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Living Polymerization of Lactams and Synthesis of Monodisperse Polyamides

J. Šebenda and J. Hauer

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
162 06 Prague, Czechoslovakia

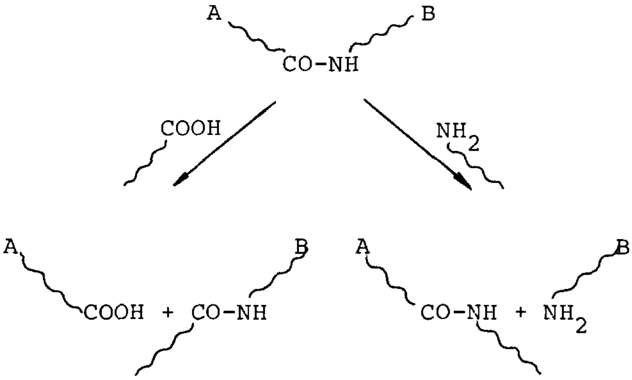
Dedicated to Prof. Dragutin Fleš on the occasion of his 60th birthday

SUMMARY

For the first time, a living lactam polymerization was proved by choosing the proper type of polymerization, lactam, growth center as well as initiator. The anionic polymerization of the disubstituted four-membered lactam (I) initiated with its lithium salt in the presence of the N-pivaloyl derivative of I acting as the growth center yielded almost monodisperse polymers of I. Subsequent additions of monomer I increased the molecular weight proportionally without appreciable changes of the MWD and number of polymer molecules.

INTRODUCTION

Although growth centers retain the ability to add lactam units for unlimited periods in hydrolytic, acidolytic and aminolytic lactam polymerizations, these cannot be considered as living polymerizations. All kinds of lactam polymerizations proceed via transamidation reactions involving various activated species (ŠEBENDA, 1972). The same type of reaction breaking the lactam amide group proceeds also at polymer amide groups and leads to a statistical MWD; e.g., in acidolytic, aminolytic, cationic and hydrolytic polymerizations:



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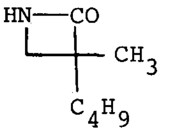
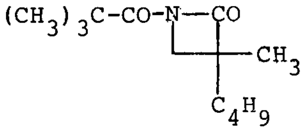
Due to the reversibility of the polymerization reaction, redistribution proceeds with all lactams also via elimination of lactam or cyclic oligomers.

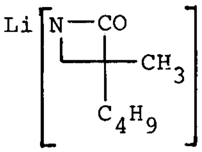
In order to meet one of the most important criteria of living polymerization, the rate of polymerization must be very much higher than the rate of the exchange and depolymerization reactions. These conditions could be fulfilled best with four-membered lactams. Since almost all kinds of lactam polymerizations are accompanied by side reactions changing the number of polymer molecules, one has to select carefully both the polymerization mechanism and the lactam structure. Acidolytic, aminolytic and hydrolytic polymerizations of four-membered lactams require rather high temperatures at which side reactions and/or changes of the number of polymer molecules cannot be avoided (BESTIAN, 1968). The only chance consists in the low-temperature anionic polymerization provided that the side reactions starting at the carbon atom next to the carbonyl group are prevented by using disubstituted lactam (I) and growth centers (II) as well as lithium lactamate (III) derived from disubstituted lactam I:



(I)



(II)



(III)

EXPERIMENTAL

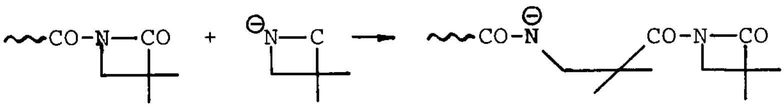
Materials. Lactam I and activator II were synthetized as described previously (ŠEBENDA et al., 1976). All solvents were dried by refluxing with $LiAlH_4$.

Polymerization. The course of polymerization was followed by the diferential calorimetric method (LUECK et.al., 1963). To a solution of I and II in THF ($7cm^3$) a 0.1 resp. 1M solution of butyl lithium in heptane was added by means of a microsyringe heated to the polymerization temperature (300 K); the temperature difference between the pure solvent and polymerization mixture was measured with a copper-constantan thermocouple and recorded after amplification with a Keithley 150B Microvolt Ammeter. After chosen periods, a sample of the reaction product was withdrawn with a syringe and neutralized with a THF solution of boric acid and then a new portion of monomer solution was added to the living polymerization mixture. Finally, the polymerization was killed by the addition of a slight excess of boric acid. Reaction conditions are summarized in Table I. All operations were carried out under dry argon in a vacuum dried equipment.

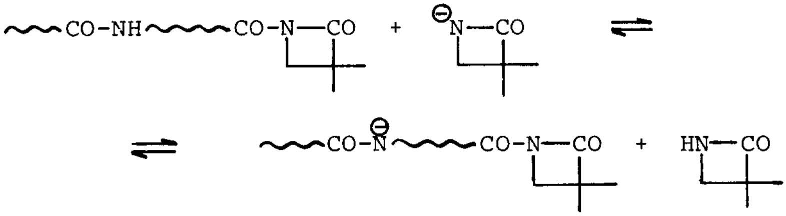
Analytical methods. The monomer content in neutralized samples was determined by GLC. The polymer was separated by evaporation of the solvent, dissolution in benzene, extraction with water and freeze-drying. Molecular weights were measured by GPC (TUZAR et al., to be published) on silanized porous glass (75, 120 and 240Å).

RESULTS AND DISCUSSION

With increasing conversion, the polymerization reaction



should be gradually slowed down because polymer amide groups entering into the equilibrium



decrease the concentration of lactam anions required for the chain growth reaction. Therefore, the initial rate of polymerization should generally differ in systems containing the same concentration of lactam I but differing in concentrations of the polymer. Hence, after addition of new monomer an equal course of polymerization observed after subsequent additions of monomer (ŠEBENDA and HAUER, 1980) cannot be regarded as a criterion of living polymerization.

For this special case of lactam polymerization, the most important criteria are a narrow MWD and a constant number of polymer molecules which should equal the initial amount of added growth centers. Fig.1 demonstrates that monodisperse polymers are obtained under the chosen reaction conditions. The molecular weight of polymers is very close to the theoretical value (Fig. 2) calculated from the equation

$$M_c = M_A + M_L(L_o - L)/A_o$$

where M_L is the molecular weight of the monomer unit, $(L_o - L)$ is the amount of consumed lactam, A_o is the amount of added growth centers and M_A is the molecular weight of the growth center.

It has to be stressed that a narrow MWD as well as agreement between the experimental and calculated molecular weights can be expected only for short reaction periods. After exhaustion of all the monomer, growth centers can react with less reactive anions of polymer amide groups, thus decreasing the number of polymer molecules and leading to branched products and a broader MWD:

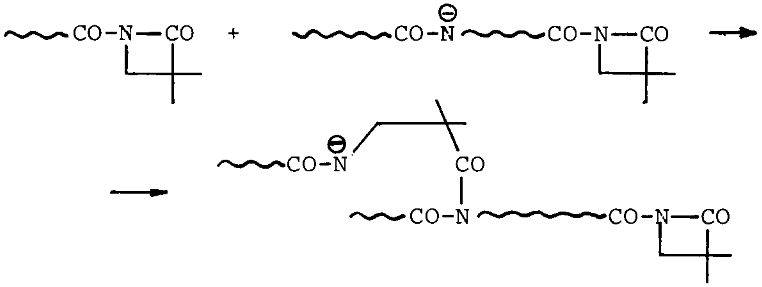


TABLE I

Polymerization of lactam I in THF at 27°C

L_o (resp. A_o and I_o) are initial concentrations (in mmol/kg) of lactam 1 (resp. growth centers II and lactamate III); in parentheses, concentrations calculated after addition of a new portion of lactam solution to a living reaction mixture are given; a new portion of I was added 5 min after the exhaustion of monomer I.

Sample	L_o	A_o	I_o	t^a, min
A1	73.7	4.75	3.82	10
A2	(68.3)	(4.59)	(3.69)	34
A3	(61.7)	(4.47)	(3.59)	54
B1	538.4	10.87	1.12	30
B2	(423.8)	(9.47)	(0.97)	100
B3	(452.0)	(8.17)	(0.84)	220
C	682.9	6.55	1.35	42
D	564.3	6.13	0.42	117

[a] Time from the addition of butyl lithium to the moment of neutralization of the given sample; all polymerization were stopped at100% conversion, except sample B3 (93%).

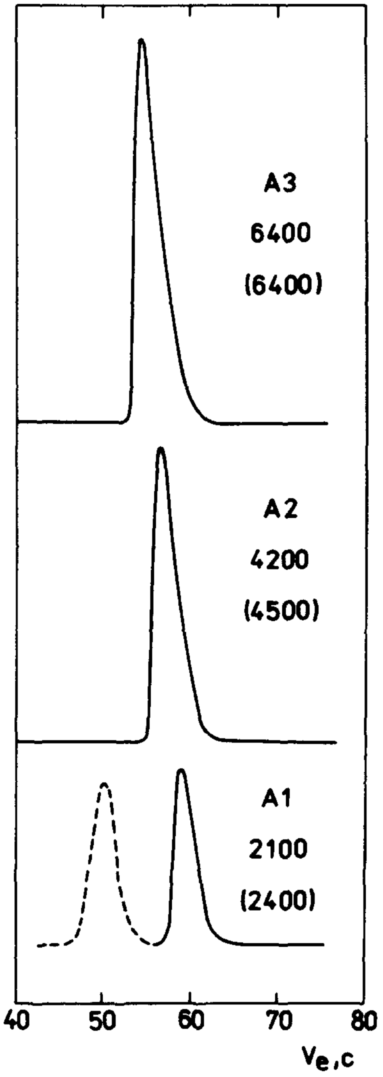
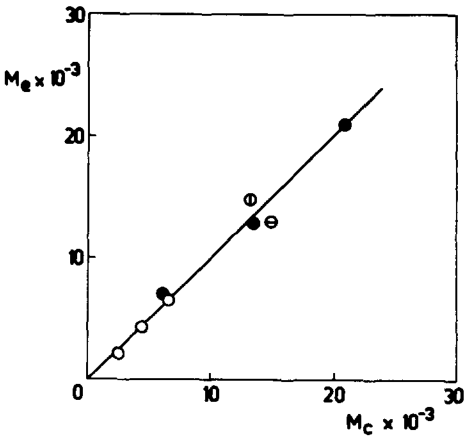


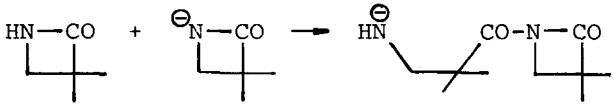
Fig.1
GP-chromatograms of samples A1 - A3.
Numbers indicate the molecular weight of the peak, numbers in parentheses are the calculated values of M_c. The dotted line represents monodisperse polystyrene with M = 8900.

Fig.2
Molecular weights from GPC (M_e)vs. calculated values (M_c).
Samples: ○ A1 - A3, ● B1 - B3, ⦶ C, ⊖ D.



Side reactions proceeding via dipole stabilized anions (BEAK and REITZ, 1978) cannot be excluded either.

As long as the lactam is present, new growth centers are formed by disproportionation:



Although this reaction is very much slower than chain growth, it may cause a broadening of the MWD.

In order to suppress the effect of all these reactions, it is recommended to work at low temperature and to use low concentrations of lactamate.

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