PREPARATION AND POLYMERIZATION OF α,α-DIMETHYL-ε-CAPROLACTAM*

J.Stehlíček, P.Čefelín and J.Šebenda

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

Received July 13th, 1973

α,α-Dimethyl-ε-caprolactam was obtained by the cyclization of methyl 6-amino-2,2-dimethylcaproate and used for hydrolytic and activated anionic polymerization. Although condensation on the carbon atom adjacent to the carbonyl group is ruled out, the process of the anionic polymerization indicates side reactions destroying the growth centres. The calorimetrically determined heat of polymerization of α,α-dimethyl-ε-caprolactam is 4·80 kcal/mol.

Of monotopically disubstituted caprolactams, only ε,ε-dialkylcaprolactams have been described[1], obtained by the Beckmann rearrangement of the oximes of 2,2-dialkylcyclohexanones in polyphosphoric acid. Although substituents generally decrease the polymerizability of cyclic monomers, these lactams polymerized already during preparation under comparatively mild conditions. It was of interest to synthesize α,α-dimethyl-ε-caprolactam (3,3-dimethyl-1-aza-2-cycloheptanone) and investigate its anionic and hydrolytic polymerization. The lactam is interesting not only from the viewpoint of the steric effect of substituents in the vicinity of the amide bond on the ring-opening polymerization, but also because of its exceptional role played in the anionic polymerization of lactams. During the anionic polymerization of lactams, which carry one or two hydrogen atoms on the carbon atom adjacent to the carbonyl group, condensation reactions[2,3] take place at this carbon atom in the corresponding N-acyl derivatives (polymerization growth centres). These side reactions lead to changes in the activity of the polymerization system, to occasional branching[4] and to a number of consecutive reactions affecting the degree of polymerization, the character of end groups and the stability of the polymer. Owing to the absence of hydrogen atoms at the α-carbon atom, the condensation reactions considered so far cannot proceed during the anionic polymerization of α,α-disubstituted caprolactam; it seemed therefore of great interest to find our whether in spite of this there may be a change in the catalytic activity. It is known that in the absence of

* Part LIII in the series Alkaline Polymerization of 6-Caprolactam; Part LII: Europ. Polymer J. in press.

hydrogen atoms in the α-position, hydrogen atoms in the β-position may also split off from carbonyl compounds in a basic medium, as it is the case *e.g.* in the reaction of pivaloyl chloride with triethylamine[5].

EXPERIMENTAL

α,α-Dimethyl-ε-caprolactam

a) The reaction mixture after hydrogenation of methyl 5-cyano-2,2-dimethylvalerate[6] (0·05 mol) was filtered, concentrated *in vacuo* and the residue was added dropwise at 160—170°C during 3 h to 45 ml of ethylene glycol with stirring[7]. Glycol was distilled off and the fraction boiling at 112°C/1·2 Torr was collected. Column chromatography on silicagel (elution with chloroform and chloroform–ether 1 : 1) followed by purification with preparative layer chromatography (Kieselgel G — Merck, 1 mm layer, development with benzene–methanol 3 : 1) and sublimation gave 28·5 mg of α,α-dimethyl-ε-caprolactam. The product was homogeneous according to thin-layer chromatography; mass spectrum M^+ 141.

b) The product after hydrogenation of 0·60 mol of methyl 5-cyano-2,2-dimethylvalerate[6] was dissolved in 550 ml of 1,2-dimethoxyethane and heated to 230°C for 4h in a stainless steel autoclave under nitrogen atmosphere. Vacuum distillation yielded 39·4 g of lactam (46·5%), b.p. 93·5°C/0·6 Torr, m.p. 87·5—88·0°C (light petroleum, b.p. 40—50°C). IR spectrum: 1377, 2985 (—C.CH_3), 1608 and 1638 (C=O), 2855, 2915, 2960 (CH_2), 3080, 3305 cm^{-1} (NH). For $C_8H_{15}NO$ (141·2), calculated: 68·05% C, 10·71% H, 9·92% N; found: 68·24% C, 10·80% H, 9·77% N. The lactam was crystallized three times from light petroleum and dried at 50°C/1Torr before polymerization.

N-*Benzoyl-α,α-dimethyl-ε-caprolactam* was obtained by benzoylation by the method B, ref.[8]; the yield was 25% (plates), m.p. 94·0—94·5°C (ether). IR spectrum: 1673, 1690 (C=O). For $C_{15}H_{19}NO_2$ (245·3), calculated: 73·44% C, 7·81% H, 5·71% N; found: 73·82% C, 7·96% H, 5·68% N.

Sodium α,α-dimethyl-ε-caprolactam. The compound was prepared in an amount needed for the polymerization from α,α-dimethyl-ε-caprolactam and a solution of sodium methoxide in methanol (1·1 : 1 molar) by a procedure described for sodium caprolactam[9]. Alternatively, the salt was prepared from lactam and sodium tert-butoxide in hexane (1·1 : 1 molar). The content of tert-butoxide was determined[10] by GLC.

Polymerization and Characterization of Products

The polymerizations were carried out in sealed ampoules filled with approximately 0·5 g of the polymerization mixture by a procedure described earlier[11]. The monomer content in the polymerizates was determined by GLC of the methanolic extract (column 1 m × 3 mm packed with 10% Carbowax 20 M on Chromosorb W 80—100 mesh, nitrogen as carrier gas 50 ml/min, temperature 185°C, benzophenone added as an internal standard). The polymerizates in the form of particles, 1 mm in size, were extracted three times for 30 min in boiling benzene and twice for 5 min in boiling water, then dried to constant weight at 50°C/1 Torr and used for the determination of end groups by conductometric titration[12] and for the determination of viscosities (*m*-cresol, 25°C, $c = 0{\cdot}5$ g/dl, Ubbelohde's viscometer).

The heat of fusion was measured with a 900 Thermal Analyzer Du Pont apparatus provided with a DSC cell. The samples in the form of granules, 1 mm in size, in aluminium capsules were

TABLE I

Polymerization of α,α-Dimethyl-ε-caprolactam

T is polymerization temperature, *t* is polymerization time, L is the monomer content in the polymerizate, [A] and [B] are concentrations of the acidic and basic end groups, respectively, in the extracted polymer.

T °C	*t* h	L, %	[A] mmol/kg	[B] mmol/kg	η_{sp}/c[a] dl/g	M.p., °C
		Catalyst 2 wt.% H_2O, 0·2 wt.% H_3PO_4				
220	403	4·25	—	68	—	204—206
	500	4·53	148	77	0·4544	202—204
235	500	6·25	—	75	—	204—206
250	90	8·00	—	76	—	204—206
	140	6·93	143	75	0·4354	205—207
265	149	8·19	—	99	—	202—204
280	70	9·21	—	121	—	204—206
	120	8·98	159	100	0·3005	201—203
		Initiator: 0·5 mol% of sodium α,α-dimethyl-ε-caprolactam; activator: 0·5 mol% of N-benzoyl-α,α-dimethyl-ε-caprolactam				
175	15	17·9	—	5	—	200—202
	30	14·2	—	6	—	205—206
	45	14·4	—	6	—	200—201
	70	13·0	—	7	—	207—209
175[b]	30	56·5	—	5	—	
	2[c]	12·6	0	3	1·1958	
200	45	16·7	—	7	—	206—207
225	45	25·4	—	9	—	206—207
		Initiator: 0·5 mol% of sodium caprolactam; activator: 0·5 mol% of N-benzoylcaprolactam				
175	10	1·79	0	12	0·5675	—
200	3	3·19	0	11	0·5558	—
225	3	4·83	13	17	0·5290	—

[a] *m*-Cresol, 25°C, $c = 0{\cdot}5$ g/dl. [b] Sodium α,α-dimethyl-ε-caprolactam from sodium tert-butoxide. [c] Added approximately 0·2 mol% of N-acetylcaprolactam.

crystallized isothermally at 170 or 180°C (in one case the crystallization proceeded nonisothermally, during spontaneous cooling of the molten sample) and melted at a heating rate of 25 K/min. The calibration was carried out by an interpolation between the melting heats of indium, $AgNO_3$, and tin.

The heat of polymerization was measured in a Calvet 2 calorimeter in ampoules (Fig. 1) inserted into a standard measuring case made of stainless steel *9*. The assembled ampoule *1* containing a thin-walled glass capsule *6* with a known amount of N-benzoylcaprolactam (approx. 0·5 mol% per lactam used) was provided with a teflon seal NZ 7 — *2* having a 1 mm bore, a stainless steel guiding stick of the stirrer *3*, a teflon connection *4* and a glass stirrer *5*. The ampoule was filled with a known amount of a solution (0·5—0·7 g) of sodium caprolactam in the respective lactam by the usual techniques[10], sealed at the capillary *8* and fixed in a measuring case *9* by means of a steel spring *7* and a teflon screw closure *10*; the guiding stick of the stirrer *3* was connected with the pull rod through a thermally insulating link. The thermostating and stabilization of the calorimeter at 171°C took 80 min. The capsule with the activator was then broken with the stirrer, and the heat evolved during the polymerization and crystallization was measured.

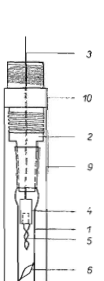

FIG. 1

Polymerization Cell for Calorimetric Determination of the Heat of Polymerization

RESULTS AND DISCUSSION

The preparation was carried out *via* substituted cyanovalerate and the respective ester of 6-amino-2,2-dimethylcaproic acid which was subjected to cyclization to yield the lactam. The synthesis differed from the procedure used earlier for α-methyl-ε-caprolactam[13] in two aspects: *a*) For the preparation of methyl 5-cyano-2,2-dimethylvalerate a new method for cyanoalkylation of the lithio esters was used[6], which considerably reduces the earlier procedure. *b*) If the method used for the preparation of α-methyl-ε-caprolactam, *i.e.* gradual addition of the amino ester to hot ethylene glycol with simultaneous removing of the alcohol by distillation was applied for the cyclization of 6-amino-2,2-dimethylcaproate, the yield was very low. However, a relatively high yield was obtained when the aminoester was heated in an autoclave under an inert gas in 1,2-dimethoxyethane as inert solvent; lactam was readily isolated from the reaction mixture by distillation.

The hydrolytic polymerization of α,α-dimethyl-ε-caprolactam (in the presence of water, 2 wt.%, and phosphoric acid, 0·2 wt.%) in a closed system proceeds at a velocity comparable to a similar polymerization of caprolactam as may be deduced from the time needed for attaining the equilibrium polymer–monomer state (Table I). The low viscosity values correspond to the relatively high concentration of the initiator used.

The anionic polymerization of the α,α-disubstituted lactam, which is particularly

interesting with respect to the impossibility of condensation in the α-position, exhibits some unexpected deviations. The possibility of formation of the C-anion in the neighbourhood of the carbonyl group and thus also condensation of N-acyl amides in the whole polymerization system were ruled out by using an initiator and an activator which were both derived from α,α-disubstituted lactam (sodium α,α-dimethyl-ε-caprolactam and N-benzoyl-α,α-dimethyl-ε-caprolactam). In spite of this, however, the polymerization proceeds very slowly (judging by the slow increase in the viscosity of the polymerization mixture) and stops at a conversion which is the lower the higher the polymerization temperature (Table I). Since sodium lactam used in these polymerizations was prepared from sodium methoxide and α,α-dimethyl--ε-caprolactam under conditions described for sodium caprolactam[8,9], it was not sure whether this salt does not retain a major amount of methoxide which would reduce the basicity of the polymerization system or cause alcoholysis of the imide growth centres, thus retarding the polymerization. Therefore, the polymerization was also carried out with sodium-α,α-dimethyl-ε-caprolactam which was obtained from sodium tert-butoxide and lactam by evaporating their hexane solution (according to the gas chromatographic analysis it contained less than 0·2 mol.% of tert-butoxide[10]), with N-benzoyl-α,α-dimethyl-ε-caprolactam as activator. In this case the polymerization at 175°C stopped even earlier (Table I). If N-acetylcaprolactam in an amount corresponding approximately to 0·2 mol% was added to this mixture prior to heating, the polymerization proceeded to a higher conversion, although not fast enough to attain the equilibrium value of conversion during the given time. If the catalytic system sodium caprolactam–N-benzoyl-ε-caprolactam is used, which does not exclude the side reactions of the C-anion in the neighbourhood of the carbonyl group, the anionic polymerization proceeds during a few minutes up to conversions

TABLE II

Heat of Fusion of Poly(α,α-dimethyl-ε-caprolactam) ΔH (cal/g)

Monomer content in the polymer: 4·5% hydrolytic, 4·8% anionic, T_m is the corrected temperature corresponding to the maximum on the DSC curve (°C).

Polymer	Preceding crystallization	T_m	ΔH
Hydrolytic	isothermal at 170°C	205·6	19·50
		207·0	19·54
Anionic	isothermal at 170°C	210·9	19·65
		206·6	19·37
Anionic	isothermal at 180°C	204·6	19·80
Anionic	non-isothermal, $T_m = 167$°C	204·6	19·23

which are in agreement with the equilibrium polymer contents for the hydrolytic polymerization. The onset of the anionic polymerization with any of the catalysts used is accompanied by a yellow colouring of the polymerization mixture; and *vice versa*, there is no polymer present in the polymerization mixture before the yellow colour appears.

Since the polymerization stops before the polymer–monomer equilibrium has been attained in the anionic polymerization of systems without the possibility of the proton dissociation in the α-position to the carbonyl group, it may be inferred that there exists a competition between the polymerization reaction and a reaction, or several reactions, deactivating the growth centres. In contrast with the 3-oxoamide structures, which are formed by condensation on the α-carbon atom and from which the growth centres are regenerated during the further process of polymerization[14], a reaction on the β-carbon atom would give structures from which no growth centres may be regenerated. The absence of the 3-oxoamide structures in the anionic polymerizates of α,α-dimethyl-ε-caprolactam is also confirmed by the negative test for the presence of amino ketones in the hydrolyzate carried out as described previously[15]. At the same time, the propagation reaction of the lactam anion with the acyllactam growth centre is probably slowed down, since the acylation of the lactam anions with the endocyclic acyl group of the growth centre is sterically hindered. A striking feature is the very small or practically zero concentration of the basic and acidic end groups determined titrimetrically in the extracted products of the anionic polymerization. However, the viscosities of the cresol solutions indicate that the products do not contain a large fraction of cyclic oligomers. The low concentration of basic groups may be assigned to the suppression of the base-catalyzed disproportionation of the lactam. This is also supported by the fact that at 170°C the polymerization of α,α-dimethyl-ε-caprolactam in the absence of the activator did not take place at all (initiator: 0·5 mol% of sodium caprolactam, 2 h). The absence of the acidic groups in extracted polymers may be caused either by the absence of side reactions leading to acidic groups or products yielding acidic groups on hydrolysis, or by the steric hindrance in the hydrolysis of the N-acyllactam end groups.

On cooling, polymers obtained by hydrolytic polymerization above 220°C become clear colourless organic glasses which after heating to 160–180°C rapidly crystallize (with evolution of heat) to yield an opaque white substance. Crystallization also occurs during extraction of the above polymers, *e.g.* with methanol. The same behaviour was observed for anionic polymers polymerized up to high conversions at temperatures above 200°C, with the difference that the clear polymers are yellow. At temperatures $\leq$200°C a crystalline polymer is obtained; the crystallization is accompanied by considerable contraction. Such tendency toward supercooling also appears during remelting of crystallized polymers, which was observed for samples used for calorimetric measurements.

The heat of fusion was determined by differential scanning calorimetry for both

anionic and hydrolytic polymerizates which had been crystallized before melting (isothermally and unisothermally) at 167–180°C and contained 4·5–4·8% of monomer. The results are given in Table II. The positions of the maxima of the DSC curves do not differ too much from the melting temperature of extracted polymers determined on the heated stage of a microscope (Table I). The average heat of fusion of polymers crystallized as indicated above is 19·5 cal/g; it was used for determining the heat of polymerization.

The heat of polymerization of α,α-dimethyl-ε-caprolactam was measured directly during the anionic activated polymerization in a calorimeter at 171°C. The method was tested on a similar polymerization of caprolactam: $\Delta H_p = 3{\cdot}84 \pm 0{\cdot}07$ kcal/mol at an assumed heat of fusion of 22·2 cal/g and a conversion of 98·7%, *cf.*[16]. The heat of crystallization mentioned above was subtracted from the thermal effect. The heat of polymerization found (4·80 kcal/mol) is higher than that of caprolactam. After substitution of 4·80 kcal/mol into Yumoto's expression[17] for the determination of the heat of polymerization from the polymer–monomer equilibria, a very low value is obtained for the parameter describing the activity of segments ($\alpha = 0{\cdot}19$). The low value of the entropy of polymerization (−1·44 e.u./mol) indicates a higher rigidity of the α,α-disubstituted polymer chain compared to the polymer of an unsubstituted lactam.

We are indebted to Dr Z. Máša and Dr R. Puffr for assistance in the calorimetric measurements and to Mrs K. Brzkovská for technical assistance.

REFERENCES

1. Nedeskov P., Taub W., Ginsburg D.: Acta Chem. Scand. *12*, 1405 (1958).
2. Bukač Z., Šebenda J.: This Journal *32*, 3537 (1967).
3. Stehlíček J., Čefelín P., Šebenda J.: J. Polymer Sci. Polymer Symposia *42*, 89 (1973).
4. Goebel C. V., Čefelín P., Stehlíček J., Šebenda J.: J. Polymer Sci. A-1, *10*, 1411 (1972).
5. Klages F., Zange E.: Ann. *607*, 35 (1957).
6. Čefelín P., Lochmann L., Stehlíček J.: This Journal *38*, 1339 (1973).
7. Kunishika S., Sakibara Y.: Japan. pat. 38–14563 (1963); Chem. Abstr. *60*, 4015 (1969).
8. Stehlíček J., Labský J., Šebenda J.: This Journal *32*, 545 (1967).
9. Čefelín P., Šebenda J.: This Journal *26*, 3028 (1961).
10. Bukač Z., Janoušová A., Lochmann L., Šebenda J.: This Journal, in press.
11. Stehlíček J., Šebenda J., Wichterle O.: Chem. průmysl *17*, 362 (1967).
12. Šebenda J., Masař B.: This Journal *31*, 3331 (1966).
13. Čefelín P., Frydrychová A., Labský J., Schmidt P., Šebenda J.: This Journal *32*, 2787 (1967).
14. Čefelín P., Stehlíček J., Šebenda J.: J. Polymer Sci. Polymer Symposia *42*, 79 (1973).
15. Stehlíček J., Čefelín P., Šebenda J.: This Journal *37*, 1926 (1972).
16. Wichterle O., Tomka J., Šebenda J.: This Journal *29*, 610 (1964).
17. Yumoto H., Ida K., Ogata N.: Bull. Chem. Soc. Japan *31*, 249 (1958).

Translated by L. Kopecká.