

# Copolymerization of 2-pyrrolidone and its methyl derivatives Thermal properties used for determination of the copolymer structure\*

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Copolymers of 2-pyrrolidone and its C-methyl derivatives were prepared with anionic catalysts. A methyl substituent on the pyrrolidone ring notably decreased polymerizability more or less according to its position. The incorporation of the methyl units depended also on the nature of the catalyst cation.

Transitions, melting points, and degradation of resulting compounds were studied and the results enabled us to determine the copolymer structure.

The data of thermal properties indicate that the nature of catalyst cation plays an important part in obtaining true random copolymers: this is confirmed by study of the incorporation ratio.

С помощью анионных инициаторов приготовились сополимеры 2-пирролидона и его С-метилированных производных. Метильная группа на пирролидоновом цикле четко понижает его полимеризационную способность. Интервал этого влияния более-менее обусловленный расположением метильной группы. Инкорпорация метилированных единиц зависит тоже от природы катиона инициатора.

Изучались температуры стеклования и плавления и деградация полученных веществ. Результаты позволили определить структуру сополимеров.

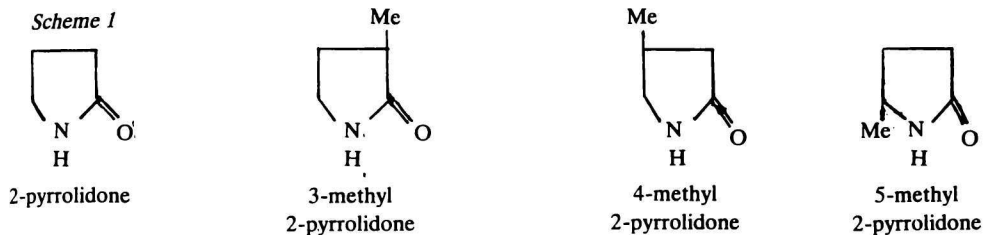
Термические свойства показали, что природа катиона инициатора играет важную роль при получении истинных статистических сополимеров: этот факт подтверждает и изучение отношения инкорпорации.

The effects of substituents on the rate of polymerization of lactams were mostly studied on 7 and more membered ring compounds. It was found that a substitution always decreases reactivity (see for example [1—7]). It is also known that a single substituent prevents the polymerization of 2-pyrrolidone and 2-piperidone [8, 9]. However, these works dealing with 5- and 6-membered lactams are rather qualitative studies.

We investigated therefore anionic homopolymerization and copolymerization of 2-pyrrolidone and its C-methyl derivatives in order to obtain further information on their reactivity (Scheme 1).

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The polymerizability of the methylated monomers as defined in our previous work [10] is very weak and consequently, the incorporation of these units in the resulting copolymers is low. The problem is whether a true copolymerization or only a termination of polybutanamide (nylon 4) chains takes place. The study of thermal properties, mainly melting points and degradations, allows to clarify this problem. This investigation permitted us to point out the role of the catalyst cation in the incorporation of methylated units. The results obtained have agreed with the mechanism proposed to explain the process of polymerization [11].

## Experimental

### *Monomers, catalysts, initiators*

A commercial 2-pyrrolidone (EGA Chemie KG) was used. Methyl pyrrolidones were obtained by catalytic reduction of  $\gamma$ -nitro acid esters, prepared by Michael condensation of nitroalkane with acrylic derivatives [12]. The monomers were purified and dried according to the method given in an earlier work [13].

Various catalysts were prepared by methods described previously: conventional alkaline salts of lactams and salts with non-metallic cation, mainly tetramethylammonium [14, 15]. They were used in the polymerization immediately after preparation.

*N*-Acetylactams [13] were used as initiators.

### *Polymerization of lactams*

The monomers were distilled directly into the dried reaction vessel under nitrogen atmosphere. The required quantity (8.0 mole % in general) of catalyst was dissolved and the initiator (2.0 mole %) introduced. The polymerization was carried out under nitrogen at 20°C (45 or 60°C, for mixtures melting at higher temperatures). After the desired time (96 hrs in general), the polymer (about 5 g) was dissolved in formic acid (50 cm<sup>3</sup>) and precipitated in ether (500 cm<sup>3</sup>), then washed with ether and dried *in vacuo* at room temperature. Reduced viscosity values determined for a concentration of 1 g/100 cm<sup>3</sup> in *m*-cresol at 25°C are given in the present article.

### *Thermal properties*

All the measurements were made with a DTA Du Pont 990 apparatus at a heating rate 20°C/min.

— Transitions: The polymer samples were melted and then quenched in liquid nitrogen in the absence of humidity. The indicated temperatures are those of the intersection of the two tangents on the curve; the values are corrected.

— Melting points and degradation: The melting points of polymers having no additional thermal history were determined. The indicated temperatures are those of the peaks after correction.

All the values were corrected with the help of a correction table supplied with the apparatus.

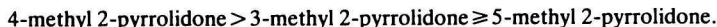
## Results

The homopolymerization of the methyl pyrrolidones, indicated by some patents [16], practically gave no polymer, whatever catalyst and initiator were used. We studied therefore more particularly the behaviour of these derivatives in copolymerization with 2-pyrrolidone.

### Kinetic results

An increase of the molar fraction of the methylated lactams in the comonomer mixture greatly decreases the yield and reduces viscosity (Fig. 1), and consequently the rate of polymerization.

Fig. 1 shows that polymerization is difficult when molar fraction of these monomers is above 0.8 and that the reactivity more or less depends on the position of the methyl group on the ring



The catalyst activity order as a function of the rate of conversion was found to be the same as that in the homopolymerization of 2-pyrrolidone [13]

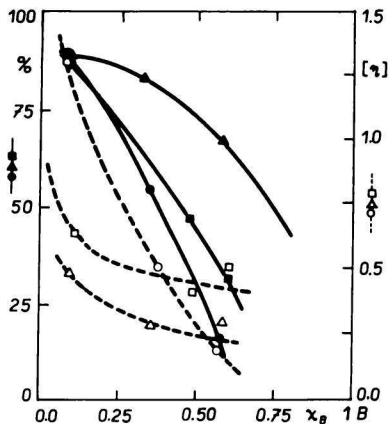
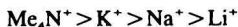


Fig. 1. Copolymerization yield (%) and reduced viscosity ( $[\eta]$ ) vs. molar fraction ( $\chi_B$ ) of methyl derivatives in the comonomer mixture.

Catalyst: tetramethylammonium cation salts of substituted lactams (8.0 mole %); initiator: *N*-acetyl 2-pyrrolidone (2.0 mole %); temperature 20°C; polymerization time 96 hrs.

□ ■ 3-Methyl; △ ▲ 4-methyl;  
○ ● 5-methyl.

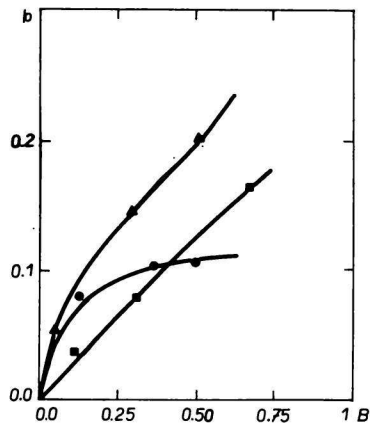


Fig. 2. Molar fraction of methylated units in copolymer ( $b$ ) vs. the initial molar fraction ( $B$ ) for copolymerization.

Catalyst: potassium cation salts of substituted lactams (8.0 mole %); initiator: *N*-acetyl 2-pyrrolidone (2.0 mole %); temperature 20°C; polymerization time 96 hrs.

■ 3-Methyl; ▲ 4-methyl; ● 5-methyl.

### Incorporation of the methylated units in copolymers

The composition of copolymers was determined by nuclear magnetic resonance [17]. The reactivity of different monomers may be classified as a function of incorporation ratio of the monomers in the copolymer (Fig. 2). The polymerizabilities of 3- and 5-methyl 2-pyrrolidone are similarly low but that of

4-methyl 2-pyrrolidone is somewhat higher. These curves, always situated under  $y = x$  line confirm the decrease of the reactivity effected by substitution on the cycle and the difficulty of homopolymerization.

The catalytic activity order as a function of incorporation ratio is different from the kinetic order: for 3- or 5-substituted derivatives the potassium cation catalysts lead to a higher ratio but for the 4-methyl 2-pyrrolidone, the incorporation ratio is similar whatever the counter-ion is.

The study of reactivity ratios,  $r_1$  and  $r_2$ , calculated from incorporation ratio data, points out the low polymerizability of the substituted monomers and the selectivity towards the incorporation of these units according to the nature of the cation catalyst [17, 18].

### Thermal properties of copolymers

#### Transitions

The transitions represent possibilities of chain movements and are related to the rigidity of the chain: for nylons, the rigidity depends on the network formed by hydrogen bonds.

Polyamides show two transitions:

- The first one, at about 0°C, is given by the methylenic links.
- The second one is the glass transition and varies from 40 to 75°C.

In the case of non-substituted polybutanamide, the glass transition is generally screened by a crystallization which occurs just after the first transition. For copolymers, we observed always the glass transition followed by a sharp crystallization peak (Fig. 3).

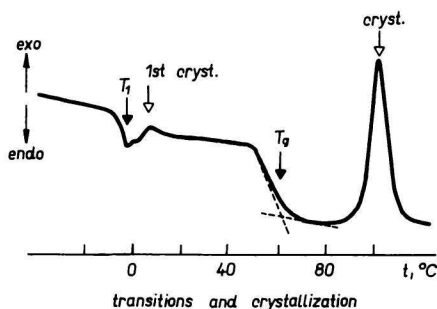


Fig. 3. A representative thermogram of melted and quenched copolymer sample as a function of temperature (heating rate 20°C/min; under  $N_2$ ).

Copolymer of 2-pyrrolidone and 4-methyl 2-pyrrolidone, obtained by polymerization with tetramethylammonium salt of 2-pyrrolidone (8 mole %) and *N*-acetyl 2-pyrrolidone (2 mole %).

The glass transition temperature increases with molecular weight up to a level for samples with reduced viscosity higher than 0.7—0.8 (Fig. 4). Fig. 5 shows the same variation of glass transition temperature vs. incorporation ratio for copolymers of different molecular weight: the shorter is the chain, the more pronounced is the bending of respective curves.

#### Melting points and degradation

The melting points of nylon 4 vary from 250 to 270°C according to the mean degree of polymerization (reduced viscosity between 0.1 and 8) [19].

The same is valid for copolymers; therefore it is necessary to compare copolymers having similar molecular weight.

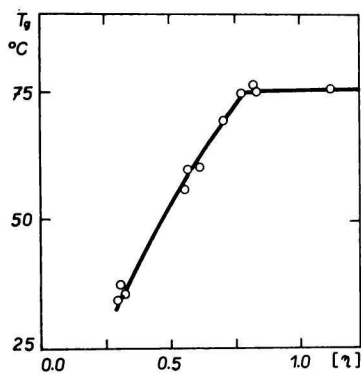


Fig. 4. Glass transition temperature ( $T_g$ ) vs. reduced viscosity ( $[\eta]$ ) of copolymer samples with an incorporation ratio  $0.05 < b < 0.06$  for the copolymers of 2-pyrrolidone with 3-, 4-, and 5-methyl 2-pyrrolidones, obtained with various catalysts.

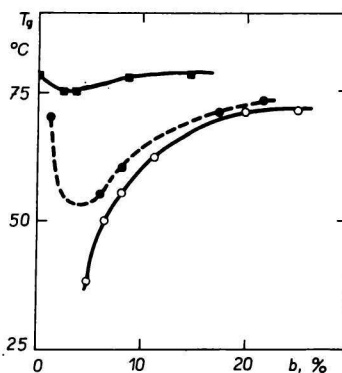


Fig. 5. Glass transition temperature ( $T_g$ ) vs. incorporation ratio ( $b$ ) for various reduced viscosities of copolymers of 2-pyrrolidone with 3-, 4-, and 5-methyl 2-pyrrolidones, obtained with various catalysts.

Viscosity: ■ >0.8; ● 0.5—0.6; ○ 0.03.

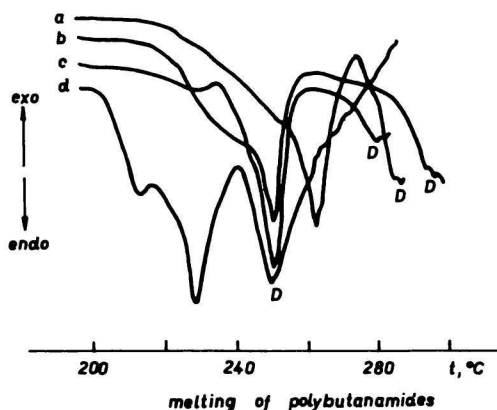


Fig. 6. Representative thermograms of polybutanamides samples having no thermal history (reduced viscosity 0.55).

a) Nylon 4 prepared with sodium cation catalyst; b) 5-methyl pyrrolidone copolymer prepared with tetramethylammonium cation catalyst; c) 3-methyl pyrrolidone copolymer prepared with potassium cation catalyst; d) 4-methyl pyrrolidone copolymer prepared with sodium cation catalyst.

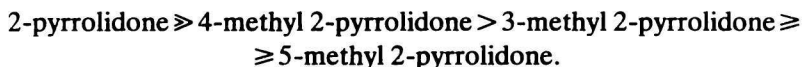
D = degradation.

The melting points of copolymers are generally below those of polybutanamide (Fig. 6), however, the influence of the incorporation ratio of methylated units does not seem to be appreciable. On the other hand, the nature of the used catalyst affects the course of the melting curves (Fig. 6). The thermogram of polymers shows that:

- Copolymers obtained with small cation ( $\text{Li}^+$  and  $\text{Na}^+$ ) catalysts have always several melting peaks, the degradation occurring immediately after melting.
- Copolymers of 3- or 5-substituted derivatives obtained with bulky cation ( $\text{K}^+$  and  $\text{Me}_4\text{N}^+$ ) catalysts generally give a single melting peak and a degradation temperature is higher by at least  $30^\circ\text{C}$ .
- Copolymers of 4-substituted lactam obtained with these bulky catalyst cations especially tetramethylammonium, as well as the copolymers obtained from a mixture containing higher ratio of methylated monomer give similar diagrams to those obtained with smaller cation.

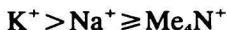
### Discussion

The non-copolymerizability of the methyl derivatives could indicate the prevention of ring opening by a substituent. In addition, these derivatives might be considered as true inhibitors of reaction since their presence appreciably modifies the polymerizability of 2-pyrrolidone; indeed a mixture with a large molar fraction of the substituted monomers does not afford the precipitation of the polybutanamide contrary to the case of 2-pyrrolidone polymerization in a solvent. The presence of methylated units in copolymers [17] indicates that the methyl substituent on the pyrrolidone cycle does not prevent the ring opening but merely decreases the reactivity of the studied lactams [10]. Besides, the same polymerizability order for the different monomers was determined both from the kinetic results and the incorporation ratio data:



On the other hand, the observed differences in catalytic activity of respective monomers give information on the selectivity by which the catalysts incorporate the methylated units [17, 18]:

- When the monomer polymerizability is very low (3- or 5-substituted derivatives) then the incorporation ratio depends mainly on the nature of the catalyst cation



The tetramethylammonium cation appears to be selective because of its large activity towards the pyrrolidone anion, while the sodium cation seems to be selective because of its low activity especially towards the methyl pyrrolidone anion.

- When the monomer reactivity is higher (4-methyl 2-pyrrolidone) the incorporation is independent of the cation nature contrary to the yield and molecular weight (kinetic results).

From these data it cannot be concluded whether methylated units are incorporated in polybutanamide chain or attached to its extremity. We calculated therefore

the average number of substituted units per chain from the molecular weight (obtained from the viscosity data [20]\*) and the incorporation ratio.

For 3- or 5-substituted derivatives, the resulting copolymers seem to have less than two methylated units per chain, except copolymers obtained with the potassium cation catalyst. This fact, together with the decrease of the molecular weight and the yield with the increase of starting molar fraction of the substituted derivative, may indicate a chain termination by methylated unit.

For 4-substituted monomer, its relatively high reactivity would lead to the formation of true statistical copolymers when sodium and lithium are used as catalyst cations. Meanwhile, low molecular weight and high yield were obtained with a bulky, especially tetramethylammonium, cation catalyst. This may indicate a possibility that transfer reaction takes place when a methylated unit is incorporated at the chain end. It might be due to the high activity of this type of catalyst [13].

The study of thermal properties of our copolymers allowed us to obtain further information concerning their structure. The fact that a glass transition followed by a pronounced crystallization is always observed much more easily than in the case of polybutanamide\*\* suggests that the presence of methylated units in the chain disorders more or less the structure of the polymer preventing the crystallization before the rearrangement of hydrogen bonds.

When the incorporation ratio is lower than 2%, the copolymer behaves in the same way as nylon 4, *i.e.*  $T_g \approx 75^\circ\text{C}$ . When the methylated unit incorporation increases, the rearrangement of hydrogen bonds might be facilitated because of the structural perturbations caused by these units: the shorter the chain, the more pronounced are the perturbations.

Glass transition temperatures do not manifest any cation effect but depend only on incorporation ratio. However, these results confirming the incorporation data do not allow to conclude on the copolymer structure contrary to the melting and degradation results.

Melting depends on the size of crystalline phase and the degradation is mainly function of chain ends: methylated unit, more cyclizable, recycles at lower temperature than pyrrolidone unit.

Multiple melting peaks and low incorporation ratios (except 4-methyl 2-pyrrolidone) observed in the case of copolymers obtained by catalysis with small cations ( $\text{Li}^+$  and  $\text{Na}^+$ ) allow to suggest imperfections [21] of the structure caused by frequent terminations by methylated unit, leading to a high polymolecularity.

The fact that copolymers with a high transfer (*i.e.* 4-methyl 2-pyrrolidone with

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\* A viscosimetric formula,  $[\eta] = 4.25 \times 10^{-3} M^{0.586}$ , was established by conductometric titration of the terminal carboxylic groups in trifluoroethanol. We utilized this formula though it is demonstrated for polybutanamide and for intrinsic viscosities  $[\eta]$  higher than 0.75.

\*\* The same phenomenon was observed with polybutanamide at a heating rate  $50^\circ\text{C}/\text{min}$  [18, 19].

tetramethylammonium cation catalyst) and those obtained from the mixture with a large molar fraction of substituted monomer melt at similar temperatures and that the degradation takes place immediately after melting is completed confirms the hypothesis of higher content of methylated units at the chain end.

These units seem to promote the transfer reaction during polymerization on account of the difficulty to open the substituted rings. They also facilitate the degradation on heating since easy recyclization of the methylated end unit initiates this reaction.

These results allow to show the important role played by the catalyst cation in order to obtain true statistical copolymers:

— With small cations ( $\text{Li}^+$  and  $\text{Na}^+$ ): The catalytic activity is too low, the resulting copolymers have methylated units at chain ends and the incorporation ratio is low except for 4-substituted derivative copolymers which are true copolymers.

— With bulky cations ( $\text{Me}_4\text{N}^+$ ): Statistical copolymers are obtained for 3- or 5-substituted derivative copolymers while for 4-substituted monomer the resulting low copolymers are identical with those obtained with small cations (3- or 5-substituted).

— With the potassium cation: Regardless the methylated comonomer they have higher incorporation ratios and are true copolymers.

## Conclusion

The presumptions concerning the copolymer composition as forwarded by the previous study of incorporation ratio, are confirmed by the arguments drawn from the analysis of thermal properties: a true random copolymerization of 2-pyrrolidone with its C-methyl derivatives is obtained with the potassium cation catalyst.

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