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CONFORMATION ISOMERISM IN POLY(N-ALKYL LAUROLACTAMS)

BY PROTON AND CARBON-13 NMR

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ABSTRACT

The amide groups of poly(N-methyl laurolactam), poly(N-ethyl laurolactam) and poly(N-benzyl laurolactam) were shown by PMR and CMR to acquire both the anti and syn conformations in $CDCl_3$ at $30^\circ C$. At $80^\circ C$, the PMR signals of the two conformations collapsed to one signal, at an intermediate chemical shift. The anti - syn PMR and/or CMR signals were displayed by carbon nuclei and protons of all the groups which are directly bonded to the amide moieties in the three polymers. The magnetic non-equivalence of the carbon nuclei and protons of a number of other groups which are not directly linked to the amide functions was also demonstrated.

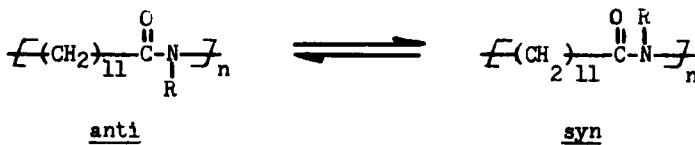
INTRODUCTION

It was demonstrated earlier in this laboratory from PMR and CMR studies on a number of N-alkyl laurolactams that their amide groups can exist in both the anti and syn conformations¹. In their PMR studies other authors have established the presence of the anti - syn isomerism in N-methyl laurolactam^{2,3}. This type of isomerism was also shown to exist in several N-substituted polypeptides⁴⁻⁹. While the amide groups

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of several unsubstituted polylactams and similar polyamides were shown to be present in the thermodynamically more stable anti conformation¹⁰⁻¹², the presence of both the anti and syn conformations was recently demonstrated in poly(N-methyl laurolactam)^{13,14}. A solution of this polymer in CDCl_3 displayed the characteristic anti - syn signals in its PMR spectra, but in the solid state the crystalline phase of the polymer was proposed to have the anti conformation only¹⁴.

The established existance of the anti - syn conformation isomerism by PMR not only in N-methyl, N-ethyl and N-benzyl laurolactams, but also in poly(N-methyl laurolactam), (I), made it logical to explore its presence in poly(N-ethyl laurolactam), (II), and poly(N-benzyl laurolactam), (III). Hence, detailed comparative PMR studies of the amide group conformation in polymers I to III were initiated. Recent application of CMR spectroscopy to the study of conformation isomerism in polymers¹⁵⁻²¹ and its demonstrated versatility in recording long range effects of the amide group isomerism in N-substituted laurolactams¹ suggested the use of this technique for studying the conformation isomerism in poly(N-alkyl laurolactams). In this communication, the PMR and CMR spectra of polymers I, II and III are reported and discussed in terms of the amide anti - syn isomerism and the chain conformation of these polymers in CDCl_3 .



I, R- = Methyl; II, R- = Ethyl; III, R- = Benzyl

EXPERIMENTAL

Synthesis of Monomers and Polymers

Following reported procedures^{13,14,22}, N-methyl, N-ethyl and N-benzyl laurolactams were prepared and polymerized to poly(N-methyl

laurolactam), (I), poly(N-ethyl laurolactam), (II), and poly(N-benzyl laurolactam), (III), respectively. Polymer I was obtained as a semicrystalline, solid material while II and III were viscous liquids at 30°C.

Analytical Methods

Reduced viscosity (η_{red}) was obtained for the polymer solutions in m-cresol (0.5 g./100 ml. solvent). Infrared spectra were prepared on a Beckman IR-9 spectrophotometer. PMR spectra of the polymers in $CDCl_3$ were recorded on a Varian HA-100 15D spectrometer at 30 and 80°C. Pulse-Fourier transform CMR spectra of the polymers in $CDCl_3$ at 30°C were obtained on a Varian CFT-20 spectrometer.

RESULTS AND DISCUSSION

As will become evident in forthcoming sections of the Discussion, the amide groups of polymers I, II and III can exist in both the anti and syn conformations. The PMR and CMR spectra of these polymers indicate that the effect of isomerism on the magnetic properties of different nuclei is not limited to those of the chemical groups which are directly bonded to the amide moieties. The CMR spectroscopy was shown to be more effective than the PMR technique in recording the magnetic non-equivalence of nuclei which are far removed from the amide function. Limited success was encountered in studying the conformation isomerism by IR spectroscopy.

In their studies of the chain conformations of N-substituted poly-peptides, Goodman and others suggested that the presence of the amide groups of these polymers, when dissolved in certain solvents, in both the anti and syn conformations at almost equal concentrations was associated with random-coil chain conformations^{4-6,23,24}. By analogy, it is proposed that when dissolved in $CDCl_3$ the chains of Polymers I,

II and III may acquire random-coil conformations, since their anti and syn NMR signals exhibited comparable peak areas.

Proton NMR (PMR)

The PMR data in Table 1 indicate that (a) all groups which are directly bonded to the amide function of Polymer I displayed both the anti and syn signals; (b) the anti and syn signals were only recorded for the methyl protons of the ethyl group in Polymer II; and, (c) in Polymer III, double signals were only observed for the methylene groups, directly bonded to the amide function. In all cases where double signals were recorded, the low field and high field ones were assigned to the anti and syn conformations, respectively. This is consistent with earlier literature assignments on similar systems²⁻⁶. The equilibrium concentration of each conformation in the three polymers at 30°C was estimated as 50% \pm 15. It is worth mentioning that the anti signal of the benzylic methylene appeared as a singlet while the syn signal was a doublet. Though the nature of this coupling is unknown, it may have been caused by one of the aromatic protons²⁵.

Upon heating any of the polymer solutions to 80°C, each of the signal pairs attributed to anti - syn conformations in the three polymers collapsed to one signal at an intermediate chemical shift (all absorptions in the PMR spectra of Polymers I to III indicated slight, non-uniform upfield shifts due to heating). This supports the proposed existence of the amide groups of Polymers I to III in both the anti and syn conformations. Though the collapse of the signal pairs at 80°C can be ascribed to the establishment of a fast conformational equilibrium at that temperature, which is associated with a rapid rotation about the C-N bond, one may not exclude (a) the presence of only one isomer at that temperature and (b) other factors which may cause chemical shift degeneracy of the anti and syn signals²⁶.

Table 1

PROTON AND CARBON-13 NMR DATA (a)

Poly(N-Alkyl laurolactams)	N-Methyl I	N-Ethyl II	N-Benzyl III
<u>PMR Data:</u>			
$(\text{CH}_2)_9$	0.8-1.8 (c)	0.9-2.0 (c)	0.9-2.0 (c)
$\text{CH}_2\text{-CO}$	2.23(t, J=?) * 2.31(t, J=?)	2.28(t, J=8)	2.31(t, J=8) * 2.38(t, J=?)
$\text{CH}_2\text{-N}$	3.27(t, J=?) * 3.35(t, J=?)	3.23(t, J=?) □ + 3.39(q, J=8) □ +	3.20(t, J=9) * 3.44(t, J=9)
-N-CO CH_2^R	2.92(s) * 2.98(s)		4.50(d, J=8) * 4.61(s)
R-Shifts	R: H	R: CH_3 1.11(t, J=?) * 1.17(t, J=?)	R: Phenyl 7.15 (c)
<u>CMR Data:</u>			
^{13}C in $(\text{CH}_2)_6$	29.1	28.8	29.3
$^{13}\text{CH}_2\text{-CH}_2\text{-CO}$ (b)	24.8, 25.1	24.9	25.3
$^{13}\text{CH}_2\text{-CO}$	32.6, 32.9	32.5	33.0
$^{13}\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-N}$ (b)	26.4	26.3	26.7
$^{13}\text{CH}_2\text{-CH}_2\text{-N}$ (b)	26.9, 28.2	26.9, 27.3	29.3
$^{13}\text{CH}_2\text{-N}$	47.3, 49.7	44.8, 47.0	45.0, 46.0
$\text{R-}^{13}\text{CH}_2\text{-N}$	33.3, 34.9	39.9, 41.6	47.1, 49.9
R-Shifts	R: H	R: CH_3 12.4, 13.7	R: 1 2 3 4 5 6 7 8 $^{13}\text{C}_3$, $^{13}\text{C}_5$: 126.2, 127.8 $^{13}\text{C}_5$, $^{13}\text{C}_6$: 126.9, 128.3 $^{13}\text{C}_6$: 127.1, 128.3 $^{13}\text{C}_1$: 137
$^{13}\text{CO-N}$	172.5	171.6	172.5

* = Two overlapping signals which collapse to one at 80°C.

+ = Overlapping signals.

a = Chemical shift in ppm .

b = Tentative assignments subject to future verification.

c = Complex multiplet.

d = Doublet

q = Quartet

t = Triplet

J = Coupling constant in Hz.

s = Singlet

Carbon-13 NMR (CMR)

The CMR spectra of the three polymers and especially Polymer II, were more demonstrative of the magnetic implications of the amide anti - syn isomerism than the corresponding PMR spectra. Each of the carbon nuclei which are directly linked to the nitrogen of the amide groups in Polymers I to III displayed two signals due to the anti and syn conformations. Of the carbon nuclei linked to the carbonyl groups in the three polymers, only that of Polymer I exhibited the two signals of the anti and syn conformations. The six carbon nuclei of the phenyl group of Polymer III exhibited seven signals in the CMR spectra instead of the classical four signals known for simple monosubstituted benzenes^{27,28}. Upon assigning the seven recorded signals, the two electronically-identical pairs of nuclei, namely $^{13}\text{C}_3 - ^{13}\text{C}_5$ and $^{13}\text{C}_2 - ^{13}\text{C}_6$ were considered responsible for two pairs of these signals. Another pair of signals was assigned to $^{13}\text{C}_4$ and only one signal was attributed to $^{13}\text{C}_1$. The double absorptions of the nuclei in the phenyl group can be considered as a consequence of the amide anti - syn isomerism. Other tentative assignments for the central nine nuclei in the polymer repeat units of I to III were made and shown in Table 1. None of the carbonyl nuclei of the three polymers revealed double signals. A few unassigned weak signals were recorded for Polymers I (29.8, 25.9 and 25.7) and II (27.8) which may be ascribed to carbon nuclei about the chain ends.

The observed chemical shift degeneracy of the anti and syn signals revealed by the carbonyl nuclei of Polymers I to III but not by their corresponding monomers¹ may be attributed to certain polar and/or steric interactions which are associated with the presence of these nuclei in a polymeric structure. The effect of these interactions seems to become more pronounced with the increase in the size and/or polarity of the

N-substituents. This argument becomes more convincing if we consider the observed chemical shift degeneracies of the $^{13}\text{CH}_2\text{-CO}$ signals in Polymers II and III, but not Polymer I. Similar trends are characteristic of the tentatively-assigned absorptions of the $^{13}\text{CH}_2\text{CH}_2\text{-CO}$ and $^{13}\text{CH}_2\text{CH}_2\text{-N}$ nuclei in Polymers I to III, shown in Table 1.

Infrared

Recent IR studies of Polymer I indicated a dependence of the relative absorbance of the N-CH_3 asymmetric (1495 cm^{-1}) and symmetric deformation frequencies (1410 cm^{-1}) on the concentration of the anti and syn conformations in the solid and liquid states¹⁴. In an oriented semi-crystalline sample of I, a split carbonyl absorption was observed at 1650 cm^{-1} . However, in the present studies, the IR spectra of the non-amorphous Polymers II and III indicated no unusual absorptions which could be related to their conformation isomerism. Both Polymers (II and III) showed a carbonyl absorption at 1650 cm^{-1} . In Polymer II, the overlapping C-H deformation frequencies of the ethyl group and the methylene groups of the main chain appeared at 1455 , 1415 , 1370 and 1340 cm^{-1} . The C-H deformations of the methylene groups in Polymer III appeared at 1452 , 1420 and 1355 cm^{-1} . An interesting set of three sharp peaks which may be assigned to the C-H stretching frequency of the aromatic ring or both the aromatic ring and benzylic methylene, were observed in the spectra of Polymer III at 3030 , 3065 and 3085 cm^{-1} .

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REFERENCES

1. S. W. Shalaby, G. E. Babbitt and R. L. Lapinski, Spectrosc. Letters, 6, 231 (1973).

2. K. M. Moriarty and J. M. Kleigman, *J. Org. Chem.*, **31**, 300 (1966).
3. R. M. Moriarty, *J. Org. Chem.*, **29**, 2748 (1964).
4. F. A. Bovey, *Polymer Conformation and Configuration*, Academic Press, New York, 1969, Chap. V.
5. J. E. Mark and M. Goodman, *J. Amer. Chem. Soc.*, **89**, 1267 (1967).
6. M. Goodman and M. Fried, *J. Amer. Chem. Soc.*, **89**, 1264 (1967).
7. P. M. Cowan and S. McGavin, *Nature*, **176**, 501 (1955).
8. F. R. Prince, *Effect of Side Chains on the Conformation of Poly-peptides and N-Substituted Polypeptides*, Ph.D. Thesis, Polytechnic Institute of Brooklyn, Brooklyn, N.Y., 1968; *Diss. Abstr.*, **B**, **29** (5), 1635 (1968).
9. W. L. Mattice, K. Kishikawa and T. Ooi, *Macromolecules*, **6**, 443 (1973).
10. N. Ogata, *J. Polymer Sci.*, **A**, **1**, 3151 (1963).
11. R. C. P. Cubbon, *Makromol. Chem.*, **80**, 44 (1964).
12. L. G. Roldan, F. J. Kahl and M. H. Riggi, *Rev. Plast. Mod. (Spain)*, **23**, 710 (1972).
13. S. W. Shalaby, R. J. Fredericks and E. M. Pearce, *J. Polymer Sci.*, **A-2**, **10**, 1699 (1972).
14. S. W. Shalaby, R. J. Fredericks, E. M. Pearce and W. M. Wenner, *J. Polymer Sci., Polymer Phys. Edit.*, (in press).
15. V. D. Mochel, *J. Polymer Sci.*, **A-1**, **10**, 1009 (1972).
16. Y. Tanaka and K. Hatada, *J. Polymer Sci., Polymer Letters Edit.*, **11**, 569 (1973).
17. G. C. Levy and G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley, New York, 1972, Chap. 7.
18. Y. Inoue, R. Chūjo and A. Nishioka, *J. Polymer Sci., Polymer Phys. Edit.*, **11**, 393 (1973).
19. K. Matsuzaki, T. Kanai, T. Kawamura, S. Matsumoto and T. Uryu, *J. Polymer Sci., Polymer Chem. Edit.*, **11**, 961 (1973).
20. Y. Inoue, K. Koyama, R. Chūjo and A. Nishioka, *J. Polymer Sci., Polymer Letters Edit.*, **11**, 55 (1973).
21. E. Kobayashi, T. Kawagoe and N. Katsuki, *J. Polymer Sci., Polymer Letters Edit.*, **11**, 239 (1973).
22. S. W. Shalaby, R. J. Fredericks and E. M. Pearce, *J. Polymer Sci., Polymer Phys. Edit.*, **11**, 939 (1973).
23. F. A. Bovey, J. J. Rayan and F. P. Hood, *Macromolecules*, **1**, 305 (1968).
24. J. E. Mark and M. Goodman, *Biopolymers*, **5**, 809 (1967).
25. V. F. Bystrov, *Russ. Chem. Revs.*, **41**, 281 (1972).
26. W. E. Stewart and T. H. Siddall, *III. Chem. Rev.*, **70**, 517 (1970)..
27. J. B. Stothers, *Appl. Spectrosc.*, **26**, 1 (1972).
28. H. Spiesecke and W. G. Schnieder, *J. Chem. Phys.*, **35**, 371 (1971).

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