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72. Limit Temperature of the Anionic Polymerization of 2-Pyrrolidone

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Summary

The following limit (ceiling) temperatures of polymerization were extrapolated from kinetic data for the anionic polymerization of 2-pyrrolidone initiated with potassium salt of 2-pyrrolidone and the initiation systems of optimum compositions: ≈ 66°C for the nonactivated polymerization, ≈ 68°C and ≈ 73°C for the polymerization accelerated with 1-(1-pyrrolin-2-yl)-2-pyrrolidone and carbon dioxide, respectively, ≈ 73°C and ≈ 76°C for the polymerization activated with N-benzoyl-2-pyrrolidone and N-acetyl-2-pyrrolidone,respectively.

Introduction

An anionic polymerization of the five-membered lactam 2-pyrrolidone (PD) renders poly(2-pyrrolidone) (PPD) - Nylon 4, which is predetermined as a textile material with respect to its pronounced hydrophilicity (1). The polymerization mechanism is similar as for higher lactams (2). Lactam anions have to be present in the system and form, by the reaction with lactam, N-acyllactam structures representing growth centres of the polyreaction. The formed polymer is insoluble in monomer at temperature employed for the polymerization. The propagation is accompanied by the separation of a partially crystalline PPD (3), so that the so called nonactivated polymerization proceeds heterogeneously, Among the known compounds, which accelerate the nonactivated polymerization , belongs above all carbon dioxide (4). Some N-iminolactams have the more pronounced acceleration effect (5), while the kinetic character of the process remain the same in all cases, i.e. the polymerization exhibits a formal kinetics of zero order. If the preformed growth centres are introduced into the polymerization system as so called activators, the polymerization is also pronouncedly accelerated. Concerning the high initial concentration of growth centres, the activated polymerization has a very fast but short initial homogeneous phase (few minutes at utmost) (6). This phase is followed by the heterogeneous phase, where the polymerization rate is similar as in the nonactivated polymerization.

The optimum temperature of polymerization ranges between 40 and 50°C for all initiation systems. PPD cannot be prepared already above 80°C and this temperature can be considered the limit temperature of polymerization process. It is not significant as the thermodynamic ceiling temperature, because the polymerization of PD cannot be characterized as an equilibrium polyreaction, above all due to the irreversible crystallization of PPD during polymerization. Consequently, the polymerizability of PD is determined by both kinetic and chemical factors. Therefore, we tried to determine the limit polymerization temperature (T_l) by a kinetic method.

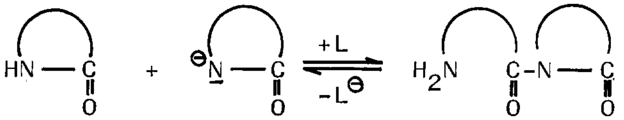
Results and Discussion

Provided that the limit polymerization temperature (T_l) is determined preferentially by kinetic factors, it should considerably depend on the type and composition of initiation system. Therefore, we determined T_l for all fundamental ways of transformation 2-pyrrolidone (PD) to the polymer (cf. Introduction).

All studied initiation systems were used in the previously found optimum concentrations (4,7,8,9) and the separately prepared potassium salt of 2-pyrrolidone (KPD) served as an initiator in all cases.

The values T_l were determined from the conversion-temperature plots obtained by both gravimetric and chromatographic analyses, where the chromatographic data are more realistic, but exhibit larger errors. The conversions at the longest studied polymerization time, 72 h, were used for extrapolations. Evaluation of the limit (pseudoequilibrium) conversions would be more accurate, but it is unjustifiable for time reasons. Also apparent rate constants cannot be used for extrapolations, because the conversion (and also viscosity) dependences unexpectedly change their course near T_l (10).

The extrapolations are summarized in Fig. 1. The lowest limit temperature, $T_l \approx 66^{o}C$, from all studied systems exhibits the nonactivated polymerization (KPD $\approx$ 3 mol-%). The growth centres are formed in this polyreaction (2) by a slow reaction /1/ followed by a fast propagation /2/, where L is the abbreviation for PD molecule



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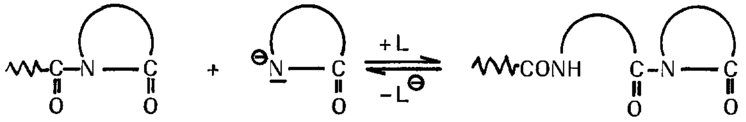

/2/

Cesation of the polymerization above T_l can be then explained by prevailing reverse reaction, i.e. aminolysis of growth centres, both inter and intramolecular, and a base catalysed depolymerization of the polymer. We rather prefer the explanation by ceasing formation of growth centres, because depolymerization is manifested at higher temperature. The effect of crystallization and separation of poly(2-pyrrolidone) (PPD)

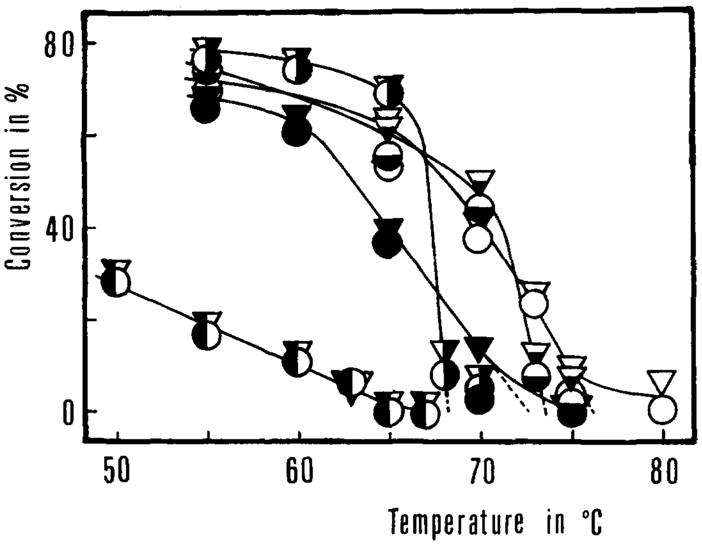

Fig.1 Dependence of the conversion attained after 72 h determined gravimetrically (circles) and by GLC (triangles), on temperature in the polymerization of 2-pyrrolidone initiated with 3 mol-% potassium salt of 2-pyrrolidone (KPD) (◐,▼), 3 mol-% KPD and 1 mol-% 1-(1-pyrrolin-2-yl)-2-pyrrolidone (◑,▼), 5 mol-% KPD and 1 mol-% CO_2 (●,▼), 3 mol-% KPD and 1 mol-% N-acetyl-2-pyrrolidone (○,▽), 3 mol-% KPD and 1 mol-% N-benzoyl-2-pyrrolidone (◒,▽)

during polymerization should be stressed, but this effect has been little investigated so far. It may be supposed that, because the above mentioned reverse reactions do not allow the polymer chains to grow to the length suitable for the formation of a crystallization nucleus, the prevented separation of PPD from the polymerization mixture contributes to the cesation of polymerization. Certainly, the degradation reaction is slowed down in the presence of solid PPD (a heterogeneous mechanism).

Importance of the semicrystalline PPD occuring in polymerization mixture follows from the fact that the conversion grows also above T_1 in the polymerization active and heterogeneous system prepared below T_1 (10).

If the nonactivated polymerization of PD (5 mol-% KPD) is accelerated with CO_2 (1 mol-%), which forms a low-soluble carboxylate of 2-pyrrolidone (4), the kinetic data reveal an increase of T_1 to 73°C. Because the carboxylate is assumed to control acidobasic equilibria (4), it has probably a positive effect both on the formation of growth centres (initiation) and propagation; the polymerization rate and also degree of polymerization are higher in comparison with the nonactivated polymerization (4). Thus, regarding the controling role of the carboxylate, or considering the carboxylate the precursor of growth centres, and supposing that its insoluble parts may act as crystallization nuclei, the increase in T_l by 7°C in comparison with the nonactivated polymerization becomes logical.

A different situation occurs with the most efficient accelerators of the nonactivated polymerization - N-iminolac - tams (5), in this case with 1 mol-% 1-(1-pyrrolin-2-yl)-2-pyrrolidone (PDPD) used with 3 mol-% KPD, where the highest reported rate of the anionic polymerization of PD is attained. PDPD probably participates very intensely in the initiation (the polymerization rate is higher by an order of magnitude in comparison with the nonactivated polymerization, while the molecular mass is low), which is very sensitive to temperature (cf. the nonactivated polymerization) and therefore $T_l \approx$ 68°C is virtually identical with the nonactivated polymerization.

If the preformed growth centres are added to the system, T_l increases. The value $T_l \approx 73^{o}C$ was extrapolated for 1 mol-% N-benzoyl-2-pyrrolidone, which is similar to T_l for potassium carboxylate (is the carboxylate, after all, a growth centre?), and $T_l \approx 76^{o}C$ was found for the same concentration of N-acetyl-2-pyrrolidone. The concentration of KPD was always 3 mol-%. Aminolysis of the added growth centres /1/ is not significant, because the concentration of amine groups is low. The depolymerization reaction does not manage to destroy the polymer, which grows very rapidly on the present growth centres and attains the length required for the formation of crystallization nuclei. The separated PPD depolymerizes more slowly and therefore T_l increases. Another possible function of the N-acyllactam centres cannot be omitted, basicity of the system is greatly changed by their addition (2), which affects most of reversible and irreversible processes in the polymerization mixture. The condensation reactions of N-acyllactam structures yield highly acidic β-ketoimide (N-acyl-β-ketoamide) structures (11).

The found dependence of T_l on the type of initiation system shows that kinetic effects pronouncedly determine the position of "ceiling" temperature in the anionic polymerization of PD.

Experimental

Purification of 2-pyrrolidone (PD) (4), the separate preparation of potassium salt of 2-pyrrolidone (KPD) from potassium tert.butoxide and PD in THF (12), and the syntheses of N-benzoyl-2-pyrrolidone (m.p. 91°C) (13), N-acetyl-2-pyrrolidone (b.p. 94°C/400 Pa) (13), and 1-(1-pyrrolin-2-yl)-2-pyrrolidone (8) were described elsewhere. The purity of all compounds was > 99.9% as checked by GLC.

Polymerizations were carried out under strictly isothermic conditions; KPD was dissolved in PD at the chosen polymerization temperature and mixed with the thermostated PD solutions of accelerating compounds in mixing ampoules, according to the procedure described for CO_2 (4).

Gravimetric and chromatographic conversions (using a methanolic extract for GLC) were determined as described in (4); intrinsic viscosity of PPD was measured in tricresol (14).

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