

Spectral and structural characterization of a cyclic trimeric model of poly(6-hexanelactam)

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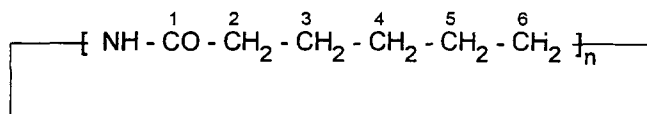
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Differential scanning calorimetry and wide angle X-ray scattering measurements of the cyclic trimer of 6-hexanelactam showed that, besides the basic crystalline form, A, obtained by slow crystallization from a water solution, the cyclic trimer can be prepared in two other crystalline forms, B and C, by heating to 174 and 216°C, respectively. According to the analysis of vibrational and nuclear magnetic resonance (n.m.r.) spectra, the amide groups are present in the *trans* structure in all the crystalline forms of the cyclic trimer and, in forms B and C, the molecules of the cyclic trimer have the same conformational structure. Based on semiempirical and *ab initio* calculations of stable conformational structures and on structural interpretations of n.m.r. and vibrational spectra, a molecular structure with symmetry C₃ was proposed for the cyclic trimer in the forms B and C. Similarly to polyamides, the forms B and C of the cyclic trimer contain an amorphous phase, the molecular structure of which depends on the thermal history of the sample. © 1997 Elsevier Science Ltd.

(Keywords: poly(6-hexanelactam); cyclic trimer; conformational structure)

INTRODUCTION

Cyclic oligomers of 6-hexanelactam (I) are important by-products emerging in the polymerization of 6-hexanelactam, in addition to open-chain macromolecules. The oligomers negatively affect properties of polyamides, and must be removed together with the unreacted monomer. On polymerization equilibrium, poly(6-hexanelactam) (PA-6) contains about 0.8–3.5% of cyclic oligomers, depending on the polymerization temperature (180–260°C)^{1,2}. More than half of the cyclics are represented by the cyclic dimer (1,8-diazacyclotetradecane-2,9-dione) and the cyclic trimer (1,8,15-triazacycloheneicosane-2,9,16-trione)².



I

The cyclic dimer and the cyclic trimer can exist in a few well-defined structural forms with different conformational structures, and thus can serve as suitable models of the

structures occurring in the amorphous and mesomorphous phases of polyamides³. Besides that, the cyclic oligomers exhibit some noteworthy physical and chemical properties, which can be caused by peculiarities of their molecular structure. The first member in the series, the cyclic dimer, has an extremely high melting point (344°C), while the melting points of the other cyclic oligomers in the series are lower by about 100°C. At the same time, the cyclic oligomers with an even number of amide groups have higher melting points than the nearest neighbours in the series with an odd number of these structure units⁴. The influence of the number of amide groups in the cycle is also reflected, e.g. in the solubility of the cyclic oligomers (solubility in water decreases in the order⁵: trimer ≫ dimer > tetramer) and in their chemical reactivity (the rate constants of acid hydrolysis decrease in the order⁶: trimer > tetramer ≫ dimer).

So far, only the structure of the cyclic dimer has been studied in detail. Two crystalline modifications of this compound were distinguished by Hermans⁷. The conformational structure of the molecule in the stable crystalline modification was determined in an X-ray crystallographic study⁸. It consists of two pairs of planar elements related by a symmetry centre. In our recent study using a combination of infra-red (i.r.), Raman and nuclear magnetic resonance (n.m.r.) spectroscopy and theoretical calculations³, an asymmetric molecular conformational structure was proposed for the high-temperature modification of the cyclic dimer.

This paper reports the isolation and spectral, as well as

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structural features of three crystalline forms of the cyclic trimer of 6-hexanelactam. The spectral and structural features of the cyclic trimer are compared to the cyclic dimer and to PA-6.

EXPERIMENTAL

Samples

The cyclic trimer of 6-hexanelactam was isolated from a mixture of monomer and oligomers obtained in the polyamide fibre production (Chemlon Humenné, Slovak Republic). After selective extraction of the monomer by trichloroethylene, the cyclic trimer was obtained by multiple fraction crystallization from water. It was identified by mass spectroscopy and, according to high pressure liquid chromatography (h.p.l.c.), its purity was 99.5%. The sample of the cyclic trimer prepared by slow crystallization from water solution is designated as A. Parts of this sample placed in an evacuated and sealed glass ampoule were heated for 15 min, either at 200°C (designated as sample B) or at 225°C (designated as sample C), and then cooled down in the air at room temperature. According to h.p.l.c. analysis, the samples A, B and C are chemically identical compounds. The sample of PA-6 was Spolamid (the product of Spolana, Czech Republic) prepared by alkaline polymerization of 6-hexanelactam; the solid-state n.m.r. spectra were reported in ref. 9.

Measurements

Differential scanning calorimetry (d.s.c.) measurements were performed using a Du Pont 2000 Thermal Analysis-d.s.c. cell instrument in the temperature range 20–260°C with a constant heating rate of 10°C min⁻¹ under nitrogen atmosphere. Before hermetic sealing, the d.s.c. cells were flushed with argon.

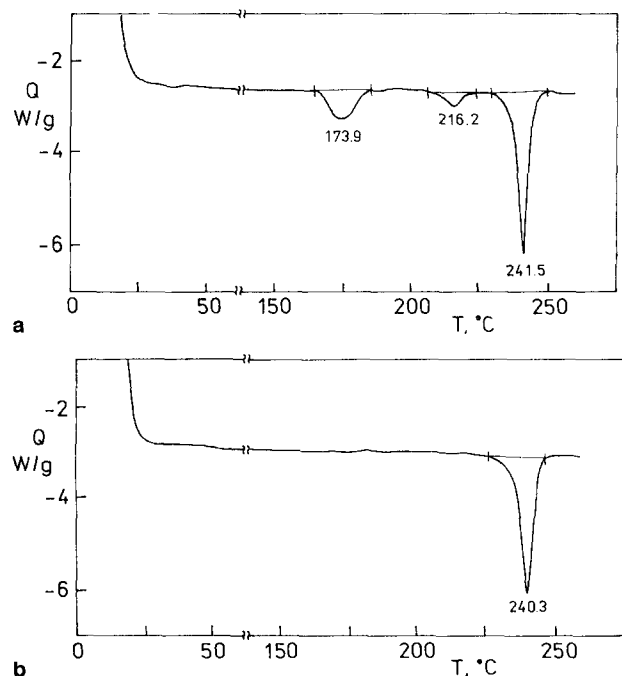


Figure 1 D.s.c. thermograms of the cyclic trimer of 6-hexanelactam: (a) sample A; (b) repeated measurement with the same sample after one week in a hermetically sealed ampoule

Wide angle X-ray scattering (WAXS) patterns were obtained using a powder diffractometer HZG/4A of Freiburger Präzisionsmechanik GmbH (Germany). Cu-K α radiation was used; diffracted radiation was recorded by means of a proportional counter.

I.r. and Raman spectra were measured on a Bruker IFS-55 Fourier transform i.r. spectrometer equipped with the Raman module FRA-106. Raman spectra were recorded at 2 cm⁻¹ resolution and the samples were excited by a 1064 nm diode-pumped Nd:YAG laser with a power of 400 mW at the sample. For the measurements of Raman spectra, the samples were used as prepared in glass tubes under vacuum. As grinding and pressing of the cyclic trimer tends to transform the crystalline modification A into high-temperature modifications, the KBr pellet technique is not suitable for the measurements of i.r. spectra. Therefore, the samples were measured in the form of suspensions in paraffin oil (Fluka AG), Voltalef 3S oil (Spectrosol) or in hexachloro-1,3-butadiene (Fluka AG) between KBr windows.

All high-resolution n.m.r. spectra of the studied substances in 2,2,2-trifluoroethanol (TFE) solution were recorded on a Bruker AC-300 spectrometer at resonance frequencies of 300.1 MHz for ¹H and 75.5 MHz for ¹³C, with a pulse angle of 30° and a pulse interval of 2.7 s in ¹H and 5.6 s in ¹³C measurements, in the temperature range 295–228 K. The solutions contained 20 mg of solute in 0.5 ml of solvent, with hexamethyl-disiloxane (HMDS) as internal standard. Acetone-d₆ in a concentric capillary was used for deuterium locking. All chemical shifts were referenced to internal HMDS (shifts δ with respect to TMS: 0.05 ppm for ¹H, 2 ppm for ¹³C).

Solid-state n.m.r. spectra were measured on a Bruker MSL 200 spectrometer at 50.3 MHz for ¹³C using a standard combination of cross-polarization (CP), dipolar decoupling (DD) and magic-angle-spinning (MAS)¹⁰. The MAS frequency was 4 kHz, the spectra were externally referenced to the signal of the carbonyl

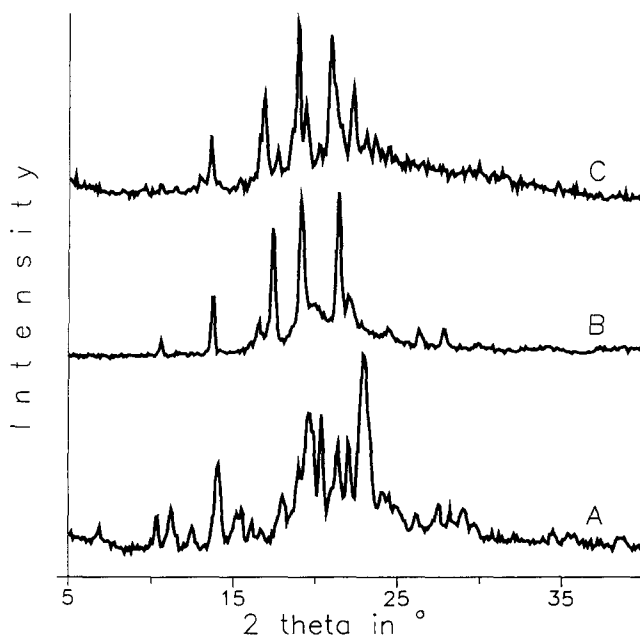


Figure 2 WAXS diffractograms of samples A, B and C of the cyclic trimer of 6-hexanelactam

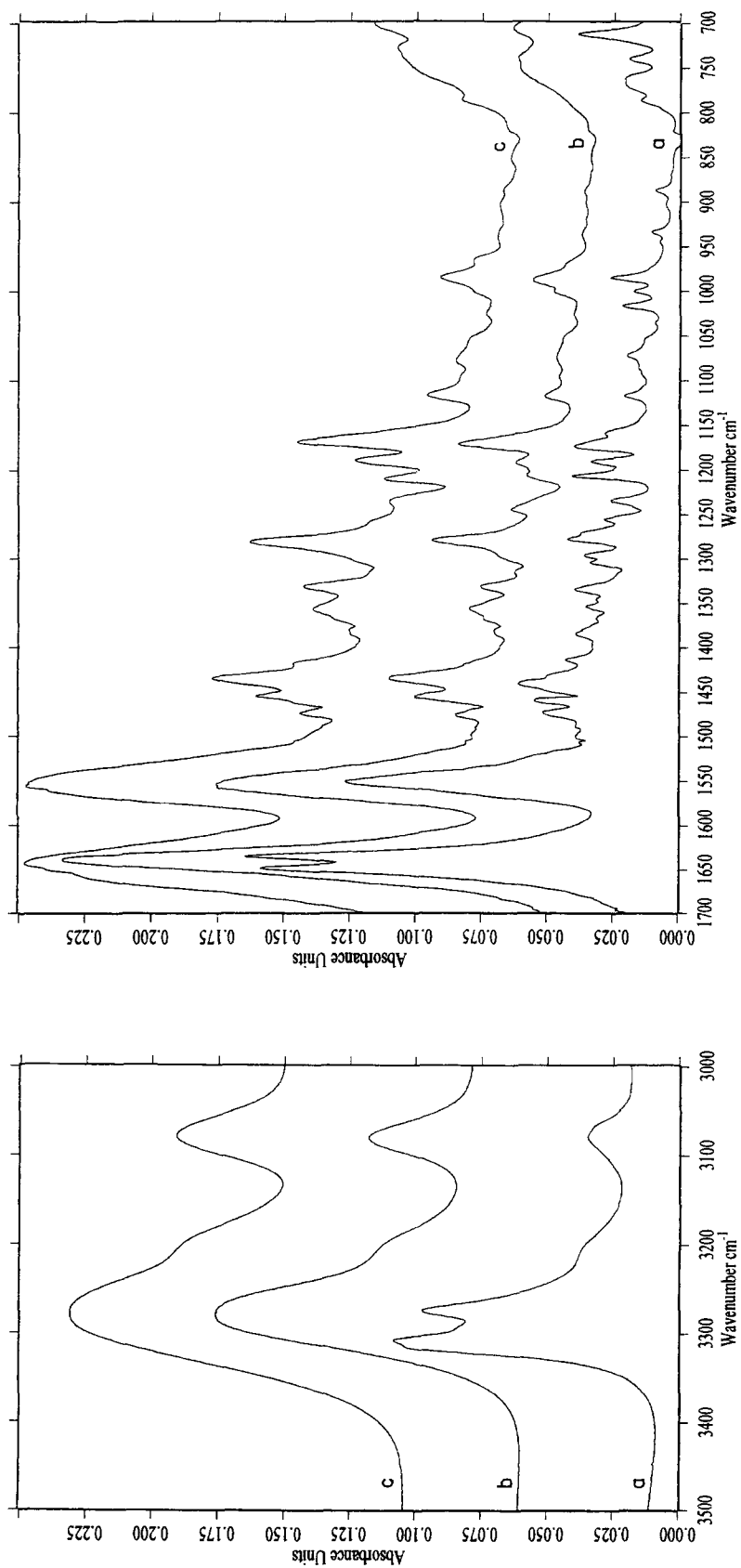


Figure 3 I.r. spectra of samples A, B and C of the cyclic trimer of 6-hexanelactam measured as suspension in paraffin oil (spectrum of paraffin oil is subtracted)

carbon of glycine ($\delta = 176.0$ ppm from TMS) by sample replacement. In addition to the conventional CP/MAS/DD spectra, the spectra emphasizing the amorphous and crystalline components were also measured using the procedures based on assumed differences in T_1^C relaxation, as previously applied to semicrystalline PA-6⁹. For revealing the amorphous component, measurements were carried out without CP, using 90° pulses at intervals of 1 s; for revealing the crystalline component, the method for T_1^C measurements with cross polarization¹¹ was applied, but spectra with too low signal-to-noise ratios were obtained.

RESULTS AND DISCUSSION

Differential scanning calorimetry and X-ray scattering

The d.s.c. thermogram of the cyclic trimer crystallized from water (sample A) shows three endotherms centred at 173.9, 216.2 and 241.5°C (*Figure 1a*). The endotherm centred at 241.5°C corresponds to the published melting point of the cyclic trimer of 6-hexanelactam⁴. After the thermal analysis, the sample of the cyclic trimer was left in the hermetically sealed ampoule at room temperature for 1 week. The d.s.c. thermogram of this sample (*Figure 1b*) shows only one endotherm corresponding to the melting point of sample A. The same result was obtained also in a repeated d.s.c. measurement with the sample stored for one week in an open ampoule in the presence of air humidity.

Direct microscopic observations during the heating of sample A (heating rate $\sim 10^\circ\text{C min}^{-1}$) showed a change in the crystal structure near 220°C. The original crystals, of rod shape, were transformed into plate crystals with sharp edges.

Sample B was analysed by d.s.c. first in the temperature range 20–200°C, 3 days after the sample preparation (no endotherm was observed). The d.s.c. thermogram measured with the same sample in the range 20–260°C, 6 days after sample preparation showed two endotherms at 219 and 241°C.

Similarly, no endotherm was detected in the d.s.c. measurements of sample C in the range 20–225°C, 3 days after preparation. In the repeated d.s.c. analysis in the range 20–260°C, performed 6 days after sample preparation, only one endotherm at 241°C, corresponding to the melting point, was observed.

From the WAXS diffractograms shown in *Figure 2* it follows that all three samples A, B and C are crystalline with crystallites larger than 40 nm. Positions of the crystal reflections indicate that A, B and C correspond to three different crystalline modifications.

The diffractogram of sample A shows a very dense series of the crystalline reflections. The profile analysis of the diffractogram indicates that this sample is completely crystalline.

In the diffractogram of sample C (*Figure 2*), the crystalline reflections are superimposed on a broad diffuse halo corresponding to the amorphous (disordered) phase of the cyclic trimer. The degree of crystallinity calculated as the ratio of the integral intensities of crystalline reflections to the total scattering is about 50%. This is a rough estimate due to the uncertainties of the scattering curve of the amorphous component.

The diffractogram of sample B exhibits, in the measured angular range, a considerably lower number of crystalline reflections compared to samples A and C. The density of the crystalline reflections is influenced by the symmetry of the crystalline unit cell and its size. In

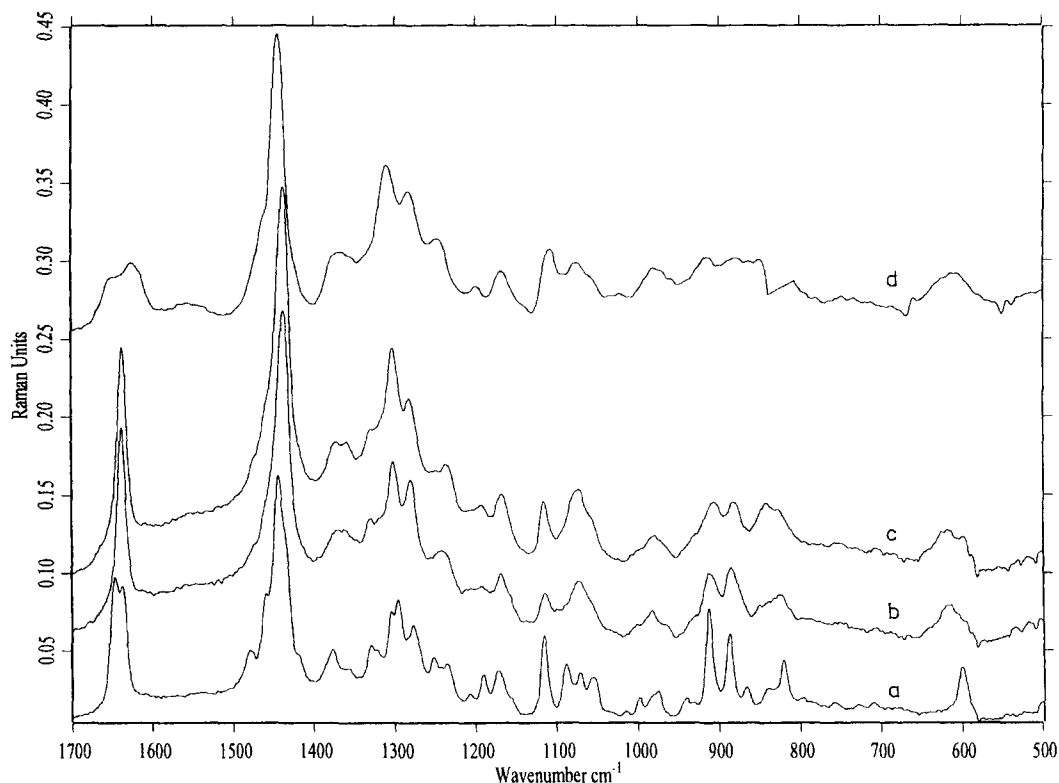


Figure 4 Raman spectra of the cyclic trimer of 6-hexanelactam: (a) sample A; (b) sample B; (c) sample C; (d) solution in trifluoroethanol (spectrum of the solvent is subtracted)

view of the fact that the samples A, B and C are chemically identical, it can be supposed that the crystalline modification B has a higher crystallographic symmetry. The crystallinity of sample B is about 70%.

Vibrational spectra

The i.r. and Raman spectra of the three modifications of the cyclic trimer are shown in Figures 3 and 4, respectively. The spectra of sample A differ markedly from the spectra of samples B and C, both in band wavenumbers and in band intensities, but only slight differences are seen between the spectra of B and C. In the spectrum of sample A, more bands are observed and they are narrower. In the i.r. spectra, a doublet at 1650 and 1636 cm^{-1} appears in the amide I region of sample A, while only one band at 1638 cm^{-1} can be observed in the spectra of samples B and C. Sharp peaks at 3317, 3306 and 3274 cm^{-1} in the N-H stretching region of sample A are replaced by a broad band at 3280 cm^{-1} in the spectra of samples B and C. Analogous features are observed in the amide I and N-H stretching regions of the Raman spectra (Figure 4). The bands at 1480, 1296, 1254, 1210, 1088, 1045 and 865 cm^{-1} in the Raman spectra and the bands at 1414, 1257 and 1017 cm^{-1} in the i.r. spectra are stronger in the spectra of sample A compared to samples B and C.

The observed differences in the spectra of samples A, B and C indicate that the conformational structure of the

trimer molecule in sample A is more complex and that the molecular conformations appearing in samples B and C are very similar.

The enthalpy difference between the *cis* and *trans* conformations in *N*-methyl-acetamide is about 2.3 kcal mol^{-1} according to the experimental data from the vibrational spectra of matrix-isolated molecules¹². The preference of the *trans* structure in the isolated amide groups is not too big, and therefore some *cis* conformations could appear in the cyclic trimer due to steric restrictions in the cycle, similar to those in the lactams with a small number (< 6) of CH_2 groups. However, vibrational spectra indicate that in the solid state the amide groups of the cyclic trimer all assume only the *trans* conformation. This conclusion is based on the intensity ratios of the amide II and amide I bands in i.r.¹³ and Raman spectra¹⁴. The ratio is ~ 0.5 in the i.r. spectra of all three samples A, B and C (Figure 3) and no amide II band is detected in Raman spectra of cyclic trimer in the solid state (Figures 4a-4c). Besides that, also the frequencies of the N-H stretching and amide I vibrations in the spectra of the solid cyclic trimer (Figures 3 and 4) agree with those of *trans* amide structures, while in the spectra of molecules with *cis* amide structure¹³ the former is lower by about 100 cm^{-1} and the latter is higher by about 20 cm^{-1} .

In the Raman spectra of the TFE solution of the cyclic

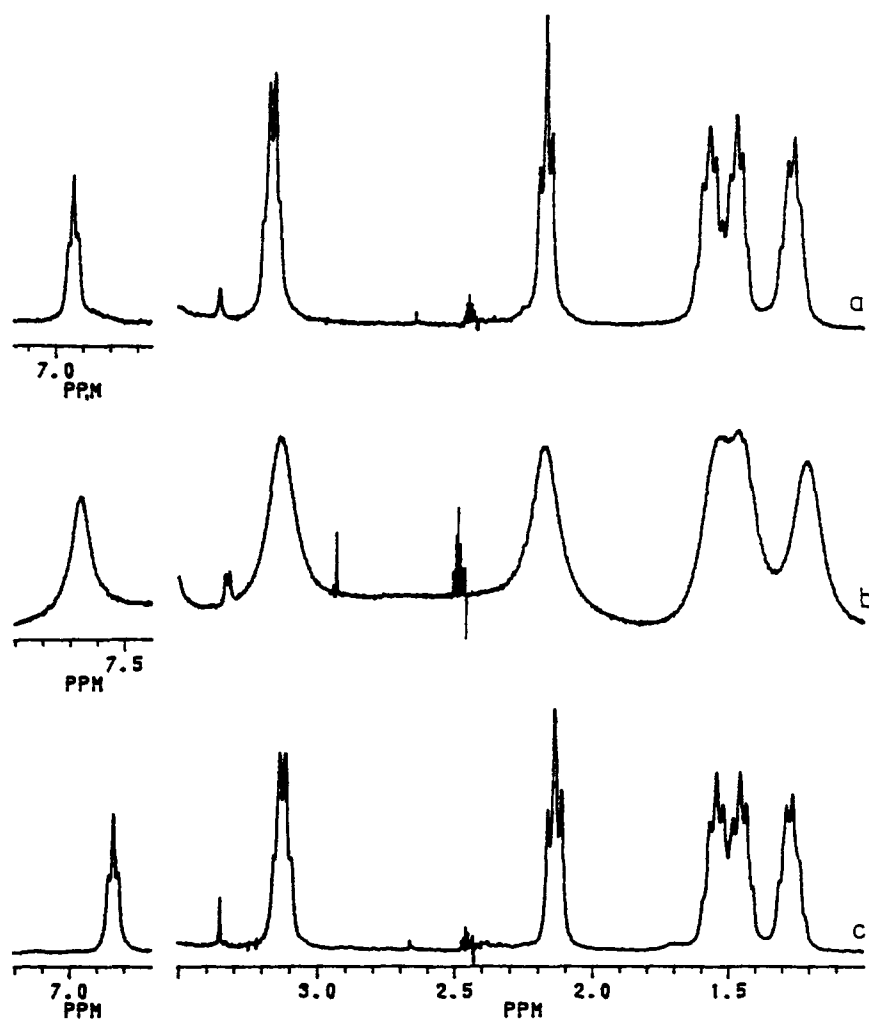


Figure 5 ^1H n.m.r. spectra of the cyclic trimer of 6-hexanelactam (a,b) and of PA-6 (c) in trifluoroethanol solution measured at 298 K (a,c) and 233 K (b)

trimer, a doublet (1625 and 1650 cm^{-1}) is observed in the amide I region, and the intensity of the amide II band at 1555 cm^{-1} is relatively high. This effect could indicate the presence of the *cis* amide structure in the solution, but more probably it is caused by strong hydrogen bonds of amide groups with TFE¹⁵.

High-resolution nuclear magnetic resonance spectra of solutions

The ¹H n.m.r. spectra of PA-6 and of the cyclic trimer are shown in Figure 5. We see that the room-temperature spectra are very similar. On cooling the solution of the trimer to the lowest accessible temperature in TFE, no new features are observed except for line broadening. The same may be stated of the ¹³C n.m.r. spectra shown in Figure 6. This indicates that the steric structure of the amide bond of the cyclic trimer in solution is the same as in the polymer, i.e. *trans*¹⁶. In the ¹³C spectrum, the broadening of the methylene carbon signals on cooling is much more pronounced than that of the carbonyl band. Disregarding a possible difference in the temperature dependence of the respective T₂ relaxation rates, we might conclude that the chemical shift of the carbonyl carbon does not much differ in various conformers of the cyclic trimer present in TFE solution, while the differences in the chemical shifts of the methylene carbons in various conformers are much larger. Also in ¹H n.m.r. spectra measured at a very low temperature, the width of the NH signal is smaller than that of the methylene proton signals, although the difference is less conspicuous.

Calculations of conformational structures

The permitted conformational structures of the isolated molecule of the cyclic trimer of 6-hexanelactam were studied by the semiempirical quantum-chemical methods AM1, PM3 and MNDO using the GAMESS set of programs^{17,18} running on a Silicon Graphics workstation Indy. A full optimization of all degrees of freedom was carried out using the gradient optimization routine in the program. The calculations were performed in C₁ symmetry.

We have calculated the enthalpy difference between the *cis* and *trans* conformations of the amide group for the linear molecule CH₃-CH₂-NH-CO-CH₂-CH₃ using the AM1 (-0.10 kcal mol⁻¹), PM3 (-0.48 kcal mol⁻¹) and MNDO (1.21 kcal mol⁻¹) semiempirical methods and the *ab initio* method with the 6-31G* basis set (2.45 kcal mol⁻¹). Comparison of the calculated values with available experimental data for aliphatic amides¹² (~ 2.0 kcal mol⁻¹) indicates that MNDO is the more suitable semiempirical method for the conformational analysis of the amides.

As vibrational and n.m.r. spectra indicate that only the *trans* amide structures are present in the cyclic trimer, in the following we do not consider trimer conformations with *cis* amide groups although, according to some semiempirical calculations, such conformations are energetically favoured.

Geometry optimizations of the cyclic trimer were run using different starting geometries of the methylene sequences and different mutual orientations of the amide groups. The most stable conformational forms of the cyclic trimer obtained by the semiempirical quantum-chemical

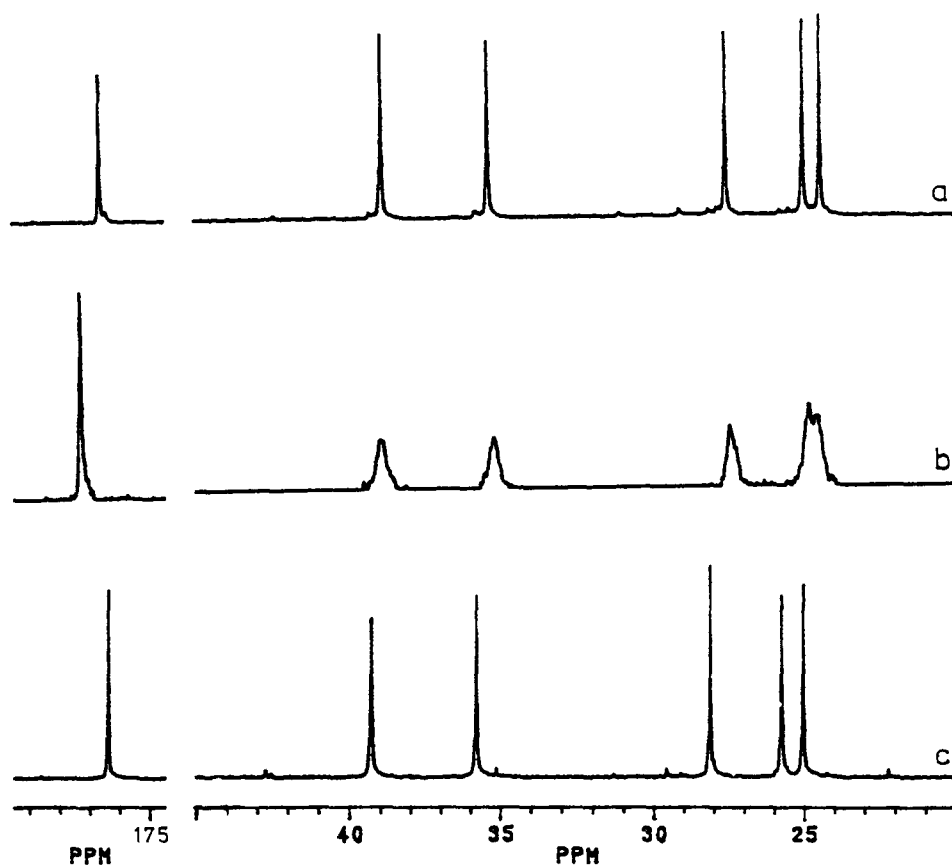


Figure 6 ¹³C n.m.r. spectrum of the cyclic trimer of 6-hexanelactam (a,b) and of PA-6 (c) in trifluoroethanol solution measured at 298 K (a,c) and 228 K (b)

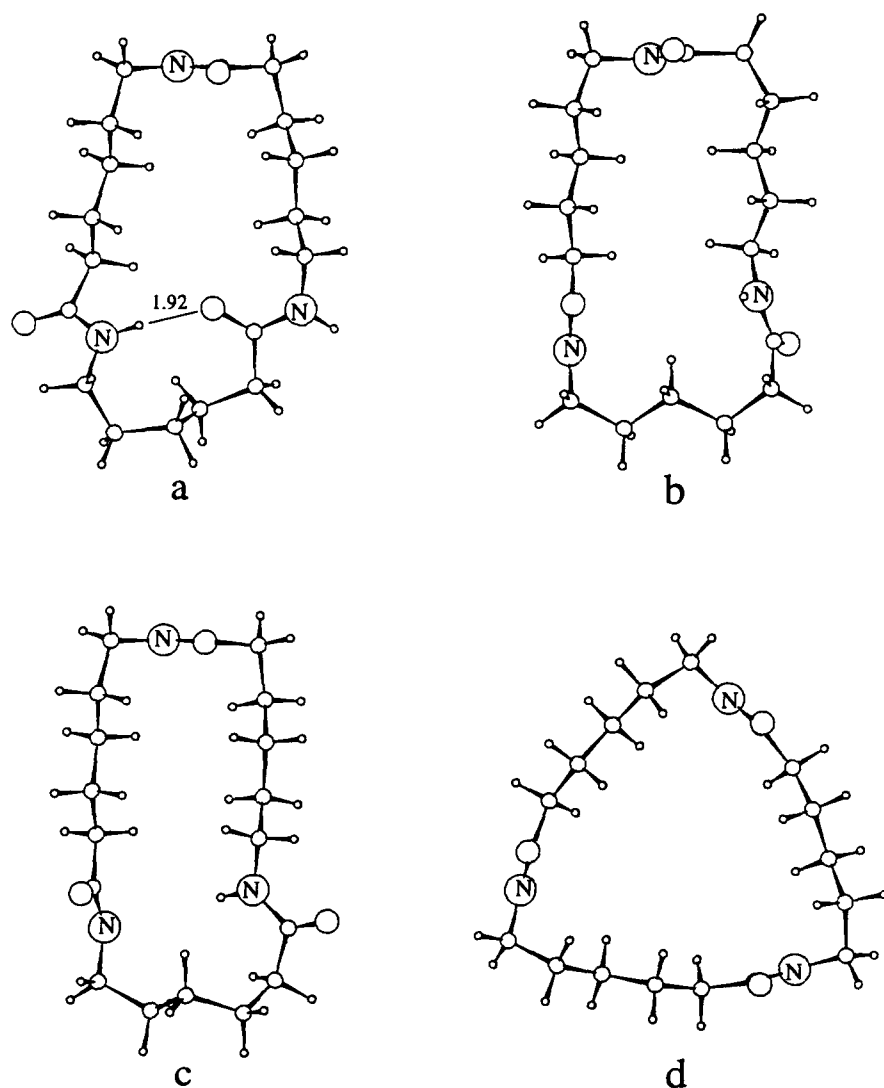


Figure 7 Energetically favoured conformational structures of the cyclic trimer of 6-hexanelactam obtained by the *ab initio* calculations with the 3-21G basis set: (a) the most stable structure stabilized by intramolecular hydrogen bonding; the other structures are less stable by 7.6 kcal mol⁻¹ (b), 10.0 kcal mol⁻¹ (c) and 10.7 kcal mol⁻¹ (d)

methods were further optimized using the *ab initio* method with the 3-21G basis set and they are given in *Figure 7*. The most stable structure shown in *Figure 7a* (total *ab initio* energy calculated with the 3-21G basis set is -1082.8222003 hartree) is stabilized by intramolecular hydrogen bonding; the other energetically favoured structures shown in *Figures 7b, 7c* and *7d* are less stable by 7.6, 10.0 and 10.7 kcal mol⁻¹, respectively. In all the structures the amide groups are planar and the methylene sequences have various conformations. Only the structure given in *Figure 7d* has a symmetry (C_3).

Solid-state nuclear magnetic resonance spectra

Conventional ¹³C CP/MAS/DD n.m.r. spectra of samples A, B and C of the cyclic trimer are shown in *Figures 8a–8c*. The spectrum in *Figure 8a* corresponds to the crystalline form A as sample A is fully crystalline according to the WAXS measurements. Samples B and C are semicrystalline and therefore, the spectra of samples B and C (*Figures 8b and 8c*) consist of mixtures of signals originating from the amorphous and crystalline phases.

In the ¹³C CP/MAS n.m.r. spectrum of sample A, eight bands and several shoulders are clearly distinguished in the region of the methylene carbons. The

spectra of samples B and C are much simpler. In the spectrum of sample C only four bands and one shoulder are observed (their chemical shifts are given in *Table 1*), and analogous bands with slightly different chemical shifts (*Table 1*) appear in the spectrum of sample B. In addition to those four bands, two shoulders at 41.0 and 25.6 ppm are detected in the spectrum of sample B (*Figures 8b*).

According to the WAXS measurements, samples B and C of the cyclic trimer contain considerable amounts of amorphous phases and are thus similar to semicrystalline polymers. Therefore, with samples B and C we have used the procedures usual for a separate measurement of the ¹³C n.m.r. spectra of the amorphous and crystalline phases in semicrystalline polymer systems^{9,19}. The spectra emphasizing the amorphous components of samples B and C are shown in *Figures 8d and 8e*, respectively. A comparison of the conventional CP/MAS n.m.r. spectrum of sample B with the spectrum of its amorphous component indicates that the shoulder at 41.0 ppm observed in *Figure 8b* originates from the amorphous phase, similarly to the shoulder at 25.6 ppm. This is further confirmed by the spectral subtraction of the amorphous component (*Figure 8d*) from the CP/

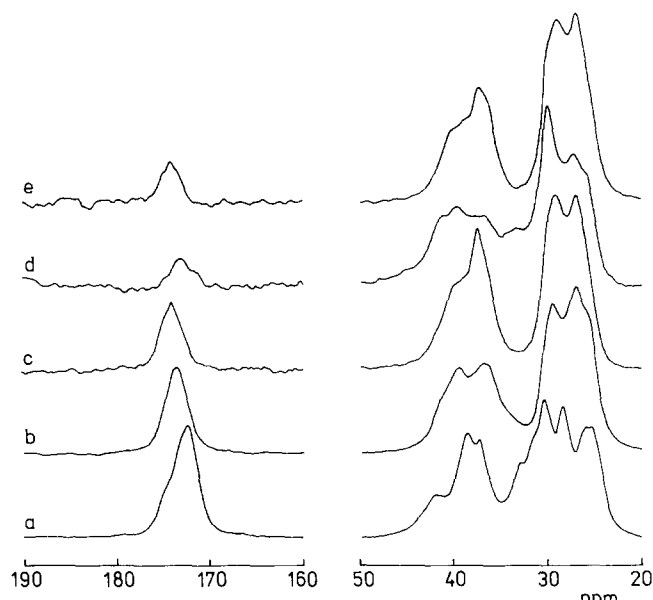


Figure 8 Solid-state ^{13}C n.m.r. spectra of the cyclic trimer of 6-hexanelactam: conventional CP/MAS/DD spectra of samples A (a), B (b) and C (c); spectra of samples B (d) and C (e) measured with single-pulse excitation with a relaxation delay of 1 s

MAS spectrum (Figure 8b). The differences in the spectra emphasizing the amorphous components of samples B and C (Figures 8d and 8e) suggest that similarly to polymers, the structure of the amorphous phase of the cyclic trimer depends on the thermal history of the sample.

The fact that only four distinguished bands appear in the n.m.r. spectra of the crystalline components of samples B and C indicates that the corresponding carbons C2–C6 in the three methylene sequences of the cyclic trimer molecule are equivalent and the molecules must have some type of symmetry (C_3). The molecular symmetry of the basic crystalline structure A is evidently lower and individual methylene sequences in the cyclic trimer exhibit different conformations.

We have made a tentative assignment of the bands in the ^{13}C CP/MAS n.m.r. spectra of the crystalline forms A, B and C in analogy to other amide compounds with five CH_2 groups in the structure unit for which the

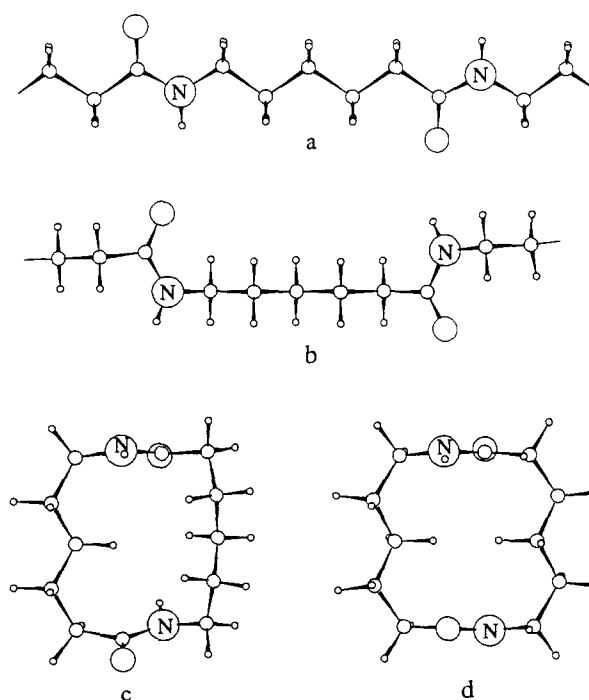


Figure 9 Conformational structures in the α -crystalline (a) and γ -crystalline (b) forms of PA-6 and in the high-temperature (c) and low-temperature (d) crystalline modifications of the cyclic dimer of 6-hexanelactam

crystalline structure and peak assignments are available, i.e. the α - and γ -crystalline forms of PA-6^{9,20} and two crystalline forms of the cyclic dimer of 6-hexanelactam³ (Table 1).

Analysis of the spectra of the α - and γ -crystalline forms of PA-6 showed^{20,21} that while the chemical shift of carbon C1 is strongly influenced by hydrogen bonding, the shifts of carbons C2–C6 are primarily affected by the conformational structures of the polymer chains; this is in agreement with the results of the temperature dependences of the ^1H and ^{13}C n.m.r. spectra of their TFE solutions (Figures 5 and 6). For carbons C2 and C4, conformations affect the chemical shifts by way of the γ -gauche interactions²², while the shifts of carbons C3 and C5 are influenced, besides by the

Table 1 ^{13}C n.m.r. chemical shifts (ppm from TMS) in the n.m.r. spectra of the cyclic dimer and cyclic trimer of 6-hexanelactam and of poly(6-hexanelactam)

	C1	C2	C3	C4	C5	C6
<i>Solid state</i>						
PA-6 α -form ^a	172.6	36.1	25.8	29.7	29.7	42.4
PA-6 γ -form ^a	172.2	37.1	29.7	29.7	33.7	38.6
PA-6 amorph. ^a	172.7	36.6	26.4	28.1	29.2	39.3
Dimer A ^b	174.7	36.4	25.9	26.9	30.9	39.0
Dimer B ^b	174.8	36.3	25.8	26.7	30.7	39.4
	171.7	37.0	29.8		34.2	
Trimer A	174.8	37.3	— ^c	— ^c	32.8	41.8
	172.3	36.0			31.5 ^c	38.5
Trimer B	173.5	36.7	27.0	29.3	30.4	39.6
Trimer C	174.2	37.6	26.8	29.4	30.0	40.4
<i>TFE solution</i>						
PA-6	178.4	37.8	27.1	27.8	30.1	41.3
Trimer	178.6	37.4	26.4	27.0	29.6	40.9
Dimer	178.8	37.4	26.5	26.6	29.7	40.5

^a Taken from the spectra shown in ref. 9

^b Taken from ref. 3

^c Bands observed in the region 25–31 ppm (25.3, 25.7, 26.3, 28.2 and 30.3 ppm) cannot be unequivocally assigned to the carbons C3, C4 or C5

γ -gauche effect, mostly by the positions of the neighbouring CH₂ groups with respect to the plane of the amide group²⁰. From Table 1 it can be seen that the rotation of the amide group in PA-6 from the position parallel to the neighbouring CH₂-CH₂ bonds (in the α -crystalline form, Figure 9a) into the perpendicular position (in the γ -crystalline form, Figure 9b) is reflected in the positions of the C3 and C5 carbon peaks shifted by 4 ppm to higher ppm values. The chemical shift of carbon C6 is affected only slightly by changes in conformational structure.

A comparison of the peak positions in the ¹³C n.m.r. spectra of the low-temperature (A) and high-temperature (B) crystalline forms of the cyclic dimer (Table 1) with the proposed conformational structures of the dimer molecule^{3,9}, shown in Figure 9, supports the above interpretation of the relationship between the carbon chemical shifts and local conformational structures.

On the basis of those data we can tentatively assign all peaks in the ¹³C n.m.r. spectra of the crystalline forms B and C of the cyclic trimer to the individual methylene carbons (Table 1). In the spectrum of form A, the peaks at 36.0, 37.3, 38.5 and 41.8 ppm are assigned to carbons C2 and C6 (Table 1). The peaks at 32.8 and 31.5 ppm can be assigned to carbon C5; the other peaks in the region 25–31 ppm originate from carbons C3, C4 and C5, but a more precise assignment is not possible by using hitherto available experimental data.

CONCLUSIONS

D.s.c. and WAXS measurements of the cyclic trimer of 6-hexanelactam showed that besides the basic crystalline form A obtained by slow crystallization from water solution, two other crystalline forms of the cyclic trimer appear in samples B and C prepared by heating sample A above the transition temperatures at 174 and 216°C, respectively. According to WAXS, sample A is completely crystalline, whereas samples B and C contain considerable amounts of amorphous phase (~50%). All crystalline forms A, B and C are stable at room temperature. By solid-state n.m.r. evidence, the amorphous phases differ in samples B and C, indicating that the structure of the amorphous phase in the cyclic trimer depends on the thermal history of the sample, similarly to polyamides. Analysis of vibrational and n.m.r. spectra showed that in all three crystalline modifications, the amide groups assume the *trans* form. The temperature dependence of solution n.m.r. spectra indicates that the chemical shifts of CH₂ groups are strongly dependent on conformational structure, and that in a common solvent (TFE) the mean conformational structure of the cyclic trimer is similar to the mean conformational structure of PA-6.

In CP/MAS n.m.r. spectra of crystalline form A, twelve partially resolved bands appear in the range 25–42 ppm: this shows that each of three monomeric units in the cyclic trimer has a different conformational structure. The positions of the individual bands indicate that in these structures, the conformations in the neighbourhood of the amide bonds are the same as those appearing in the α - and γ -crystalline forms of PA-6. The occurrence of such a complex, unsymmetrical conformational structure of the cyclic trimer is confirmed in i.r. and

Raman spectra of form A by the appearance of bands corresponding to three types of hydrogen bonds.

Although the WAXS evidence and microscopic observation of the crystal shape suggest that forms B and C are crystallographically different, according to vibrational and n.m.r. spectra the conformational structure of the cyclic trimer in both these forms is very similar. The circumstance that 15 CH₂ groups of the cyclic trimer are manifested by only four resolved bands in ¹³C CP/MAS n.m.r. spectra indicates the equivalence of the three monomeric units, and thus molecular symmetry C₃. Only one such stable conformational structure of C₃ symmetry was found by semiempirical and *ab initio* calculations (Figure 7d), and the band positions in n.m.r. spectra are in agreement with this structure. The proposed symmetrical conformational structure is supported by the i.r. and Raman spectra of samples B and C, where only a single broad band appears in the range of N–H stretching vibrations, indicating a single type of hydrogen bonds.

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