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Polymerization of Lactams, 21*)

Effect of Activating Agents on the Anionic Polymerization of 2-Pyrrolidone

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SUMMARY:

The activated anionic polymerization of 2-pyrrolidone (**1a**) was studied by using *N*-potassium-2-pyrrolidone (**1e**) as initiator in a 1:1 mole ratio with *N*-acetyl- (**1b**), *N*-benzoyl- (**1c**), and *N*-pivaloyl-2-pyrrolidone (**1d**), *N*-benzoyl-8-octanelactam (**2a**) or *N*-benzoyl-12-dodecanelactam (**2b**) as activators in the heterogeneous stage of the polymerization process under isothermal conditions.

Introduction

On the basis of laws concerning the anionic polymerization of lactams, particularly caprolactam[1], and of published data on the anionically activated polymerization of 2-pyrrolidone (**1a**), it is possible to assume that in addition to the perfect purity of the components of the polymerization system[2], to the experimental performance[2,3], to the temperature[2,4–6], and to the concentration and ratio of the initiation system components[3], the course of the polymerization of **1a** also depends on the nature of the activator. Many activators have been claimed in patents. *N*-acyllactams, primarily *N*-acetyl-2-pyrrolidone (**1b**)[4,6–9], *N*-benzoyl-2-pyrrolidone (**1c**)[2,7,10], *N*,*N*′-adipolydipyrrolidone[11], lower lactones[4,8], and carbon dioxide[6,12] have been extensively used as activators for the polymerization of **1a**, mostly in combination with the alkaline salt of **1a**.

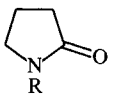
In most papers the course of the polymerization of **1a** has been studied at constant time and temperature for different mole ratios of activator and initiator[4,7–9]. It has been shown that the time dependence of conversion and intrinsic viscosity[2,6,10,11] cannot be mutually compared at different concentrations and compositions of the initiation system neither at different experimental performance and purity of the system[2,10].

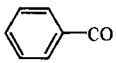
The initial unusually rapid homogeneous stage of the polymerization of **1a** takes only several minutes[10]. Thus, it is possible to expect that the rapid conversion of *N*-acyllactam structures by secondary condensation reactions[1] corresponds primarily to this short time period. During the further heterogeneous stage of the polymerization, the course of the secondary condensation reactions requiring (according to a considered analogy with the caprolactam polymerization) the interaction of two *N*-acyllactam groups, is certainly partially restricted. It is also possible to consider that the initial rapid homogeneous stage exerts a remarkable effect on the course of the subsequent heterogeneous polymerization stage. Thus, it is possible to expect, with

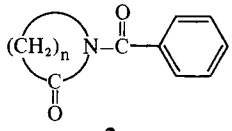
*) Part 20: cf.[21].

respect to the low optimum polymerization temperature (40°C), that in the case of **1a** the effect of the structure of the activator will be remarkably more expressed than it is in the case of the polymerizations of higher lactams[1,13,14]. At higher temperatures the growing centres, which decayed at the beginning of the polymerization can be recovered again by side reactions[2].

In this work we investigated the effect of *N*-acyllactams **1b–d, 2a, b** on the course of the anionic bulk polymerization of **1a**.



1a : R = H
b : R = H_3C–CO
c : R = 
d : R = $(H_3C)_3C$–CO
e : R = K



2a: n = 7
b: n = 11

Experimental Part

2-Pyrrolidone (**1a**) (from Fluka) was purified by double crystallization of its monohydrate and subsequent distillation[2]; bp 110°C at 267 N/m^2 (2,67 mbar). GLC purity: 99,95%; water content 0,01 mole-% (after drying over "Nalsit 4A" molecular sieves).

N-potassium-2-pyrrolidone (**1e**) was prepared by the reaction of KOH with **1a** in xylene[3] and was recrystallized from pyridine in an inert atmosphere.

N-acetyl-2-pyrrolidone (**1b**) was prepared by the reaction of excess acetic anhydride with **1a**[15]. It was purified by double rectification; bp 94°C at 400 N/m^2 (4 mbar).

N-benzoyl-2-pyrrolidone (**1c**) was prepared by the reaction of benzoyl chloride with **1a** in dry benzene and triethylamine[2]. It was purified by precipitating five times the solution of *N*-benzoylpyrrolidone in toluene with diethyl ether (mp 91°C).

N-benzoyl-8-octanelactam (**2a**) was prepared by the same procedure as *N*-benzoyl-2-pyrrolidone (**1c**). The crude product was recrystallized five times from the mixture of cyclohexane and n-heptane (volume ratio 1:1), mp 55,5°C.

N-benzoyl-12-dodecanelactam (**2b**) was prepared similarly as *N*-benzoyl-2-pyrrolidone (**1c**). It was purified by recrystallization from cyclohexane (six times), mp 73–74°C.

N-pivaloyl-2-pyrrolidone (**1d**) was prepared by the reaction of pivaloyl chloride with **1a** in dry benzene and triethylamine. After distillation it was purified by double rectification, bp 92–93°C at 400 N/m^2 (4 mbar).

The purity of the activators was determined by using the GLC, GPC, NMR, and conductometric titration methods. The content of impurities was in no case higher than 0,5% by weight, and the absence of acidic substances could be demonstrated. Before use, the activators were dried either over molecular sieves (from Linde, 5A) or for 24 h at 13,3 N/m^2 at ambient temperature.

The polymerizations were carried out under isothermal conditions at 40°C in glass ampoules with separated compartments for the solutions of activator and initiator in the monomer. The polymerization was started by intensive stirring of both preliminarily conditioned solutions. All operations associated with the preparation of the polymer, were carried out in dry nitrogen.

The polymer content (in percentage) was determined by extraction of the polymerized sample with ethanol (five times, each extraction 20 min, total ethanol volume about 1 dm^3 per 10 g of the polymer). After washing with diethyl ether polypyrrolidone was dried to a constant weight. Its viscosity was measured at 25 ± 0,01°C in the Ubbelohde viscosimeter with the capillary II, according to the standard procedure, in *m*-cresol. The intrinsic viscosity was calculated from the relative viscosity according to *Loepelmann*'s relationship[16].

The concentration of basic groups in the polymer was determined by conductometric titration with 0,01 M HCl in a mixture of 60% phenol, 13% water, and 27% ethanol (by vol.).

The molecular weight of polypyrrolidone was calculated according to the relationship found by *Tuzar* et al.[17].

Results and Discussion

In *N*-acyllactams the substituent determines the electron density at the nitrogen, which activates the endocyclic carbonyl group. Thus, depending on the substituent, different effects on the rate of the lactam anion addition to the *N*-acyllactam in the first reaction step have to be expected[1,14]. In this reaction, in some cases the steric effect of the substituent will be manifested to a certain extent and further, the substituent can also affect the thermal stability of the polymer[18].

Simultaneously, even at a low concentration of acyl groups, it is impossible to rule out their effects on the acidity of the polymerization system. Therefore, we can expect an alternation of all the acid-base equilibria in the system which control the active concentration of lactam anions, and thus also the polymerization rate.

When using activators which have no active α-hydrogen in the acyl group, we can expect a partially reduced possibility of condensation reactions of the *N*-acyllactam groups in the initial step of polymerization (acetyl vers. benzoyl); the condensation reactions will be limited to the sterically less attainable endocyclic $-CH_2-$ group in the neighbourhood of the carbonyl group of the lactam. All these effects will be remarkably manifested primarily in the homogeneous stage of the polymerization, which is in many directions a governing stage for the further polymerization of **1a** in the heterogeneous system. Since it is difficult to follow the short homogeneous stage, we studied the effect of *N*-acetyl-(**1b**), *N*-benzoyl-(**1c**), and *N*-pivaloyl-2-pyrrolidone (**1d**) on the polymerization of **1a** in the heterogeneous stage. For comparison of time dependence of the conversion and intrinsic viscosity (for the above mentioned activators **1b–1d** and for a 1:1 mole ratio with *N*-potassium-2-pyrrolidone (**1e**) (0,40 mole-%) see Figs. 1 and 2.

The Figs. show that the initial polymerization rate in the heterogeneous step depends on the substituent of the activator and increases in the sequence **1b** < **1c** < **1d**. For the intrinsic viscosity (polymerization degree) at the beginning of the time interval of interest (5 h) the

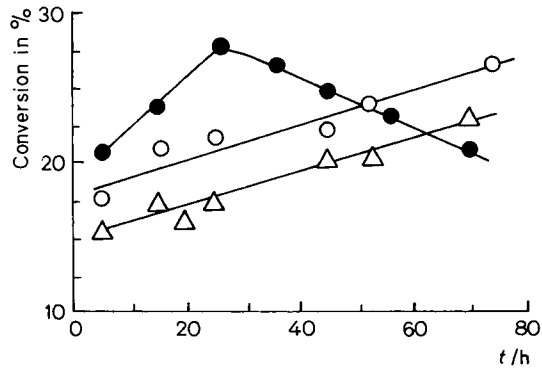


Fig. 1. Time (t) vs. conversion curves for the polymerization of 2-pyrrolidone (**1a**) initiated by 0,4 mole-% *N*-potassium-2-pyrrolidone (**1e**) and activated by 0,4 mole-% of *N*-acetyl-2-pyrrolidone (**1b**) (△), of *N*-benzoyl-2-pyrrolidone (**1c**) (○), of *N*-pivaloyl-2-pyrrolidone (**1d**) (●); temp.: 40 °C

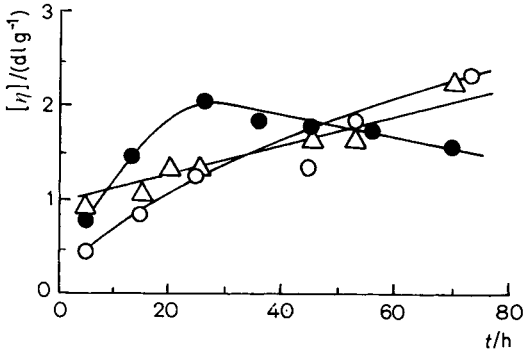


Fig. 2. Time (t) vs. intrinsic viscosity ($[\eta]$) curves for the polymerization of 2-pyrrolidone (**1a**); for symbols see legend of Fig. 1

order was found to be **1c** < **1d** < **1b**; after 70 h **1d** < **1b** < **1c**. The lowest efficiency (with respect to the conversion) of **1b** is due to the highest activity for condensation reactions due to the presence of α-hydrogens adjacent to endo- as well as exocyclic carbonyl groups. Thus, a rapid decrease of growing centres occurs via the side reactions. Slightly higher values of intrinsic viscosity as compared to **1c** may also result from condensation reactions between polymer chains.

1c and **1d** have no active hydrogen in the neighbourhood of the exocyclic carbonyl group. Thus, they are characterized by a reduced tendency to condensation reactions of the Claisen type which is manifested in both cases by an increased conversion as compared to **1b**.

We can, however, assume that during the heterogeneous polymerization of this kind the rate of polymerization and the values of the intrinsic viscosity may also be determined by the parallel effects of propagation and crystallization rates. In the case of activation with **1d** higher initial values of conversion and intrinsic viscosity may be assumed at the beginning of polymerization due to the lower possibility of the side reaction and to the reduced tendency to the crystallization for sterical reasons. The branching at the end of the chain (pivaloyl group) could lead to a slight delay of crystallization and thus also to a prolongation of the homogeneous stage at which the polymerization is remarkably more rapid. The time dependence of the polymerization of **1a** activated with **1d** revealed a unique character; the dependence of conversion and intrinsic viscosity on the time are characterized by a maximum. For longer polymerization times (above 40 h) a depolymerization from the end of the chains may be considered, in contrast to all polymerization dependences for **1a**, known so far. Repeated reacylations in the neighbourhood of the pivaloyl substituent, leading to an enhancement of the concentration of low molecular particles and thus to an increase of the portion of extractable components, seem to be improbable.

Comparison of the course of polymerization in the presence of *N*-benzoyl-8-octanelactam (**2a**), and *N*-benzoyl-12-dodecanelactam (**2b**) shows the best results for **2a** (Figs. 3 and 4). The polymerization in the initial stage activated with **2a** or **2b** is essentially more rapid and shows higher values of intrinsic viscosity of the polymer than in the case of activation with **1c**. When elucidating these phenomena it is possible to consider a higher rate of the primary and secondary reacylation growing reaction of the pyrrolidone anion with the *N*-benzoyllactam group. Similarly we can consider that the primarily formed polymer is actually a copolymer, and it is possible to take into account a hindered crystallization process and thus a longer

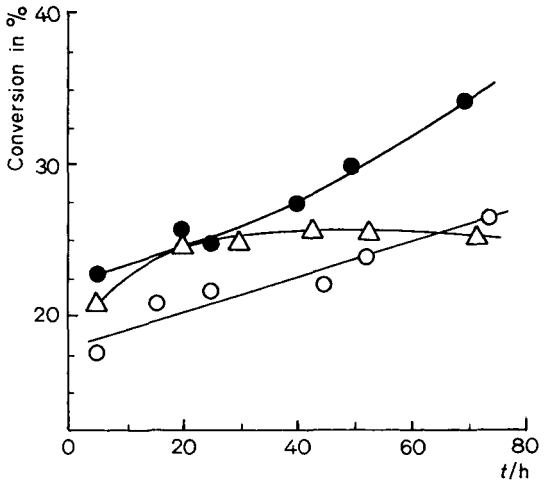


Fig. 3. Time (t) vs. conversion curves for the polymerization of 2-pyrrolidone (**1a**) initiated by 0,4 mole-% *N*-potassium-2-pyrrolidone (**1e**) and activated by 0,4 mole-% of *N*-benzoyl-2-pyrrolidone (**1c**) (○), of *N*-benzoyl-8-octanelactam (**2a**) (●), of *N*-benzoyl-12-dodecanelactam (**2b**) (△); temp.: 40°C

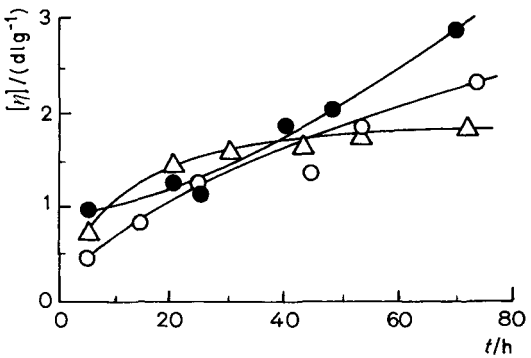
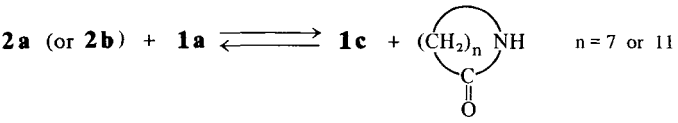


Fig.. 4. Time (t) vs. intrinsic viscosity ($[\eta]$) curves for the polymerization of 2-pyrrolidone (**1a**); for symbols, see legend of Fig. 3

time of residence of the growing chain in the rapid homogeneous stage. In both cases we can consider higher values of conversion and intrinsic viscosity.

The following exchange reaction can be taken into account between **2a** or **2b** and the monomer **1a** (or its anion):



which may be controlled by the acidity, which is assumed for **1a** to be the highest of all the lactams used[19]. However, the experiments show that the addition of the pyrrolidone anion to the exocyclic carbonyl group does not take place, or that its rate is much lower than that of the addition of the lactam anion to the endocyclic carbonyl of the *N*-acyllactam structure. In the opposite case the initial composition of the polymers should be identical

and only in the latter stage the rates differ by the action of the released more difficultly copolymerizing lactams[3]. The rate of the recyclization, i.e., the parameter which is important for the thermal stability of the polymer[20], is also associated with the size and thermodynamical stability of the ring of the corresponding activator.

An anomalous dependence of conversion and intrinsic viscosity was found in the polymerization activated with **2b** in which the polymerization was stopped at a certain degree of conversion. This may be attributed to so far unidentified reactions leading to a decay of growing centers.

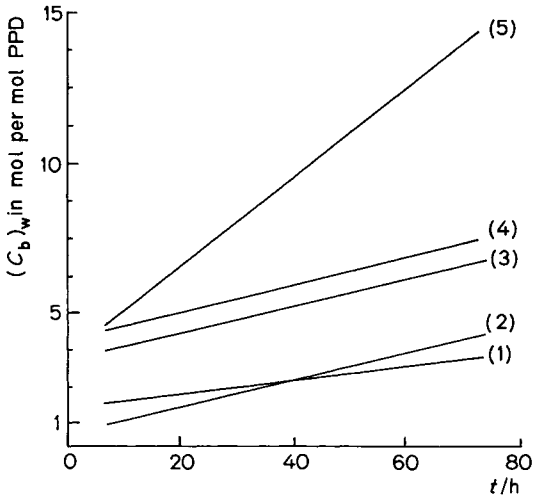


Fig. 5. Time (t) vs. content of basic groups in polymer (c_b) (referred to amount of polymer in mol) for the polymerization of 2-pyrrolidone (**1a**) initiated by 0,4 mole-% *N*-potassium-2-pyrrolidone (**1e**) and activated by 0,4 mole-% of (1): *N*-benzoyl-2-pyrrolidone (**1c**), (2): *N*-benzoyl-8-octanelactam (**2a**), (3): *N*-benzoyl-12-dodecanelactam (**2b**), (4): *N*-acetyl-2-pyrrolidone (**1b**), (5): *N*-pivaloyl-2-pyrrolidone (**1d**)

The type of activator also affects the content of basic groups in polypyrrolidone (Fig. 5). However, the content of basic groups is related neither to the conversion nor to the intrinsic viscosity of the polymerization series. The process which determines the different content of basic groups cannot be established on the basis of the present knowledge on the reactions occuring during the polymerization of **1a**. It will probably be associated with a competition between the propagation rate of the side condensation reactions or possibly of further splitting of thus formed products and particularly the rates of disproportionation between the polymer chains. In this case it is also necessary to consider the simple aminolysis of the *N*-acyllactam structures, the rate of which will be dependent on the type of substituent.

On the basis of the data presented here, we can consider a remarkable effect of the initial rapid polymerization stage on the course of the heterogeneous stage of the activated polymerization of **1a**. Since the effect of the type of activator is remarkably manifested even in the heterogeneous stage of the polymerization, its action in the homogeneous polymerization stage, which is more rapid at least one order of magnitude, will probably determine the further course of the polymerization.

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