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Cyclic diamides with $(CH_2)_x$ segments: Phase transitions in the solid state

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Summary

Cyclic diamides with various CH_2 segment lengths were synthesized. Cyclo-(octamethylene sebacamide) **I**, x = 8, was investigated as a model system by means of calorimetry, X-ray diffraction and Raman spectroscopy with special emphasis on its phase behaviour. In the low temperature phase the molecules exist as collapsed rings where the amide groups are located in the folds and the straight stems consist of nondisordered CH_2 segments. During the solid phase transition at about 84°C a strong increase of conformational disorder (4 additional gauche defects per molecule) occurs which does not change significantly during subsequent melting. It is shown that the conformation of the molecules in the high temperature phase is similar to that in the melt (liquid-like). In spite of conformational disorder the linewidth of the X-ray reflection peaks is smaller in the high temperature phase compared to that in the solution crystallized phase.

Introduction

Mesophases and mesophase transitions in flexible chain molecules are of considerable interest to understand the defect structure of conformationally disordered molecular crystals. Whereas numerous mesophase transitions are only due to changes in crystal symmetry with a small excess enthalpy and entropy, a dominant solid phase transition with large transition quantities caused by conformational disorder occurs in some systems below melting. Experimental investigations of the molecular defect structure in similar phases exhibited in cycloalkanes have been reported (1), (2). A theoretical description of the conformational disorder based on Monte-Carlo-simulation was published recently (3), (4).

Cyclic oligoamides with variable CH_2 segment lengths represent an appropriate model system that allows the investigation of defect structure in the mesophases on a molecular level by means of different experimental methods such as X-ray, calorimetry and

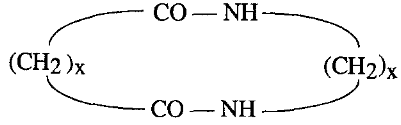

fig. 1: cyclo-(octamethylen sebacamide) **I**, x = 8

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Raman spectroscopy. A series of cyclic diamides have been synthesized. The results of the experimental investigations of the system cyclo-(octamethylene sebacamide) **I**, x = 8, are reported here as a representative example. The system considered exhibits a strong solid-solid phase transition at about 84°C (after first heating the solution crystallized (sc) sample above 130°C) from the low temperature phase (LT) into the conformationally disordered high temperature phase (HT). Melting occurs at about 208°C without further significant increase of the intramolecular disorder.

Experimental

Synthesis of cyclo-(octamethylene sebacamide)

1000 ml abs. toluene were placed in a 4 l three-necked round-bottomed flask equipped with a mechanical stirrer and two precision dropping funnels (Normag). One dropping funnel was filled with a $4.0 \cdot 10^{-2}$ m solution of sebacoyl dichloride in abs. toluene, the other with a $8.0 \cdot 10^{-2}$ m solution of 1.8-diaminooctane in the same solvent. At room temperature 500 ml of either solution of acid dichloride (4.78 g, 20 mmol) and diamine (5.77 g, 40 mmol) were added dropwise synchronously and at a constant rate with intensive stirring within 6 hours. Subsequently, stirring was continued for 60 min. From the filtered precipitate (9.16 g) 3.75 g of the raw product were isolated by extraction with tetrahydrofuran or toluene in a Soxhlet apparatus. After treatment with boiling water for 2.5 hours 3.48 g of cyclodiamide were obtained, which were purified further by GPC on Sephadex LH-20/methanol and recrystallized from methanol. Another 0.42 g of cyclodiamide can be isolated from the toluene filtrate (overall yield: 54.9 %, lit. (5): 20 %).

m.p.: 209°C (lit. (5): 205°C)
IR (KBr, cm^{-1}): 3285 (NH), 1635 (CO, amide I), 1545 (amide II)
^{1}H-NMR ($CDCl_3$, TMS, δ in ppm): 5.56 (NH), 3.29 ($N-CH_2$), 2.18 ($CO-CH_2$)
MS (m/e): $M^+ = 310$

$C_{18}H_{34}N_2O_2$ (310.48)	Calc.	C 69.63	H 11.04	N 9.02
	Found	C 69.70	H 11.06	N 9.19

Physical measurements

In order to characterize the phase transitions as well as the structure and intramolecular conformation of the molecules differential scanning calorimetry (DSC), X-ray powder diffraction as well as Raman spectroscopy have been performed extensively. For the thermal investigations a DSC 2 (Perkin-Elmer) calorimeter was used. These measurements were performed under nitrogen atmosphere. X-ray diffraction data were collected on Siemens D500 and D5000 powder diffractometers using nickel-filtered CuKα radiation (λ = 1.54188 Å) covering for 2θ a range from 8 to 50°. For high temperature patterns the powder was placed on a Pt-Rh heating element. Lattice parameters and space groups were obtained by a space group sensitive indexing process (6) using ZnO as an internal standard. Raman spectra of the sample in 2 mm capillaries were recorded on a Spex 1403 double monochromator equipped with a PMT and a CCD array as detector systems. The output of the argon-ion laser at 514.5 nm was adjusted to provide not more than 100 mW at the sample to prevent local heating. Temperature was adjusted by a controller with an accuracy of ±1 K.

Results and discussion

Synthesis of Cyclic Diamides

Cyclodiamides of the diamine/dicarboxylic acid type **I** (fig. 1) were synthesized according to the method introduced by Stetter (7) from dicarboxylic acid dichlorides and α,ω-diamines in moderately diluted solution. Cyclization was performed by dropwise synchronous addition of solutions of the acid chloride and the diamine in toluene to a large volume of the same solvent. In order to neutralize the hydrogen chloride released during the amide coupling the diamine was added in double stoichiometric amounts. As the first example, the synthesis of the cyclodiamide (1.10-diaza-cycloeicosane-11.20-dione) **I**, x = 8, of sebacic acid and octamethylendiamine was performed (5). The reaction of the acid chloride and the amine starts immediately at room temperature. A precipitate is formed consisting of 1.8-diaminooctane dihydrochloride, the desired cyclodiamide **I**, x = 8, and in addition linear oligoamides with acid chloride or amine end groups. These are formed according to the following scheme on account of intermolecular growth reaction competing with the desired intramolecular ring closure.

In case of cyclizations from linear precursors the chain propagation can be restricted almost completely by decreasing the educt concentration (dilution principle). In the present case, however, this is only possible to a certain extent. The linear monoamide **II** (fig. 2) appropriate for cyclization must be formed in a preceding bimolecular reaction from dicarboxylic acid dichloride and diamine. Therefore, the rate of the reaction is strongly decelerated in case of too low concentrations as well.

Cyclic oligoamides with the n-fold ring size of **I**, x = 8, can be formed from long-chain linear precursors with amine and acid chloride end groups (cyclooligomerization, formation of **III**, n = 2, 3, ...). For statistical reasons (probability of intramolecular reaction of the chain ends) their formation tendency strongly decreases with increasing n. Nevertheless, in the synthesis of **I**, x = 8, the homologous 40-membered cyclotetraamide (**III**, n = 2) could be detected in the mixture obtained.

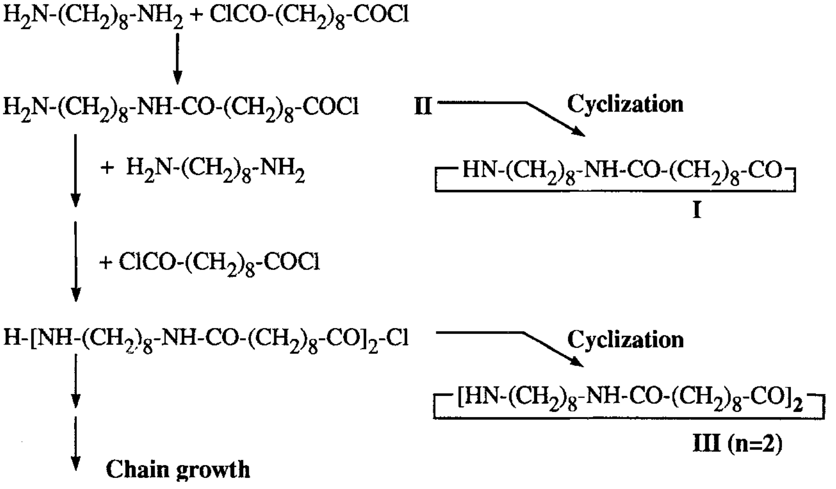


fig. 2: Scheme of the reaction of sebacoyl dichloride and 1.8-diaminooctane (chain growth vs. cyclooligomerization)

The cyclodiamide **I**, x = 8, was extracted from the reaction mixture with tetrahydrofuran or toluene. In this procedure also the cyclic tetraamide (**III**, n = 2) as well as small quantities of diamine dihydrochloride are dissolved. The amine salt can be removed from the raw extract by boiling water, while the cyclotetraamide remains mostly unsolved. Recrystallization from methanol or acetone has no sufficient purification effect as well. The cyclotetraamide shows far less solubility compared to the cyclodiamide and can be detected in all fractions. In order to obtain chromatographically pure **I**, x = 8, the cyclotetraamide (2.0 weight-%) was separated by GPC on Sephadex LH-20/methanol. Another recrystallization from methanol or sublimation at 160°C/0.04 mbar did not lead to a further rise of the melting point (209°C). The multistep purification procedure is justified by our efforts to obtain a really monodisperse oligomer.

The cyclic amide was proved to be pure using TLC, HPLC, and GPC. The structural assignment was confirmed by IR, ^{1}H-NMR and mass spectrometry. The elementary analysis is in good conformity with the calculated values.

Thermal behaviour (calorimetry)

In the DSC diagram cyclodiamide I, x = 8, recrystallized from methanol shows an intensive endothermic phase transition into a solid high temperature phase (HT) during the *1st heating* (fig. 3) at 125.9°C (98.6 J/g). Melting is performed at 208.8°C with a melting enthalpy of 120.9 J/g. During the *1st cooling* recrystallization spontaneously occurs at 176.3°C. At 82.4°C, 26.8 J/g are released with exothermic transition. During the *2nd heating* (fig. 3) the phase transition into the high temperature phase (HT) starts already at 84.0°C. The energy absorption of 29.2 J/g is obviously lower than in case of (first) heating the substance crystallized from solution. On the other hand, temperature as well as enthalpy in the melting process are almost identical with the values determined during the 1st heating process (207.6°C, 121.4 J/g). The phase transition into the HT-phase observed at 84.0°C can be reproduced in the *3rd and 4th heating cycle*. All scans were performed at a constant heating rate of 5 K/min.

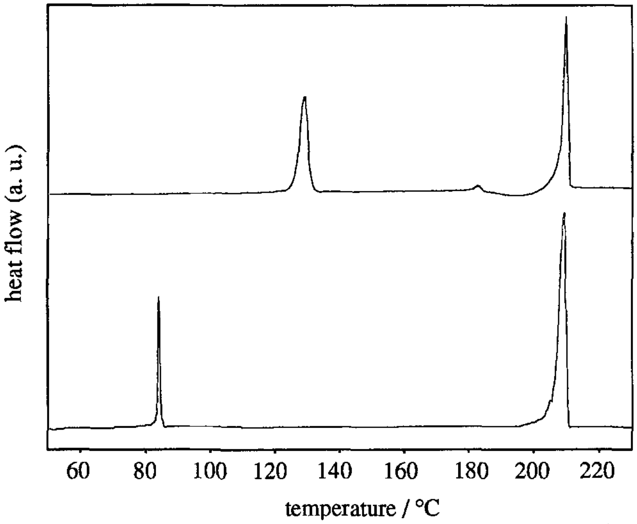


fig. 3: DSC of I, x = 8; above: 1st melting (crystallized from methanol); below: 2nd melting

The phase transition into the HT-phase detected by calorimetric methods is not visible under the microscope. The melting of the small crystal needles is not preceded by any sublimation. The clear melt spontaneously solidifies upon cooling to give an ice-like crystal layer.

Structure determination (X-ray diffraction)

Point symmetries:

Due to the configuration of the amide groups inversion symmetry can be excluded. A mirror plane perpendicular to the CH_2 elements requires a fully eclipsed (cis) conformation since the number of the CH_2 units is even. As preliminary molecular modeling calculations (BIOSYM) have shown, the lowest of the energy minima is obtained in case that the CH_2 groups (not situated within the folded region) are in all-trans (anti) conformation. Thus twofold or unique symmetry are the only point symmetries to be taken into account.

Lattice parameters:

The solid state phase transitions as shown by calorimetry can also be observed by X-ray powder diffraction. The powder crystallized from solution shows at room temperature a distinctly different pattern compared to that in the high temperature phase (HT) at 120°C and also to the low temperature phase (LT) obtained after first heating above 120°C and subsequent cooling. Similar to the calorimetric experiments the patterns obtained in the HT-phase and in the LT-phase are reproducible by alternating heating and cooling the sample regardless whether the heating process is extended to the melt or only to a temperature just above the HT-phase transition. The LT-phase therefore can be regarded as quasi-melt crystallized.

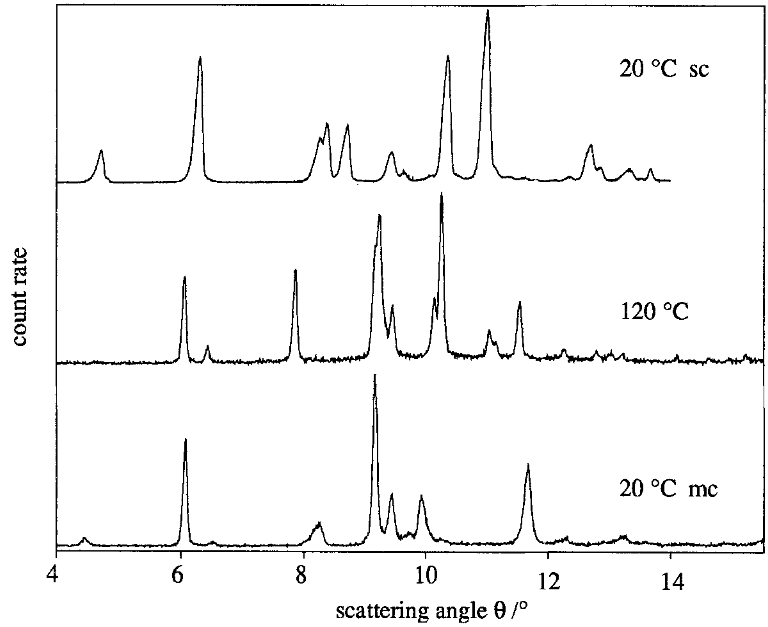


fig. 4: Powder diffraction patterns of the different phases (sc/mc: solution/melt crystallized)

The following results are obtained by the indexing process:

Phase	Lattice parameters / Å	Crystallographic density / kg / m^3	Space group (no.)	Required point symmetry	Figures of merit (8), (9)
20°C solution cryst.	a = 21.172 b = 4.841 c = 18.753	1072	Pna2$_1$ (33) [Pnam (62)]*	1 m	M_{20} = 24 F_{20} = 65
120°C (HT-phase)	a = 11.139 b = 9.586 c = 18.844	1023	Pbcn (60) [Pbca (61)]*	2 or $\bar{1}$ $\bar{1}$	M_{18} = 20 F_{18} = 42
20°C melt cryst. (LT-phase)	a = 10.605 b = 9.547 c = 19.449	1044	Pnca (60) Pbnn (52)	2 or $\bar{1}$ 2 or $\bar{1}$	M_{12} = 23 F_{12} = 21

*Space groups rejected because of point symmetry discussed above.

All phases show only few lines. Therefore, a space group determination can not be performed unambiguously without taking into account point group symmetry. Both space groups which fit the LT-phase require the same point symmetry. Thus, no final statement can be made in this case.

The full width at half maximum (FWHM) of the reflection peaks obtained in the solution crystallized phase exceeds distinctly that obtained in the HT- as well as in the LT-phase. As the FWHM is coupled directly with reciprocal crystallite size the crystals - similar to an annealing process - are supposed to grow bigger in the HT-phase. Focussing on the lattice parameters it is evident that the b-axis does not change its length significantly (apart from a factor 2 due to transitions in the symmetry elements). This repeat unit of about 4.8 Å is well known in structures showing hydrogen bonding between amide groups (10). The circles in fig. 5 represent the CH_2 units perpendicular to the amide plane. This model proposes the amide groups to be localized in the ring fold, according to Raman spectroscopic data and to the lattice parameters reported above. This leads to the conclusion that the direction of the CH_2 axis is approximately parallel to the a-axis of the unit cells.

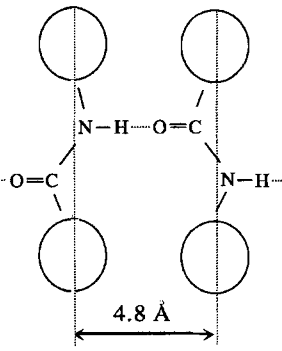
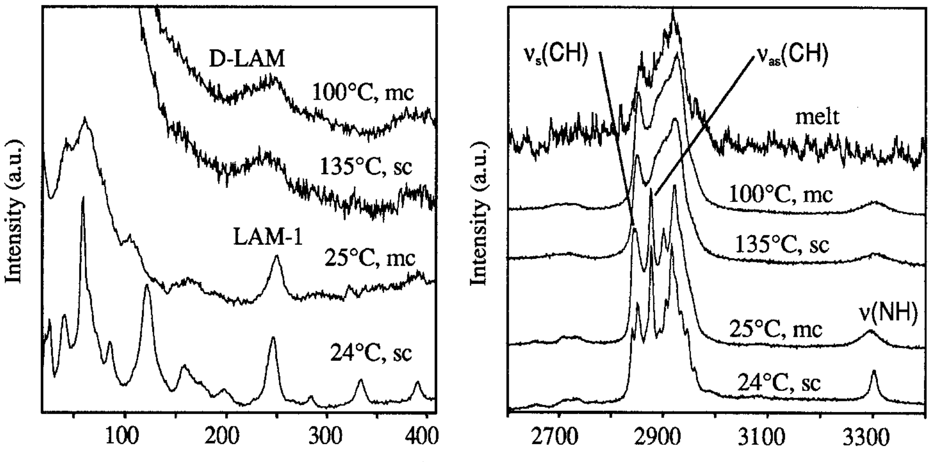


fig. 5: Hydrogen bonding of sec. amide groups

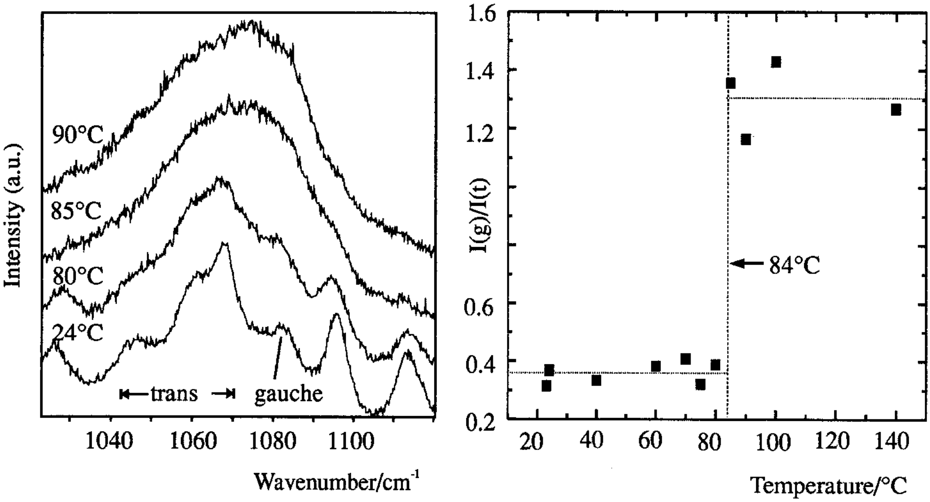
Intramolecular conformation (Raman spectroscopy)

Temperature dependent Raman spectra were recorded for the cyclodiamide **I**, x = 8 (fig. 6). In the low frequency region an accordion-like mode (LAM-1) at 246 cm^{-1} is detected. This vibration mode is well known from linear chain molecules where its wavenumber shows a linear dependence on the reciprocal chain length. The wavenumber of the LAM-1 of cyclodiamide **I**, x = 8 (20 ring atoms) lies between the cyclic alkanes $(CH_2)_{18}$ and $(CH_2)_{22}$ (11). This indicates that in the LT-phase the molecule exists - similar to these cycloalkanes - as a collapsed ring. The two aliphatic chains are arranged parallel, connected by tight folds with the conformation -ggtgg-. In the HT-mesophase the LAM broadens and shows increased conformational disorder (D-LAM, distorted LAM (12) at 241 cm^{-1}). In the CH stretching region a breakdown of the ν_{as} (CH) band at 2880 cm^{-1} is observed in the HT-phase. This confirms the increased conformational disorder in this mesophase. The melt-like broad bands indicate the appearance of a mixture of different conformers in the HT-phase (13). The ν(NH) as well as the ν(C=O) band are shifted only slightly at the mesophase transition. Thus a change of the hydrogen bond structure during the HT-phase transition can be excluded.



Low frequency

CH- and NH-stretching



CC-stretching (melt crystallized)

Intensity ratio in the ν(CC) region (mc)

fig. 6: Raman spectra and gauche defect concentration (sc/mc: solution/melt crystallized)

This is consistent with the X-ray investigations mentioned above.
The conformational disorder can be determined in the ν(CC) region (14). At the mesophase transition a strong increase of the intensity of the gauche defect band at about 1080 cm^{-1} is detected. Based on the calibration of the intensity ratio (I_{gauche}/I_{trans}) with data from the cyclic alkanes (15) the number of gauche defects can be calculated. In the low temperature phase two gauche defects exist per aliphatic chain. The two other gauche bonds of the tight fold must be located at the amide groups (CH_2-CO and CH_2-NH respectively) that are located in the folds. In the mesophase two additional gauche defects are built into each aliphatic chain (probably a -gtg$^-$- kink).

Acknowledgements

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