CONFORMATIONAL STRUCTURE OF *N*-METHYL-8-OCTANELACTAM AND POLY(*N*-*M*ETHYL-8-OCTANELACTAM) AS STUDIED BY NMR, INFRARED AND RAMAN SPECTROSCOPY AND BY THEORETICAL CALCULATIONS

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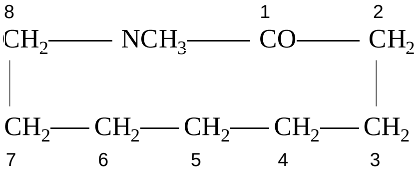
Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

It was proved by ^{1}H and ^{13}C NMR spectra that in *N*-methyl-8-octanelactam in $CDCl_3$ solution, the amide bond assumes only the cis form. Mirror inversion about the plane of the amide bond occurs with an activation enthalpy $\Delta H^{\#}$ = 44.7 kJ/mol. Molecular mechanics and quantum mechanical calculations yielded four favoured conformational structures for the isolated molecule. By vibrational spectra, one of two distinguishable structures strongly predominates. From ^{1}H NMR spectra, this predominant conformation was identified with one of the calculated stable forms. By ^{13}C NMR evidence, poly(*N*-methyl-8-octanelactam) in tetrachloroethane solution contains equal populations of the cis and trans amide forms; the structure of this polymer in the rubbery solid state seems to be similar to its structure in solution.

In our studies of *N*-methyl-12-dodecanelactam, a combination of NMR and vibrational spectroscopy with theoretical calculations was used for the determination of the conformational structures of the amide group and of neighbouring methylene sequences[1–3]. Using these results, conformational structure of the chains in semicrystalline poly(*N*-methyl-12-dodecanelactam) could be determined[3]. In this paper we use a similar approach in the structural analysis of poly(*N*-methyl-8-octanelactam) and *N*-methyl-8-octanelactam (*I*) as a model.



I

The aim of this work was to determine conformational preferences on the amide and neighbouring bonds, together with the assignment of the signals in liquid-state ^{13}C NMR spectra which served as an aid in the assignment of solid-state high-resolution NMR spectra and structure determination of the corresponding amorphous polymer.

EXPERIMENTAL

N-Methyl-8-octanelactam was synthesized from 8-octanelactam (BASF) by methylation with dimethyl sulfate[4] and purified to 99.95% (GC) by distillation on a rotary-spiral Nester–Faust column (40 TP) at 101 °C and 130 Pa.

Polymerization of *N*-methyl-8-octanelactam (12.8 mmol) was initiated with octanoic acid (0.26 mmol) and carried out at 260 °C for 240 h in an ampoule sealed under nitrogen. The yield of polymer obtained by the HPLC determination of the remaining monomer was 98.7%. The concentration of carboxylic end groups, analyzed by conductometric titration, corresponded to the degree of polymerization 0.49.

Solution (liquid-state) NMR spectra were recorded on a Bruker ACF-300 spectrometer, at resonance frequencies of 300.1 MHz for ^{1}H and 75.5 MHz for ^{13}C. The studied lactam was measured as ≈10% solution in $CDCl_3$, the polymer in 1,1,2,2-tetrachloro(1,2-$^{2}H_2$)ethane (TCE). All chemical shifts are referenced to internal hexamethyldisiloxane (HMDS; δ shifts with respect to TMS: 0.05 ppm for ^{1}H, 2 ppm for ^{13}C). The pulse angle was 30°, and the pulse interval was 4.5 s in ^{1}H and 6.5 s in ^{13}C measurements.

^{1}H-^{1}H COSY spectra[5] were measured at 300 MHz with 1 024 points and 256 increments, with zero filling to 512 points and 16 scans per increment. Sinebell weighting functions in both dimensions were used before FT, and symmetrization procedure was applied to the final spectrum. ^{1}H-^{13}C COSY (HETCOR) spectra[6] were measured at 75.5 MHz with 4 096 points and 400 scans per increment; 128 increments with zero filling to 256 points. The relaxation delay was 1 s, the polarization transfer delays were 3.9 and 1.95 ms.

Infrared and Raman spectra were recorded on a Bruker IFS-55 FT-IR spectrometer equipped with the Raman module FRA-106. Low-temperature IR spectra were measured using a RIIC variable temperature cell. Raman spectra were recorded at 2 cm^{-1} resolution and the samples were excited by a 1 064 nm diode-pumped Nd : YAG laser at a power of 400 mW at the sample. Low-temperature spectra were measured using a Bruker variable temperature Raman glass cell.

Solid-state NMR spectra were measured on a Bruker MSL 200 spectrometer at 50.3 MHz (^{13}C) using the standard combination of dipolar decoupling (DD) and magic-angle spinning (MAS) with and without cross polarization (CP) with experimental parameters conventional for amorphous polymers[7]. The spectra were externally referenced to the signal of the carbonyl carbon of glycine (δ = 176.0 ppm) by sample replacement. As poly(*N*-methyl-8-octanelactam) is not quite solid it had to be measured in KEL-F rotors of our own construction[8] at spinning rates not exceeding 3 000 s^{-1}.

RESULTS AND DISCUSSION

NMR Spectra

The ^{1}H-^{13}C HETCOR spectrum of *I* measured in $CDCl_3$ solution at room temperature is shown in Fig. 1, together with the peak assignment which for the proton spectrum follows from a ^{1}H-^{1}H COSY experiment. Contrary to the previously studied *N*-methyl-

12-dodecanelactam[1,2], both the ^{1}H and the ^{13}C spectra measured at room temperature show a single N–CH_3 peak, corresponding to only one, presumably the cis form of amide, as expected.

The high-resolution ^{1}H NMR spectra of *I* measured at various temperatures are shown in Fig. 2. At room temperature, the signals of protons on carbons 2 and 8 are multiplets, with fine structure of AA′XX′ type[9]; this indicates equalization of ^{1}H chemical shifts of the two protons on each carbon by rapid mirror inversion about the plane of the amide bond. The vicinal coupling constants remain nonequivalent, with $J_{AX} = 9.15$ Hz; $J_{AX}' = 3.25$ Hz for signal 2, and $J_{AX} \geq 7.4$ Hz; $J_{AX}' \leq 4.4$ Hz for signal 8.

With decreasing temperature, the fine structure of signal 8 first disappears, and the peak splits into two at the lowest temperatures. The signals of groups 3, 4, 6 and 7 also undergo broadening and splitting, while the signals of groups 2 and 5 only lose their fine structure, but remain relatively sharp. This indicates that the chemical shift difference between the two protons on carbon 2, and also on carbon 5 is small, if any, in each of the limiting mirror forms. The fine structure of signal 5 is conspicuously symmetrical at room temperature and below, but some of this symmetry is lost at +60 °C.

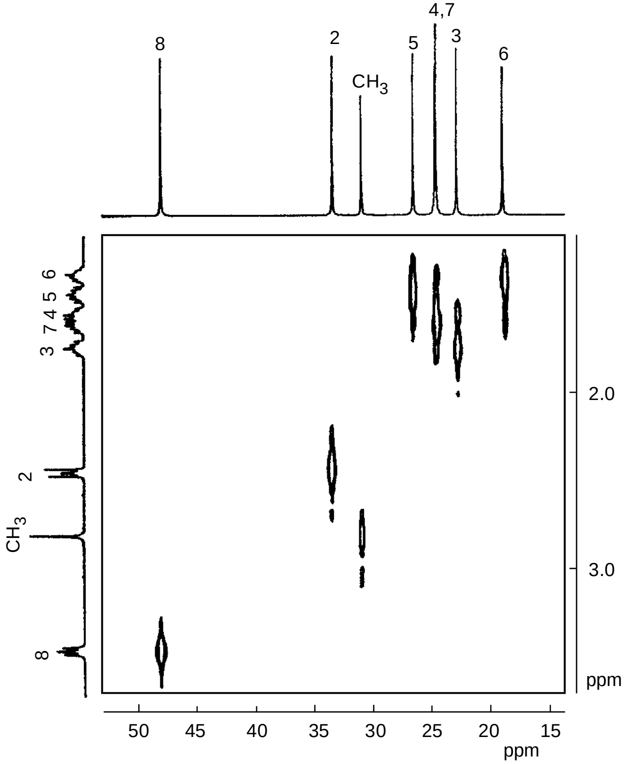


FIG. 1
^{1}H-^{13}C HETCOR spectrum of *I* in $CDCl_3$ solution at 25 °C

The barrier to the mirror inversion was estimated from the broadening and splitting of signal 8 by comparing the experimental line shapes with those simulated by means of the relation[10]

$$S(\omega) = \mathrm{Im}\{-\mathrm{i}C\tau[2p_1p_2 - \tau(p_1\alpha_2 + p_2\alpha_1)]/(p_1p_2 - \tau^2\alpha_1\alpha_2)\} \ , \qquad (1)$$

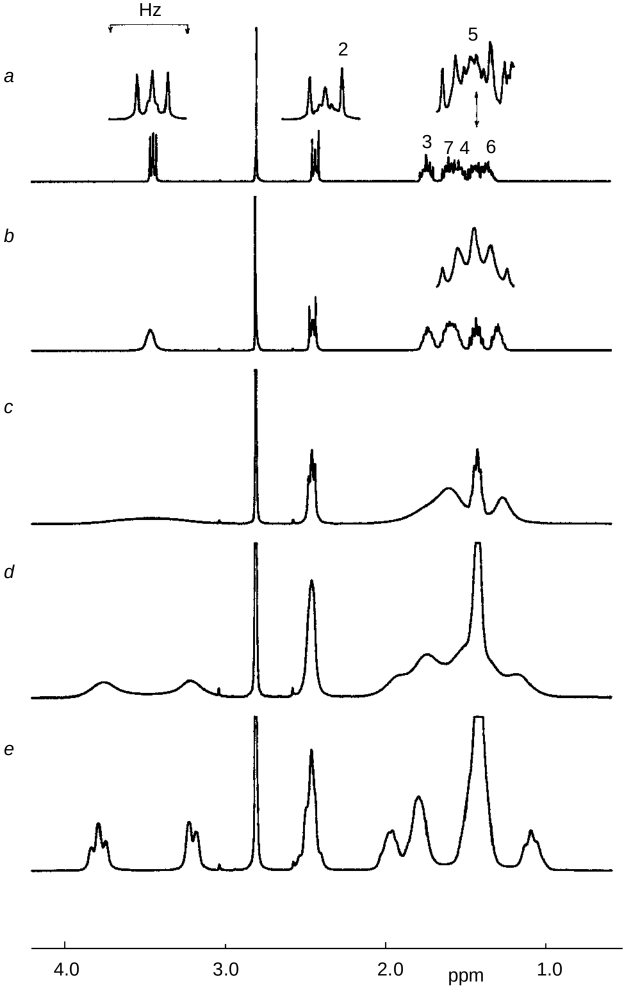


FIG. 2
^{1}H NMR spectra of *I* in $CDCl_3$ solution at: *a* 60 °C; *b* –3 °C; *c* –33 °C; *d* –43 °C; *e* –60 °C. The shift scale for all expanded spectra is shown in Fig. 2*a*. The intensity scales for various spectra were individually adjusted

where p_1, p_2 are the populations of the two mirror forms and $\alpha_1 = -[i(\omega_1 - \omega) + 1/T_2 + p_2/\tau]$, with $p_1 = p_2 = 1/2$, $T_2 = 0.1$ s, and $\tau_1 = \tau_2 = 2\tau = k^{-1}$. The rate constant of the mirror inversion, k, is related to the activation enthalpy by means of the Eyring equation

$$\ln\left(\frac{kh}{k_B T}\right) = -\frac{\Delta H^{\#}}{RT} + \frac{\Delta S^{\#}}{R} \ , \qquad (2)$$

where k_B and h are the Boltzmann and Planck constants, and the other symbols have their conventional meaning. From the line shapes between –23 and –43 °C (250–230 K), $\Delta H^{\#}$ is estimated as equal to 44.7 kJ/mol.

At –60 °C, the low-field component of signal 8 appears as a triplet, the high-field component as a doublet of relatively broad lines, with a splitting of ca 13.5 Hz. Each of the corresponding protons must be coupled to one geminal and two vicinal protons; thus for the proton resonating at low field, one of the vicinal couplings must be comparable to the geminal coupling, and the other must be small; for the proton resonating at high field, both vicinal couplings must be small and lost in the line width.

Infrared and Raman Spectra

Raman spectra of neat *I* measured at 25 °C and –140 °C are shown in Fig. 3. It is seen that weak bands at 581, 502 and 343 cm^{-1} observed in the spectrum at 25 °C are not detected in the spectrum measured at –140 °C. This indicates that at least two distinguishable conformational structures are present in liquid *I* at room temperature, and the bands mentioned above correspond to the conformationally sensitive vibrational modes of a less stable structure of *I*.

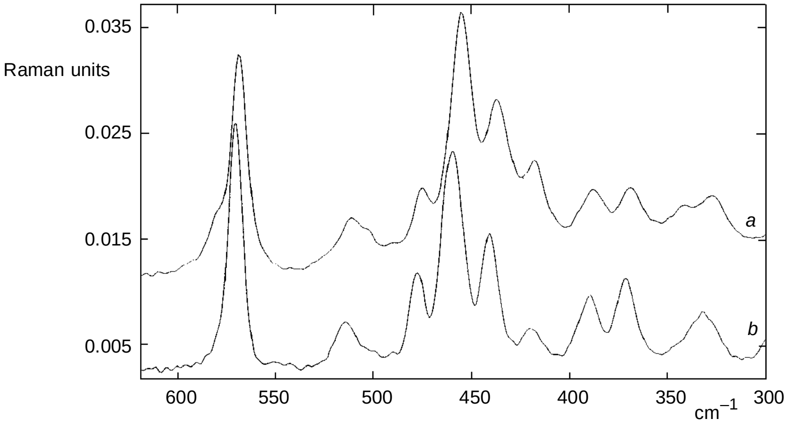


FIG. 3
Raman spectra of neat *I* at 25 °C (*a*) and –140 °C (*b*)

Infrared spectra of a 5% solution of *I* in $CHCl_3$ were measured in the temperature range from 25 °C to –140 °C (Fig. 4). It can be seen that with decreasing temperature of the sample the intensities of the bands at 1 156 and 1 094 cm^{-1} decrease while those of the bands at 1 162, 1 033 and 986 cm^{-1} increase; these temperature changes of the band intensities probably correspond to the population changes of conformational structures of *I* detected in Raman spectra. From Fig. 4 it can be seen that intensity changes of the bands appearing in the spectra of the solution in the liquid state (Figs 4*a*–4*d*) continue at temperatures below the freezing point of $CHCl_3$. This indicates that the equilibration of the conformational structures of *I* is relatively fast also for molecules of *I* embedded in the matrix of solid chloroform.

Assuming the presence of only two conformational structures, the enthalpy difference ΔH can be determined from the plot of ln *K* versus 1/*T* according to the equation

$$\ln K = \Delta H/RT - \Delta S/R \ , \qquad (3)$$

where *K* is the ratio of the band absorbances and ΔS is the entropy change. It is assumed that ΔH is not a function of temperature. The integrated intensities of the overlapping bands in the doublet at 1 162 and 1 156 cm^{-1} were obtained by a least-squares separation using the Bruker program OPUS. Based on the slope of the plotted data, a value of 3.3 kJ/mol was obtained for ΔH. Using ΔH it can be estimated that the popu-

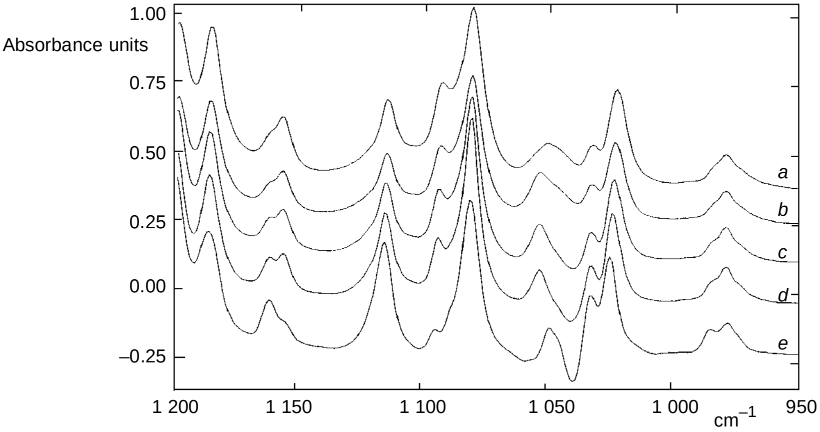


FIG. 4

Infrared spectra of *I* in $CHCl_3$ solution (0.05 g/ml) at: *a* 25 °C, *b* 0 °C, *c* –25 °C, *d* –50 °C, *e* –140 °C. Bands of the solvent are subtracted lation of the less stable conformer of *I* at 25 °C is approximately 20%. This is in good agreement with an estimated value which can be obtained from the intensity ratios of the bands in the conformationally sensitive doublets in the Raman spectra.

Calculations of the Conformational Structures

The conformational structures of isolated molecule *I* were studied by a molecular mechanics method (MM2 force field[11]), by the semiempirical AM1 molecular orbital calculations[12] and by the *ab initio* calculations[13,14] with the 3-21G basis set. Stable structures of *I* were found by a detailed inspection of the potential energy surface using different starting geometries both with the cis and trans forms of the amide group. A full optimization of all degrees of freedom was carried out.

Several structures of *I* differing in conformation of the methylene sequences were found both for the cis and trans forms. Stable conformational structures found for *I* with cis amide group are shown in Fig. 5. The calculated molecular parameters for the fa-

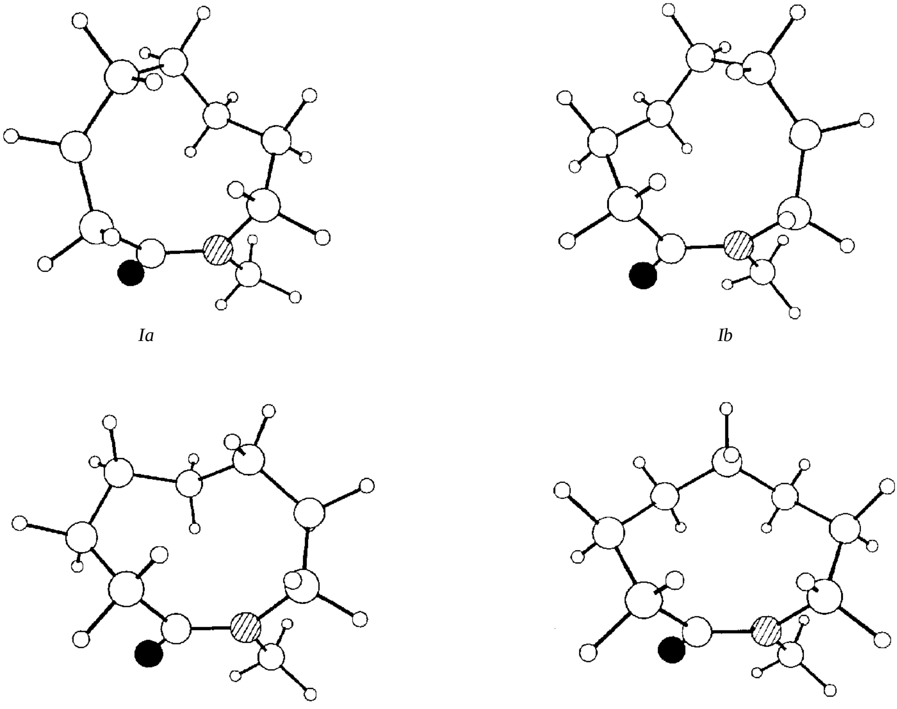

Ia *Ib* *Ic* *Id*

FIG. 5

Ab initio optimized geometries of stable cis forms *Ia*, *Ib*, *Ic* and *Id* of *N*-methyl-8-octanelactam obtained with the 3-21G basis set voured conformational structures of *I* are summarized in Table I. For the trans form of *I*, structures analogous to the cis form (Fig. 5), with similar conformations of the methylene sequences, were predicted by the calculations. As the heats of formation of

TABLE I
Calculated molecular parameters of the stable structures of *N*-methyl-8-octanelactam (*I*) with cis amide group

Parameter		*Ia*	*Ib*	*Ic*	*Id*
			Heat of formation (kJ/mol)		
MM2		–298.49	–293.02	–288.13	–286.00
AM1		–256.86	–253.48	–256.69	–249.76
			Relative energy[a] (kJ/mol)		
3-21G		0.0	0.95	4.19	6.18
			Torsion angle θ[b]		
C_2–C_3	H_1,H_3	82(0.02)	53(0.36)	81(0.02)	45(0.50)
	H_1,H_4	163(0.91)	169(0.96)	163(0.91)	162(0.90)
	H_2,H_3	35(0.67)	66(0.17)	37(0.64)	72(0.10)
	H_2,H_4	75(0.04)	50(0.41)	78(0.04)	44(0.52)
C_8–C_7	H_1,H_3	49(0.43)	83(0.01)	71(0.11)	42(0.55)
	H_1,H_4	165(0.93)	163(0.91)	173(0.99)	158(0.86)
	H_2,H_3	67(0.15)	33(0.70)	46(0.48)	73(0.09)
	H_2,H_4	48(0.45)	82(0.02)	70(0.12)	42(0.55)
C_5–C_4	H_1,H_3	55(0.33)	62(0.22)	90(0.00)	114(0.17)
	H_1,H_4	59(0.27)	177(1.00)	26(0.81)	129(0.40)
	H_2,H_3	170(0.97)	53(0.36)	155(0.82)	1(1.00)
	H_2,H_4	55(0.33)	62(0.22)	89(0.00)	115(0.18)
C_5–C_6	H_1,H_3	60(0.25)	53(0.36)	130(0.41)	117(0.21)
	H_1,H_4	175(0.99)	61(0.24)	15(0.93)	127(0.36)
	H_2,H_3	55(0.33)	168(0.96)	114(0.17)	1(1.00)
	H_2,H_4	60(0.25)	54(0.35)	131(0.43)	117(0.21)

[a] With respect to the global minimum *Ia* at –477.3652749 hartree. [b] Dihedral angle between vicinal C–H bonds in the bond sequence (H_1,H_2)–C_j–C_k–(H_3,H_4) as calculated with the 3-21G basis set; the value of $\cos^2 \theta$ is given in parentheses.

the trans structures are higher by more than 25 kJ/mol (MM2) compared to the most stable geometry of *I*, they are not considered in the following discussion.

Correlation of Calculated Structures of I *with Spectroscopic Data*

According to infrared and Raman spectra, of the four conformational structures favoured by theoretical calculations, probably only two distinguishable forms are actually present at room temperature; at temperatures near to the freezing point of chloroform, one of these two forms predominates very strongly.

The structure of the preferred conformer should correlate with the main features of NMR spectra; of these, the vicinal coupling patterns in ^{1}H NMR spectra are the most important. As the exact form of the dihedral angle dependence of the vicinal coupling constants in *I* is unknown, these constants were only interpreted in terms of a simple $A \cos^2 \theta$ relation. The $\cos^2 \theta$ values for the relevant vicinal angles are included in Table I.

For the protons on carbon 8 at low temperature, the pattern characteristic of a "frozen" mirror form exhibits one large and one small coupling for one proton, and two small couplings for the other. From Table I, this situation is consistent with structures *a* and *c*, hardly with *d* and certainly not with *b*.

At high temperature, where rapid equilibration of the two mirror forms occurs, the difference between the averaged vicinal couplings, $J_{AX} = 1/2(J_{12} + J_{34})$ and $J_{AX}' = 1/2(J_{13} + J_{24})$ is larger for the protons on carbon 2 and smaller for those on carbon 8. From Table I, structures *a* and *c* would be expected to show such behaviour.

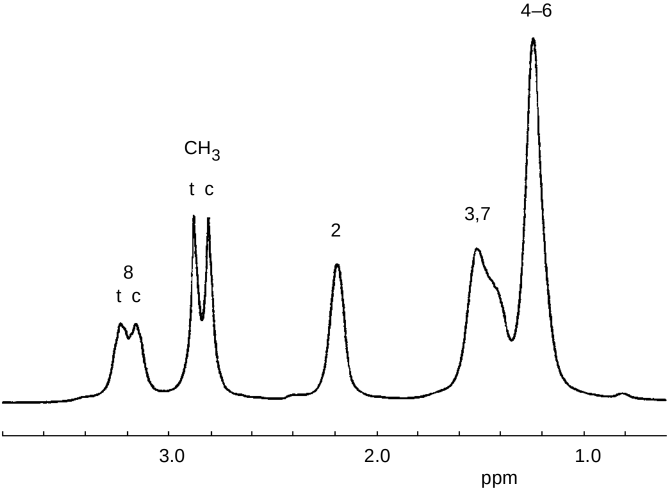


FIG. 6
^{1}H NMR spectrum of poly(*N*-methyl-8-octanelactam) in TCE solution at 25 °C

At room temperature and below, the coupling pattern of the protons on carbon 5 is conspicuously symmetrical, indicating similar coupling to protons on carbons 4 and 6. From Table I, this would occur in structure *a*.

The chemical shift difference of the protons on carbons 2 and 5 remains very small at all temperatures. By inspection of models, this seems plausible for both proton groups only in form *a*, even in its "frozen" form; in "frozen" form *c*, equivalence of proton chemical shifts in group 5 seems highly improbable, in view of the position of one of the protons very close to the amide bond.

From this analysis, form *a* appears as the most favoured conformer, while some amount of form *c* could appear at elevated temperatures.

Structure of Poly(N-methyl-8-octanelactam)

The ^{1}H and ^{13}C NMR spectra of poly(*N*-methyl-8-octanelactam) in TCE solution at 25 °C are shown in Figs 6 and 7*a*, respectively. The spectra are fully analogous to those of

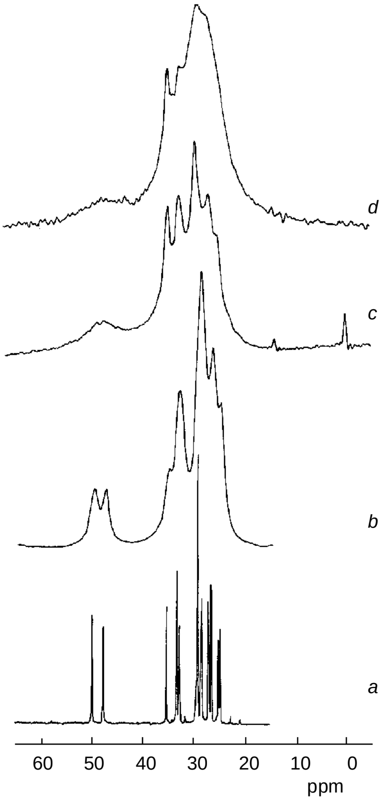


FIG. 7
^{13}C NMR spectra of poly(*N*-methyl-8-octanelactam): *a* conventional solution spectrum; *b* solution spectrum with 100 Hz line broadening; *c* solid state spectrum measured with single pulse excitation with a relaxation delay of 1 s; *d* conventional CP/MAS/DD spectrum with contact time 1 ms

poly(*N*-methyl-12-dodecanelactam)[3] and can be interpreted accordingly. Contrary to cyclic *I*, at room temperature the polymer contains approximately equal amounts of the cis and trans forms. From the indicated coalescence of the N–CH_3 and N–CH_2 doublets, probably also the dynamics of cis–trans isomerization is similar to that in poly(*N*-methyl-12-dodecanelactam).

Solid-state ^{13}C NMR spectra of the rubbery polymer measured without and with cross-polarization are shown in Figs 7*c*, 7*d*. These spectra are almost identical, any difference between them is evidently caused only by slightly differing line widths. The solid-state spectra do not markedly differ from the solution spectrum recorded with a line broadening of 100 Hz (Fig. 7*b*). The broadening of the N–CH_2 doublet at ca 50 ppm in the solid-state spectra is caused by residual dipolar interaction with ^{14}N, similarly as in other polyamides[3]. The presence of the line at 35 ppm, corresponding to trans CH_3 carbons, indicates that also in solid polymer both cis and trans forms exist in comparable amount, similarly as in solution. Some differences in relative line intensities could be caused by the circumstance that in the solid-state spectrum, different signals are broadened to a various extent.

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