

ALKALINE POLYMERIZATION OF 6-CAPROLACTAM. II.*

EFFECT OF THE ACTIVATOR/INITIATOR RATIO ON THE MOLECULAR WEIGHT DISTRIBUTION

M. KAPUŚCIŃSKA^a, E. ŠITTLER^{b*} and J. ŠEBENDA^b

^a *Institute of Synthetic Fibers, Technical University, Łódź, Poland and*

^b *Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06, Prague 6*

Received February 6th, 1973

In anionic polymerizations with a high activator/initiator ratio, most of the strong base is consumed in side reactions very quickly already during the polymerization so that the re-equilibration with respect to chain length is substantially slowed down. Therefore, the molecular weight distribution at the end of polymerization is fairly narrow ($\bar{M}_w/\bar{M}_n \approx 1.2$) and only small changes in the molecular weight distribution occur during extended heating. On the other hand, large variations of the molecular weight distribution occur in polymers prepared with equimolar amounts of initiator and activator. Due to the fact that the strong base survives much longer, new polymer molecules are formed by disproportionation reactions both during polymerization and after the attainment of the monomer-polymer equilibrium. After very long heating periods, crosslinking reactions predominate and increase the amount of the high molecular weight fraction.

The intrinsic viscosity of anionic caprolactam polymers is a complicated function of the reaction conditions, namely the concentration of catalytic components (initiator and activator), time and temperature¹⁻⁷. Viscosity changes occurring in anionic polymers can be attributed to changes in the molecular weight distribution, to the formation of new polymer molecules by disproportionation and to the decrease in the number of polymer molecules by condensation reactions. The complex set of these reactions finally leads to a stable viscosity depending mainly on the initial concentration of active base¹⁻⁵.

Gechele and Stea⁸ found that anionic caprolactam polymers prepared below the melting temperature of the polymer have a fairly narrow molecular weight distribution and observed a progressive broadening of the latter during extended heating at 220°C. The broadening is supposed to be due both to transamidation and branching⁸. On the other hand, Králíček and coworkers³ observed that the initially broad molecular weight distribution is getting narrower after extended periods of heating at 250°C and slowly approaches a Flory-Schulz distribution. So far, however, no values of the \bar{M}_w/\bar{M}_n ratio were reported for anionic polymers.

Recently it was found^{6,7} that at a given temperature the viscosity changes are governed mainly by the initiator concentration and therefore, it is of great interest to decide whether the changes of intrinsic viscosity are due to the changing number

* Part XLVIII: This Journal 38, 2274 (1973).

* Present address: Silon, Planá n. Luž., Czechoslovakia.

of polymer molecules or molecular weight distribution. It is the scope of the present work to study the effect of the activator/initiator ratio on the changes of the molecular weight distribution of anionic caprolactam polymers. In order to correlate the changes of viscosity, molecular weight distribution and number of polymer molecules, two different polymers were investigated: one "living" system (series A) in which the catalytically active base was expected to survive for a long period and one practically "dead" system (series B) in which virtually all active base is consumed in side reactions already during the first minutes. Although the polydispersity could be also estimated from light scattering (\overline{M}_w) and osmometric measurements (\overline{M}_n), the fractionation was preferred since the \overline{M}_w and \overline{M}_n values cannot be determined with a sufficient accuracy for low molecular weight polyamides.

RESULTS AND DISCUSSION

Fractionation

The most effective fractionation of polyamides has been achieved by the distribution of the polymer between two immiscible liquid phases^{9,10}. The problem of end group association during the fractionation of hydrolytic polymers has been circumvented either by the addition of acetic acid to the polymer solution¹¹ or by acylation of the amine groups prior to fractionation¹². In the present work, the problem of association during the fractionation is not as serious as for hydrolytic polymers, since anionic polymers usually do not contain equal concentrations of amine and carboxyl groups¹³, at which the effect of association is maximum. Therefore, the classical fractionation method suggested by Turska⁹ was used without any precautions to suppress association.

In the fractionation of anionic polymers, the significance of the results obtained is somewhat devalued by the fact that the polymers are slightly branched^{6,13} so that the macromolecules are separated not only according to their molecular weight. Gechele and coworkers¹⁴ found that in the mixture of a linear and a branched high molecular weight fraction, the branched one is much more soluble and can be eluted separately. However, this difference is strongly depressed in mixtures with low molecular weight fractions and in polydisperse polymers¹⁴. Hence it can be expected that the presence of branched molecules will not affect seriously the fractionation with respect to the molecular weight (without distinguishing linear and branched molecules). However, the presence of branched macromolecules leads to somewhat lower $\overline{M}_w/\overline{M}_n$ ratios.

The material lost during fractionation (2–5%) was added to the fractions proportionally to their weight. The integral distribution curves were constructed according to Schulz¹⁵ from plots of $(0.5 W_{i+1} + \sum W_i)$ vs (M_{i+1}) . The intrinsic viscosity in sulfuric acid ($[\eta]_a$) was calculated from a single viscosity measurement (at 0.25 g : 100 ml) using $k_H = 0.24$ (ref.¹³). In order to be able to apply the equation

$$\overline{M} = 2.52 \cdot 10^4 [\eta]_c^{1.342} \quad (1)$$

derived for fractions of anionic polymers in cresol¹⁶, the intrinsic viscosity in sulfuric acid was converted into the corresponding value in cresol ($[\eta]_c$) using data from ref.¹³:

$$[\eta]_c = 0.878[\eta]_a^{0.946} \quad (2)$$

Intrinsic viscosities were measured in sulfuric acid in which the extent of end group association is much lower than in cresol¹¹. The molecular weights of fraction 1 of sample B-1 and fraction 1 of sample B-3 were checked by osmometry in *m*-cresol at 60°C (Hewlett-Packard instrument). The osmometric values (13400 and 24400) agree with those calculated from Eqs (1) and (2) (14600 and 25800).

Although one could draw even bimodal differential distribution curves from some fractionation data (sample B-2 in Fig. 1), curves with one maximum seem to be more justified with respect to the limited number of fractions and their unequal weight (Fig. 2–5).

Molecular Weight Distribution in Anionic Polymers

The chain growth in anionic caprolactam polymerizations proceeds very much faster than the formation of new growth centers by disproportionation. When the concentration of growth centers at the beginning of polymerization is comparable with that of the lactam salt, the formation of new growth centers is negligible. In addition, the redistribution through depolymerization is ten times slower than the chain growth and the anionic transacylation between macromolecules is not too much faster than the polymerization. Therefore, the molecular weight distribution at the end of poly-

TABLE I

Characterization of Polymers

Catalyst: sodium caprolactam and N-butyrylcaprolactam (0.30 and 0.30 mol. %, resp., in series A; 0.10 and 0.28 mol. %, resp., in series B).

Sample	Time min	Yield %	$[\eta]_a$ dl/g	$\frac{\bar{M}_w^a}{\bar{M}_n}$	Sample	Time min	Yield %	$[\eta]_a$ dl/g	$\frac{\bar{M}_w^a}{\bar{M}_n}$
A-1	5.5	90.8	2.21	1.35	B-1 ^b	3	67.0	2.06	1.16
A-2	30	90.6	2.35	1.02	B-2	5	72.3	2.01	1.16
A-3	600	91.0	1.21	1.34	B-3	30	85.1	2.23	1.17
A-4	1 800	91.6	1.36	1.25	B-4	120	90.4	2.13	1.16
A-5	6 800	91.4	1.34	1.09	B-5	600	91.0	2.23	1.21

^a $\bar{M}_w/\bar{M}_n = \Sigma W_i M_i / \Sigma (W_i/M_i)$. ^b Concentration of N-butyrylcaprolactam 0.30 instead of 0.28 mol %.

merization is fairly narrow (Table I) and is close to a Poisson distribution resulting from an irreversible chain growth at a given number of growth centers. The Flory-Schulz distribution can be attained only very slowly through a great number of transacylation reactions.

Distribution in "Dead" Polymers

It has been established⁷, that at temperatures above 200°C the catalytically active lactam and polymer amide anions disappear very quickly when the ratio of the initial concentrations of activator/initiator is higher than 2.5. As expected, only small changes of the molecular weight distribution occur during extended heating of such polymers since the active base has been consumed almost entirely already during the first minutes (Fig. 2 and 3). The extent of disproportionation reactions increasing the number of polymer molecules is very small (curve 2 in Fig. 6) and also the re-equilibration with respect to the length of polymer molecules proceeds only very slowly. As a result, the molecular weight distribution moves only slowly towards the most probable one (Fig. 2).

Molecular Weight Distribution in "Living" Polymers

It has to be pointed out that the term "living" does not refer to the growing end groups but to the active base which is present in these systems for longer periods than in the preceding ones. We have to bear in mind, however, that even in the "living" anionic caprolactam polymers, the concentration of the catalytically active base gradually decreases⁷.

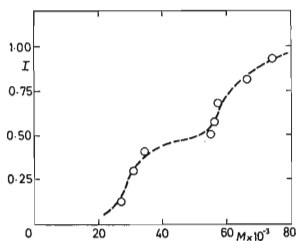


FIG. 1

Integral Distribution Curve of Sample B 2
Polymerization conditions are given in
Table I.

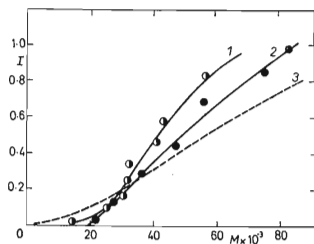
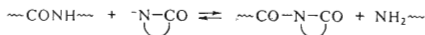


FIG. 2

Integral Distribution Curves of Samples
B 4 (1), B 5 (2), and the Flory-Schulz
Distribution for $M_n = 30000$ (3)

Changes in the "living" system (Fig. 4 and 5) are much more pronounced than in the "dead" one (Fig. 2 and 3). During the first hour, the molecular weight distribution is getting narrower (curves 1 and 2 on Fig. 4) and the low molecular weight portion is diminishing.

In the second period, the formation of new polymer molecules by disproportionation



shifts the curve to lower molecular weights without affecting appreciably the polydispersity (curve 3 on Fig. 4 and curve 1 on Fig. 5). This period is connected with the presence of the catalytically active lactam and polymer amide anions.

After very long heating periods, the strong base practically disappears and condensation reactions leading to branching and crosslinking start to predominate. As a result, the amount of the high molecular weight fraction increases (curve 2 on Fig. 5) and the formation of an insoluble gel fraction is becoming very probable.

Changes in the Number of Polymer Molecules

For reaction periods up to two hours, the number of polymer molecules formed per one added growth center (Fig. 6) is slightly higher (0.63–0.84) than the value 0.55 found under similar conditions earlier⁶. This could be due to the fact that in the latter case the molecular weight was calculated from the equation derived for a Flory-Schulz molecular weight distribution.

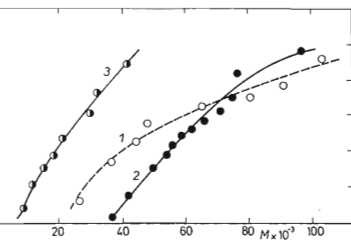
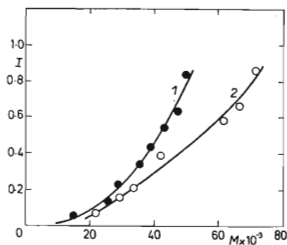


FIG. 3

Integral Distribution Curves of Samples B-1 (1) and B-3 (2)

FIG. 4

Integral Distribution Curves of Samples A-1 (1), A-2 (2) and A-3 (3)

Due to the very low concentration of active base the total number of polymer molecules in the "dead" system increased only very slightly (Fig. 6). In the "living" system, on the other hand, the strong base survived for a much longer period and increased the number of polymer molecules more than twofold during 30 h. Later, however, crosslinking reactions predominated and the number of polymer molecules sharply decreased (Fig. 6), although the intrinsic viscosity remained fairly constant (Table I). Hence, the constant viscosity attained after very long heating periods²⁻⁴ only pretends a constant number of molecules. The actual situation in such polymers can be described only in terms of molecular weight distribution.

EXPERIMENTAL

Polymers. In a solution of 0.2 (or 0.6) mmol of sodium caprolactam¹⁷ in 0.2 mol of dry caprolactam was dissolved 0.6 mmol of N-butylcaprolactam¹⁸ at 80°C. Then the reaction vessel (17 mm i.d.) with the reaction mixture was immersed in a thermostated salt bath ($220 \pm 0.3^\circ\text{C}$) for periods indicated in Table I. Filings of the polymer were extracted with boiling water (3×100 ml/g polymer) and dried at $50^\circ\text{C}/20$ Torr.

Fractionation. The extracted polymers (4 g) were dissolved in 200 ml of phenol-tetrachloroethane (1 : 1 w/w) and then heptane was added in such an amount as to precipitate about 50% of the polymer. Each fraction was then redivided into two until 8 or 12 fractions were obtained. The required amounts of precipitant were determined in preliminary tests. After each addition of n-heptane, the turbid mixture was stirred for 4 hours at 25°C and then left standing for the

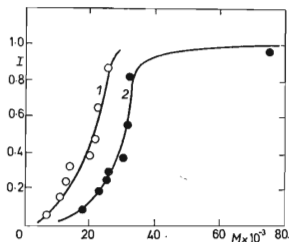


FIG. 5

Integral Distribution Curves of Samples A-4 1 and A-5 2

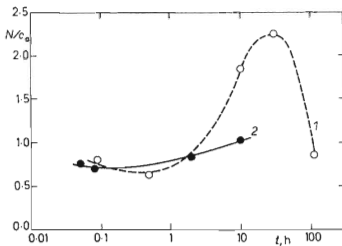


FIG. 6

Number of Polymer Molecules formed per One Added Growth Center (N/c_a) in Polymers of Series A (1) and B (2)

$N = 10 p \Sigma_i (w_i/M_i)$; c_a is the initial activator concentration (in mol/kg) and p yield of polymer (in %).

separation into two clear liquid phases. The lower one was then isolated, the polymer was precipitated, washed with ethanol and extracted 8 hours in a Soxhlet apparatus with ethanol, filtered off and dried *in vacuo* at 60°C to a constant weight.

Viscosity measurements. The viscosities of 0.25% (w/v) solutions of the polymers in 96% sulfuric acid were measured in Ubbelohde viscometers at 25°C.

We thank Dr C. V. Goebel, The Polymer Corporation, for the osmometric determination of molecular weights.

REFERENCES

1. Griehl W., Schaaf S.: *Makromol. Chem.* 32, 170 (1959).
2. Králíček J., Šebenda J.: *J. Polymer Sci.* 30, 493 (1959).
3. Králíček J., Červený L., Zimmer L.: *Sborník Vysoké školy chemicko-technologické, Praha, Org. Chem. and Technol. C* 9, 5 (1966).
4. Gechele G. B., Stea G.: *European Polymer J.* 1, 91 (1965).
5. Gechele G. B., Martinis G.: *J. Appl. Polymer Sci.* 9, 2939 (1965).
6. Šebenda J., Kouřil V.: *European Polymer J.* 7, 1963 (1971).
7. Šebenda J., Kouřil V.: *European Polymer J.* 8, 437 (1972).
8. Stea G., Gechele G. B.: *European Polymer J.* 1, 213 (1965).
9. Turska E., Matuszewska-Czerwik J.: *Polimery* 8, 13 (1963).
10. Biernacki P., Chrzczonowicz S., Włodarszyk M.: *European Polymer J.* 7, 739 (1971).
11. Králíček J., Maroušek V.: *Sborník Vysoké školy chemicko-technologické, Praha, Org. Chem. and Technol.*, in press.
12. Raffler G., Reinisch G.: *Angew. Makromol. Chem.* 29, 57 (1971).
13. Goebel C. V., Čefelín P., Stehlíček J., Šebenda J.: *J. Polymer Sci. A-1*, 1411 (1972).
14. Mattiussi M., Manescalchi F., Gechele G. B.: *European Polymer J.* 5, 105 (1969).
15. Schulz G. V.: *Z. Physik. Chem. (Frankfurt) B* 47, 155 (1940).
16. Tuzar Z., Kratochvíl P., Bohdanecký M.: *J. Polymer Sci. C* 16, 633 (1967).
17. Čefelín P., Šebenda J.: *This Journal* 26, 3028 (1961).
18. Šebenda J., Stehlíček J.: *This Journal* 28, 2731 (1963).