence of CO_2 (RODA,1981b); the obtained polymer can be melt-spun without major problems (PETERS and GERVASI,1972). The polymerization can be markedly accelerated similarly to the other lactams (ŠEBENDA,1972) by adding activators, N-acyllactams in most cases. In such an activated polymerization the slow heterogeneous stage is preceded by a short and very fast homogeneous stage of polymerization. With respect to side reaction accompanying the activated polymerization the thermal stability of PPD is very low (RODA et al.,1981a).

This means that one of the key problems of the polymerization of PD consists in finding a fast acti-

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vator which at the same time would provide a thermally stable polymer. A vast amount of compounds have been tested and patented which introduce or form propagation N-acyl-2-pyrrolidone sites; in fact, however, with the exception of the not quite unambiguous effect of CO_2 (BARNES,1973), all attempts to prepare PPD possesing satisfactory thermal stability have failed.

Recently,BOUR(1979) has pointed out the positive activation effect of 1-(azacyclohept-1-en-2-yl)-2-oxoazacycloheptane(CLCL): already after 10 h of polymerization high yields of melt-spun polymer were obtained.

A structural analog of CLCL, viz.,1-(1-pyrrolin-2-yl)-2- pyrrolidone (PDPD), has also been mentioned as an activator of the anionic polymerization of PD (GLICKMANN and MILLER,1962; NEY and ZOLLINGER,1962). No conclusions regarding its effect can be drawn, because any detailed data on its polymerization activity are inaccessible.

The investigation of the activation effect of PDPD has brought surprising result which are reported in this paper.

Results and Discussion

Table 1 shows that already after 5 h of polymerization (40°C) high conversions are reached, at a lower concentration of the initiation system than recommended for the activation of the polymerization with N-acyllactams (RODA et al.,1978a).

TABLE 1

Polymerization of 2-pyrrolidone initiated by KPD and PDPD at 40°C; polymerization time 5 h

KPD(mole-%)	PDPD(mole-%)	Conversion(%)
0.52	0.53	20.56
1.00	0.49	34.11
1.65	0.46	56.45
2.00	0.53	76.06
3.13	0.53	74.65
0.52	1.05	32.85
1.04	1.05	71.21
3.12	0.97	73.64

The conversion dependences in Fig.1 illustrate the effect of change in the KPD concentration at ≈0.5 mole-% PDPD on the course of polymerization. Quite unexpectedly, the polymerization is characterized by a linear rise in conversion with the polymerization time, exhibits zero-order formal kinetics, similar to the much slower non-activated polymerization and to the polymerization in the presence of CO_2. The values

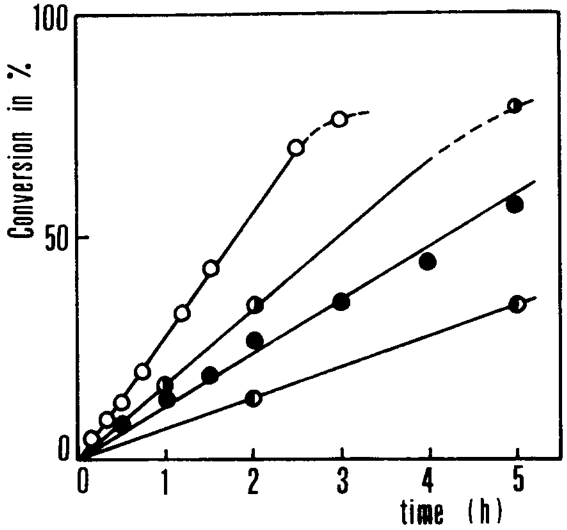

Fig.1 Conversion vs. time dependences for polymerization of 2-pyrrolidone by 2-oxo-1-pyrrolidinylpotassium and PDPD (in mole-%) at 40°C: (◐) 1.00; 0.49; (●) 1.57; 0.47; (◑)2.03; 0.52; (○) 2.65; 0.57.

TABLE 2

Apparent rate constant (k_a) of polymerization of 2-pyrrolidone initiated by KPD and PDPD at 40°C

KPD(mole-%)	2.65	2.03	1.57	1.00
PDPD(mole-%)	0.57	0.52	0.47	0.49
k_a (mol.kg^{-1}.min^{-1})	5.28	3.36	2.26	1.33

of the apparent rate constants, cf.Table 2, were used in the determination of the order of the polymerization reaction with respect to the initiator (≈1.4). With respect to the complicated mechanism of the anionic polymerization of lactams (ŠEBENDA,1972), the non-integer reaction order does not seem surprising, but its value is markedly different from the order with respect to the initiator determined for non-activated polymerizations and for polymerizations in the presence of CO_2 (≈0.8) (RODA,1981b).

The molar mass of PPD characterized by [η] of cresol solutions increases relatively slowly after an initial stepwise rise ≈90 cm^3.g^{-1} and at conversions > 50 % exceeds the value 120 cm^3.g^{-1}, sufficient for the processing of the polymer.

Already very few experimental data demonstrate the expectional effect of PDPD on the anionic polymerization of PD. At 2.65 mole-% KPD and 0.57 mole-% PDPD,

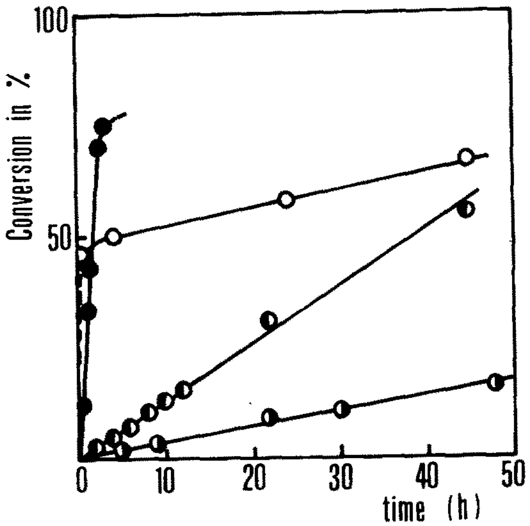

Fig.2 Comparison of conversion curves for main types of anionic polymerization of 2-pyrrolidone initiated by 2-oxo-1-pyrrolidinylpotassium (KPD) at 40°C: (●) 2.65 mole-% KPD; 0.57 mole-% PDPD; (○) 3.03 mole-% KPD; 0.99 mole-% N-benzoyl-2-pyrrolidone-"activated polymer"; (◑) 4.58 mole-% KPD; 1.40 mole-% CO_2-"CO_2polymer"; (◐) 3.16 mole-% KPD; "non-activated polymer".

more than 70% of conversion is reached already after 3 h, while by employing other routes of polymerization of PD such an economically advantageous conversion is reached only if the polymerization time increases by at least one order of magnitude. The situation is demonstrated for 40°C in Fig.2, where the "PDPD" polymerization is compared with the so-called fast activated polymerization, non-activated polymerization and polymerization accelerated by the presence of CO_2. A comparison with the data of BOUR(1979) is also of importance - PDPD is more efficient than CLCL (2.5 mole-% KPD, 0.62 mole-% CLCL, 50°C, 8 h, ≈ 70 % PPD).

It is interesting that also at a high rate the polymerization with PDPD is controlled by the basic rules of non-activated polymerization (RODA,1978b).If PDPD were a "real" polymerization activator, the reaction would have to exibit a homogeneous stage (cf. Fig.2), which however has not been proved. The acceleration is probably due to the effect on the formation of propagation sites; the only possibility of increasing their production consists in an increase in the concentration of lactam anions. In this case PDPD should be as a regulator of both the dissociation and acid-base equilibria in the system. This regulating ability is indirectly confirmed by the GLC analysis of extracts: at a 40% conversion, at least 65% of the original PDPD remains unincorporated, and moreover the result is distorted by a partial hydrolysis of PDPD.

The kinetic scheme will of course be complicated: expect the order with respect to the initiator ≈ 1.4, the activation energy 13.3 $kJ.mol^{-1}$ (2.03 mole-% KPD; 0.52 mole-% PDPD) is much lower (cf.Table 3) than

TABLE 3

Temperature dependence of polymerization of 2-pyrrolidone initiated by 2.03mole-% of KPD and 0.52mole-% PDPD

Temperature(°C)	30	40	45	50	60
Conversion,1h(%)	11.25	16.53	21.28	29.35	8.62
Conversion,2h(%)	20.07	32.97	41.58	42.42	16.25

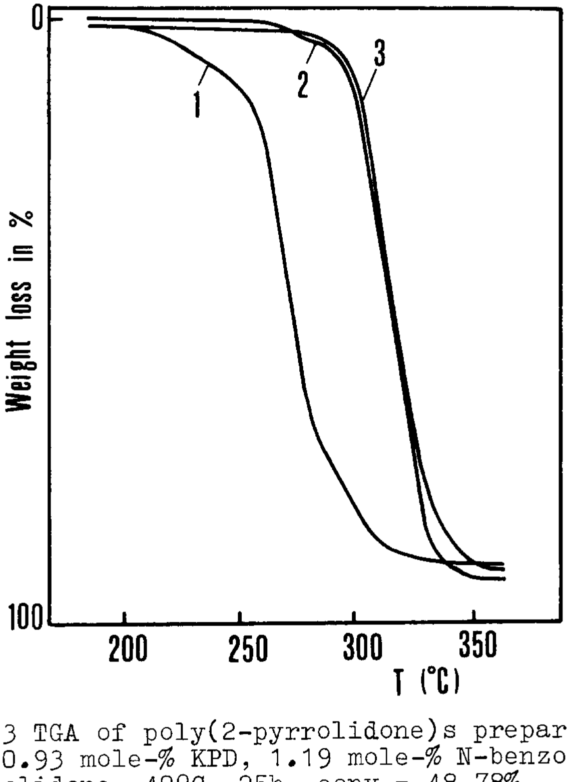

Fig.3 TGA of poly(2-pyrrolidone)s prepared:
(1) 0.93 mole-% KPD, 1.19 mole-% N-benzoyl-2-pyrrolidone, 40°C, 25h, conv.= 48.78%, [η]= 141 $cm^3.g^{-1}$;
(2) 2.65 mole-% KPD, 0.60 mole-% PDPD, 40°C, 3h, conv.= 75.77%, [η] = 140 $cm^3.g^{-1}$;
(3) 7.60 mole-% KPD, 0.60 mole-% CO_2, 50°C, 161h, conv.= 72.40%,[η]= 799 $cm^3.g^{-1}$;
rate of heating 10 $K.min^{-1}$, under the atmosphere of argon, 50 $cm^3.min^{-1}$.

with the other routes of polymerization of PD (40-80 kJ.mol^{-1}). It should also be mentioned that the complexity of the system is enhanced by the known crystallization of PPD during the polymerization process.

The thermal stability (characterized by TGA) of polymers obtained in the presence of PDPD resembles that of spinnable polymers prepared in the presence of CO_2 and is considerably higher than that of PPD obtained with N-acyllactams as activators, Fig.3. This finding gives more support to the already observed exceptional effect of PDPD on the anionic polymerization of PD.

Experimental

1-(1-Pyrrolin-2-yl)-2-pyrrolidone was prepared according to NEY and ZOLLINGER(1962) by the dehydration of PD by P_2O_5 at 200°C. The purity of PDPD was checked by IR spectroscopy, elemental analysis and GLC, m.p. 61°C.

For PD purification, polymerization procedure in mixing ampoules, determination of conversion and intrinsic viscosity $[\eta]$ in cresol see RODA et al.(1981a).

Solution of 2-oxo-1-pyrrolidinylpotassium in 2-pyrrolidone was prepared in situ from a methanolic solution of KOH (RODA et al.,1981a).

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