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Thermal catalytic depolymerization of polyamides

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Summary

The formation of cyclic diamides of polyamides 4,6 and 6,6 by thermal catalytic depolymerization of the corresponding polyamides was investigated. This method was optimized by changing external factors, like: concentration of catalyst; depolymerization temperature; — time; working under nitrogen flow and under a high vacuum (10^{-5} mbar). The catalyst sodium-2-ethylhexanoate was used to accelerate the reaction. The different multi-component depolymerization products were analyzed by reversed phase HPLC. The formation of cyclic diamides of polyamides 4,6 and 6,6 was 10, respectively 20 wt.-%, under optimum conditions, which is not sufficient to be used as feed stock for new (co)polyamides.

Introduction

The literature on the synthesis of cyclic diamides with special emphasis on the 12-membered 1,6-diazacyclododecane-7,12-dione (*c-4*) reveals that several methods have been applied. Especially the high-dilution procedures (1,2) and Beckmann and Schmidt rearrangements (3,4,5,6,7) suffer from serious drawbacks, e.g.: special design apparatus required; usage of large quantities of benzene; exclusion of water and CO_2; starting materials not readily available; and multistep syntheses required forming isomeric cyclic oligomers which are difficult to separate. Although not yet applied to the synthesis of *c-4*, two procedures looked promising for the preparation of *c-4*.

(A) Cyclic diamides having 12-20 ring atoms have been prepared by simple pyrolytic depolymerization of polyamides in the presence of metallic sodium as a catalyst (8). Polyamide 4,6 (PA 4,6) was heated with about 1 % of sodium in a distillation flask in an oil-pump vacuum at 270-300°C to yield 9 % *c-4*. Langhammer *et al.* (9) have converted successfully different polyamides (PA 8, PA 12, PA 6,6, PA 11,6, and PA 12,12) into cyclic oligomers at 280-330°C within 1-3 hours. These anionic depolymerizations were catalyzed by small amounts of salts of different carboxylic acids.

(B) Despite the simplicity of the synthesis, as described in a slightly different manner in 1939 by Du Pont (10), the condensation of dimethyl —, diphenyl —,

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or dibutyl adipate with 1,4-diaminobutane, respectively 1,6-diaminohexane did not yield the desired cyclic diamides *c-4* or 1,8-diazacyclotetradecane-9,14-dione (*c-6*), but instead low molecular-weight PA 4,6, respectively PA 6,6 was obtained, beside other oligomeric materials (11).

Already in 1938, Greenewalt (12) described the hydrolytic polymerization of the 14-membered cyclic diamide *c-6* and the corresponding cyclic tetra-amide 1,8,15, 22-tetra-aza-2,7,16,21-tetra-oxocyclo-octacosane (*c-66*) to form PA 6,6. More recently, Vogl and Knight (13) prepared poly(hexamethylene oxamide) and related polyoxamides by ring-opening polymerization of the appropriate cyclic diamides, while Iwakura *et al.* (7) polymerized the appropriate cyclic diamide hydrolytically in the solid state to linear poly(trimethylene malonamide).

The aim of this study was to investigate the possibilities of anionic depolymerization of PA 4,6, as compared to PA 6,6, to produce conveniently the cyclic diamide *c-4*. This cyclic diamide can then be used as feed stock in the synthesis of new (co)polyamides (14).

Experimental

Materials

Polyamide 4,6 (Stanyl® KS300, DSM, The Netherlands) and polyamide 6,6 (Ultramid® A3, Bayer, Germany) were used without further purification. Sodium-2-ethylhexanoate (ICN Biomedicals, USA) was used as a catalyst. All chemicals were thoroughly dried in a vacuum oven overnight at elevated temperature prior to use.

Depolymerizations

The thermal catalytic depolymerizations were conducted in predried glass vessels with a total volume of about 100 mL. These vessels were filled with 5 g of polyamide with the optional presence of catalyst and connected to a vacuum line (10^{-5} mbar). In an other experimental set-up, glass vessels were used in which a capillary was made —reaching to the bottom of the vessel— for the addition of dry nitrogen (flow ≈1 L/hr). The evaporating depolymerization products were trapped with liquid nitrogen and removed from the trap by dissolution in methanol. The methanol and any volatile by-products were evaporated by Rotavap. The depolymerization rates were determined by weighting the collected depolymerization products and the remaining polyamide after 30 or 60 min.

Characterization and analysis

Reversed phase HPLC measurements were carried out with a Gilson 811 high pressure liquid chromatography instrument in combination with two pumps Gilson 302 and 305, using one column Nucleosil 120-5 C_{18} (250 mm length x 4 mm i.d.). The HPLC oparating conditions consisted of an acetonitrile gradient in 10 m*M* H_3PO_4 mobile phase (from 0 to 45 % in 30 min) and a flow rate of 1.0 mL/min at room temperature.

Results and discussion

In the study of Langhammer *et al.* (9), for PA 6,6 an optimum in the depolymerization rate was found, being reportedly 80.7 wt.-%/hr with addition of 6 mol-% sodium hexanoate as catalyst. The depolymerization products were composed of more than 50 wt.-% of *c-6* and about 25 wt.-% of *c-66*. In order to find the optimum conditions for the depolymerization of PA 4,6, as compared to PA 6,6, with respect to the formation of *c-4* and *c-6*, the temperature dependence as well as the catalytic activity of Na-2-ethylhexanoate on the depolymerization and specifically on the formation of the cyclic diamides were investigated.

For the thermal depolymerization of PA 4,6 or PA 6,6, in the presence of Na-2-ethylhexanoate as catalyst, a reaction mechanism, as postulated by Langhammer *et al.* (9), is assumed. This mechanism involves propagation and depolymerization steps. The anionic reaction is initiated by deprotonation of an amido group, followed by an attack at the neighbouring carbonyl group which subsequently yields a species able to start depolymerization. A second propagation reaction is the nucleophilic substition at the next carbonyl group, which directly leads to the starting species. The so formed amine anion is able to attack either the neighbouring carbonyl group or the next carbonyl group to yield subsequently cyclic diamides, or cyclic oligo-amides.

The depolymerization products were characterized for *c-4*, respectively *c-6* by reversed phase HPLC (see Figure 1). The main product in the depolymerization products of PA 4,6 was a cyclic urea derivative next to *c-4*. This cyclic urea derivative was isolated and identified as being 1,3-diazacycloheptane-2-one by NMR and mass spectroscopy. Some oligomers, including linear ones, were identified using the HPLC chromatogram of a water-soluble-extract of Stanyl as reference. In the depolymerization products of PA 6,6, the main product was *c-6*.

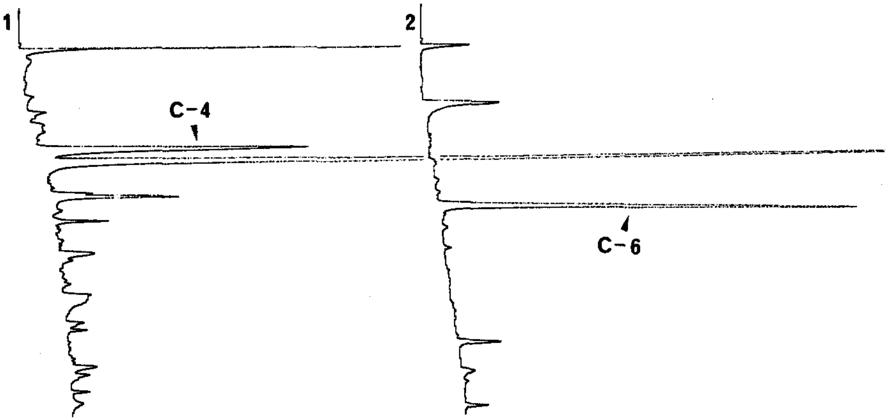

Figure 1:
Example HPLC chromatograms of the depolymerization products of PA 4,6 (1) and PA 6,6 (2).

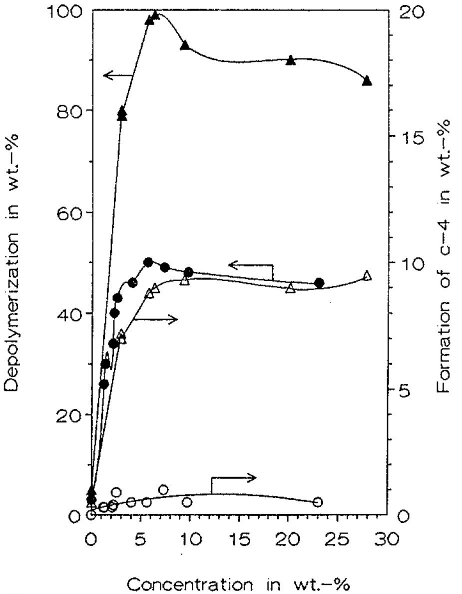

Figure 2:
Catalytic activity of ethylhexanoate on the depolymerization (▲,●) and the formation of *c-4* (△,○) for the depolymerization of PA 4,6 for 60 min, at 330°C under N_2 (circles) and vacuum (triangles).

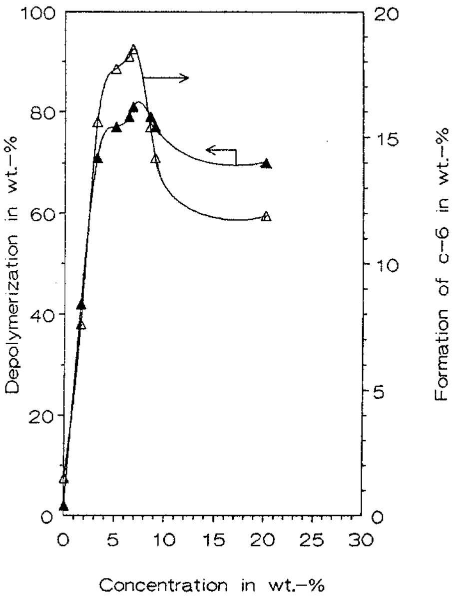

Figure 3:
Catalytic activity of ethylhexanoate on the depolymerization (▲) and the formation of *c-6* (△) for the depolymerization of PA 6,6 for 60 min, at 305°C under vacuum.

Figures 2 and 3 show plots of varying concentrations of Na-2-ethylhexanoate versus depolymerization and formation of cyclic diamides for PA 4,6 and PA 6,6. It was proven that the catalyst Na-2-ethylhexanoate enhanced the depolymerization significantly and preferentially the formation of cyclic diamides (as also evidenced in Figures 4 and 5). For the depolymerization under vacuum a maximum at 5.5 wt.-% of catalyst was found for PA 4,6 and a maximum at 7 wt.-% of catalyst was found for PA 6,6. These values are in agreement with reported optimum concentrations of catalyst for depolymerizations of PA 6,6 (9) or PA 6 (15).

At the present moment there is no adequate explanation for the fact that for PA 6,6 the formation of *c-6* was decreased by addition of more than 7 wt.-% of catalyst, while for PA 4,6 a plateau value was reached —this plateau value for PA 4,6 stays below the end value for PA 6,6. Minor differences in the configuration of the cyclic diamides possibly have an effect on the reactivity towards further degradation/reaction. The cyclic diamide *c-6* shows possibly an enhanced reactivity due to the presence of two non-vicinal *gauche*-bonds and a less favourable dipole orientation (16,17).

For PA 4,6 also the depolymerization under nitrogen flow was investigated. For this set-up, the depolymerization and formation of *c-4* was significantly lower as compared to the depolymerization under vacuum, possibly due to an insufficient removal of depolymerization products.

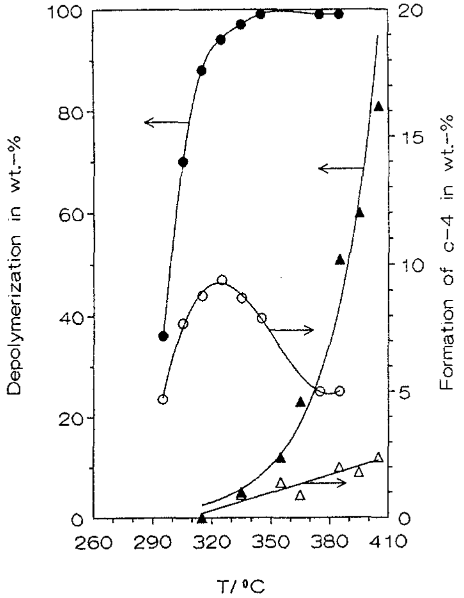

Figure 4:
Temperature dependence of the depolymerization (▲,●) and the formation of *c-4* (△,○) for the depolymerization of PA 4,6 for 30 min, under vacuum without catalyst (triangles) and with 6 wt.-% catalyst (circles).

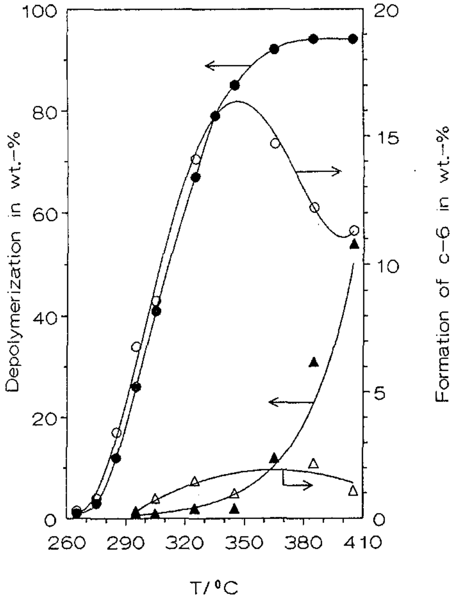

Figure 5:
Temperature dependence of the depolymerization (▲,●) and the formation of *c-6* (△,○) for the depolymerization of PA 6,6 for 30 min, under vacuum without catalyst (triangles) and with 7 wt.-% catalyst (circles).

Figures 4 and 5 show plots of the depolymerization and formation of cyclic diamides for PA 4,6 and PA 6,6 as a function of depolymerization temperature. For the catalyzed depolymerization of PA 4,6 an optimum in *c-4* formation was found at 325°C, for the uncatalyzed depolymerization the most *c-4* was formed at the highest temperature (i.e. 405°C). For the catalyzed depolymerization of PA 6,6 an optimum in *c-6* formation was found at 345°C, for the uncatalyzed depolymerization the most *c-6* was formed at 365°C. The amount of *c-4*, which was formed, was lower than the amount of *c-6*, possibly due to the fact that the 14-membered *c-6* is slightly more stable than the 12-membered *c-4*. In recent semi-empirical quantum chemical calculations on symmetrical cyclic diamides (18), a small degree of eclipsing of the hydrogen atoms was found for *c-4*, indicating a less stable configuration. Furthermore, increasing the temperature above the optimum increases the degradation of cyclic oligo-amides to low molecular-weight linear oligomers, as evidenced quantitatively by reversed phase HPLC.

Conclusions

The optimum reaction temperatures for depolymerization of PA 4,6 with 5.5 wt.-% catalyst for 30 min was 330°C, yielding 10 wt.-% *c-4* and for depolymerization of PA 6,6 with 7 wt.-% catalyst for 30 min was 345°C, yielding 20 wt.-% *c-6*. On a commercial basis, though, the above-mentioned depolymerizations of polyamides do not yield quantitatively pure cyclic diamides to be used as a feed stock for new synthetic routes to (co)polyamides.

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