J. CHEM. SOC. FARADAY TRANS., 1990, 86(9), 1561–1567

Vibrational Spectra of *N*-Acylglycine Oligomers and the Long *N*-Acyl Chain Effect

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Trimers, tetramers and pentamers of *N*-acylglycine oligomer acid types with various acyl chains, their potassium or sodium salts, and their *N*-deuterated salts have been prepared. The vibrational spectra of these molecules have been measured and compared with those of polyglycine I (PGI; extended β form) and polyglycine II (PGII; helical form). Only a conformation similar to PGII exists in the solid state for these compounds. The long acyl chains induce a further PGII-like structure in the NH···O=C and peptide skeletons. This effect is reflected markedly in the NH and ND stretching, amide I and II and low-frequency regions.

Membrane proteins can be crystallized as protein–detergent complexes in the presence of detergent molecules,[1–3] and surfactant molecules promote the ordered packing of the proteins.[4,5] Recently, the structure of the detergent assembly in the crystals of a bacterial photosynthetic reaction centre complex has been demonstrated[6] and provides a model for the interaction between the lipid bilayer and the complex.

The interaction between lipid and membrane protein may change the conformation of a protein molecule, since water-soluble proteins synthesized in the cytoplasm have to change their conformations in order to enter the hydrophobic interior of a membrane. Therefore, the possibility of conformational change in the protein molecule induced by the hydrophobic environment is present in the lipid–membrane protein complex. However, very little is known about how the conformational change of the peptide can occur in such a hydrophobic environment. A study of the conformational change of simple peptides incorporated into the hydrophobic region might aid the understanding of this mechanism.

The *N*-acylsarcosinate anion, as well as other simple amide compounds, has possible *cis* and *trans* conformations about the C—N bond of the peptide group. Takahashi *et al.*[7] reported NMR spectroscopic studies that showed that the *trans* conformation of the sarcosinate anion is more stable in the micellar state than in the monomolecular state. It has also been confirmed that incorporation of the sarcosinate anion into micelles of sodium dodecyl sulphate (SDS) induces an increase in the proportion of the *trans* conformer of the anion. However, many problems on the conformational changes of molecules incorporated into such micelles (model membranes) still remain unresolved, and further study is desirable in connection with the functional appearance of biomembranes.

In our previous paper,[8] the conformations of *N*-acetylglycine oligomer acid types (trimer, tetramer and pentamer) and their potassium (K) salts were investigated by vibrational spectroscopy and X-ray diffraction. A solid A (PGII-like helical structure) ⇔ solid B (PGI-like extended β structure) conversion is possible for the oligomeric acid types. For the K-salts, only the PGII-like structure was found to exist in the solid state and in aqueous solution. This observation demonstrated that the carboxylate anion of these oligomers contributes markedly to the stabilization of the PGII-like structure.

In globular proteins, short α-helices in the range 6–20 residues are usually found, and research into specific stabilizing factors is now a focus of interest. Baldwin and co-workers[9] and Schoemaker *et al.*[10,11] have demonstrated the critical role of the charged group in the stability of the helical structure of the C-peptide fragment (residue 1–13) of ribonuclease A.

In order to aid the understanding of the role of the hydrocarbon chain in the lipid–protein complex, we synthesized *N*-acylglycine oligomers with various acyl chains, their K- or Na-salts and their *N*-deuterated salts. The conformation of glycine oligomer parts has been investigated and the long acyl chain effect on the peptide conformations is discussed in detail. In particular, a comparison of the vibrational spectra of these oligopeptides with the observed[12,13] and calculated results[14,15] of PGI and PGII has been made.

Experimental

N-Acylglycine trimers with various acyl chains were prepared by a method similar to that of Ingersol and Babcock[16] in aqueous acetone medium using freshly distilled acid chlorides and triglycine. Tetramers were prepared as follows. First, ethyl esters of the corresponding *N*-acyltetraglycine were prepared by condensation of *N*-acyltriglycine and glycine ethyl ester by the method of Ionova *et al.*[17] The corresponding ethyl esters were solvolysed and then converted into free acids by neutralization. Pentamers were prepared in the same manner using glycylglycine ethyl ester instead of glycine ethyl ester.

The potassium and sodium salts of these oligomers were prepared from the corresponding acid types and potassium or sodium hydroxide in methanol. *N*-Deuterated salts of these oligomers were prepared by D_2O exchange. The abbreviations for 53 molecules used are listed in table 1.

Samples were identified by elemental analysis; the agreement between the calculated and observed values for *N*-acylglycine oligomers was within 0.5–0.6%.

Raman spectra below 4000 cm^{-1} were taken with a JEOL JRS-400D Raman spectrometer using 514.5 nm excitation. Infrared spectra were recorded on a Perkin-Elmer 1700 Fourier-transform infrared spectrometer (4000–400 cm^{-1} with the sample dispersed in KBr discs) and on a Hitachi FIS

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Table 1. Abbreviations[a] for *N*-acylglycine oligomers[b]

		trimer ($m = 3$)	tetramer ($m = 4$)	pentamer ($m = 5$)
acetyl ($n = 0$)	AcGH	AcG3H-A[c]	AcG4H-A[c]	AcG5H-A[c]
	AcGK	AcG3K	AcG4K	AcG5K
	AcGK (ND)	AcG3K (ND)	AcG4K (ND)	AcG5K (ND)
propanoyl ($n = 1$)	PrGH	PrG3H	PrG4H	PrG5H
	PrGK	PrG3H	PrG4K	PrG5K
	PrGK (ND)	PrG3K (ND)	PrG4K (ND)	PrG5K (ND)
butanoyl ($n = 2$)	BuGH	BuG3H	BuG4H	BuG5H
	BuGK	BuG3K	BuG4H	BuG5K
	BuGK (ND)	BuG3K (ND)	BuG4K (ND)	BuG5K (ND)
pentanoyl ($n = 3$)	PeGH	PeG3H	PeG4H	PeG5H
	PeGK	PeG3K	PeG4K	PeG5K
	PeGK (ND)	PeG3K (ND)	PeG4K (ND)	PeG5K (ND)
hexanoyl ($n = 4$)	HeGH	HeG3H	HeG4H	HeG5H
	HeGNa	HeG3Na	HeG4Na	HeG5Na
	HeGNa (ND)	HeG3Na (ND)	HeG4Na (ND)	HeG5Na (ND)
octanoyl ($n = 6$)	OcGH	OcG3H	OcG4H	OcG5H
	OcGNa	OcG3Na	OcG4Na	OcG5Na
	OcGNa (ND)	OcG3Na (ND)	OcG4Na (ND)	—

[a] H, K, Na and ND denote acid type, potassium salt, sodium salt and *N*-deuterated sample, and the numbers (3–5) in abbreviations indicate the residue number. [b] $CH_3(CH_2)_nCO(NH{-}CH_2{-}CO)_m{-}OH$. [c] These samples were treated with saturated LiBr–H_2O solution.

double-beam grating spectrometer (400–50 cm^{-1} with the sample dispersed in Nujol and sandwiched between two polyethylene windows).

X-Ray diffraction powder patterns were obtained by the use of an RAD-RC diffractometer with counter monochromator (Cu K_α, 60 kV, 200 mA).

Results and Discussion

X-Ray Diffraction Powder Patterns of *N*-Acylglycine Oligomers

X-Ray diffraction powder patterns were measured for *N*-acylglycine oligomer acid types and the pentamer salts, and were compared with those of PGI (extended chain) and PGII (helix).[18] Reflections at 4.18–4.29, 4.18–4.24 and 4.20–4.21 Å are observed for the acid types of trimer, tetramer and pentamer, respectively. The pentamer salts also have the reflections at 4.14–4.22 Å. These reflections correspond to that at 4.15 Å for PGII. Reflections at 3.40 and 4.35 Å for PGI were not observed for these molecules. Thus, from the X-ray diffraction powder patterns, both acid types and the salts of the longer acyl chain derivatives are found to take the PGII-like structure.

Vibrational Spectra of *N*-Acylglycine Oligomers and their Salts

The Raman and IR spectra of *N*-acylglycine oligomer acid types with various acyl chains, their K- or Na-salts and their *N*-deuterated salts were measured and compared with those of PGI, PGII and PGII(ND) in the solid state.[12–15] Characteristic bands of PGII and PGII(ND) were observed for these oligomers. Fig. 1 and 2 show the representative Raman spectra of PeGH and PeGK(ND) oligomers and the bands characteristic of PGII and PGII(ND) are marked with asterisks. For ease of discrimination between the PGI- and PGII-like structures, the characteristic bands of the PGI- and PGII-like *N*-acetylglycine pentamer acid types are briefly summarized in table 2.

The Raman bands for PeGH oligomers arising from glycine CH_2 groups are observed in common at 2978 and 2944, 1420–1421, 1386–1387, 1261–1262 and 889–891 cm^{-1}, and are assigned to the asymmetric and symmetric stretching, bending, wagging, twisting and rocking modes, respectively. Raman bands at 1136–1137 and 1030–1033 cm^{-1} for PeGH oligomers are assigned to the skeletal stretching modes of the peptide.

For a series of PeGK(ND) oligomers, Raman bands of the glycine CH_2 groups are observed in common at 2974–2976 and 2938–2939, 1417 and 1271–1274 cm^{-1} and are assigned to the asymmetric and symmetric stretching, bending and twisting modes, respectively. Common bands at 985–993 and 875 cm^{-1} are due to the CH_2 rocking modes coupled with the skeletal stretching modes. Raman bands at 1127–1134

Table 2. Observed characteristic frequencies (cm^{-1}) of PGI- and PGII-like *N*-acetylglycine pentamer acid types[a]

PGI-like (extended)		PGII-like (helical)	
Raman	IR	Raman	IR
	1685 m		
1666 s			
		1653 s	1651 vs
	1633 vs		
			1558 s
1520 w	1523 s		
1460 s			
	1433 s	1430 s	
			1423 m
1400 w	1410 m		
		1384 s	1379 m
		1281 w	1281 m
		1262 s	
		1245 m	1242 m
1217 m	1218 w		
1158 m			
		1135 w	
		1034 s	1028 m
1016 vs	1016 m		
		887 vs	
621 w	621 w		
598 w	598 w		
		570 w	571 w

[a] From ref. (8). s, strong; m, medium; w, weak; and v, very.

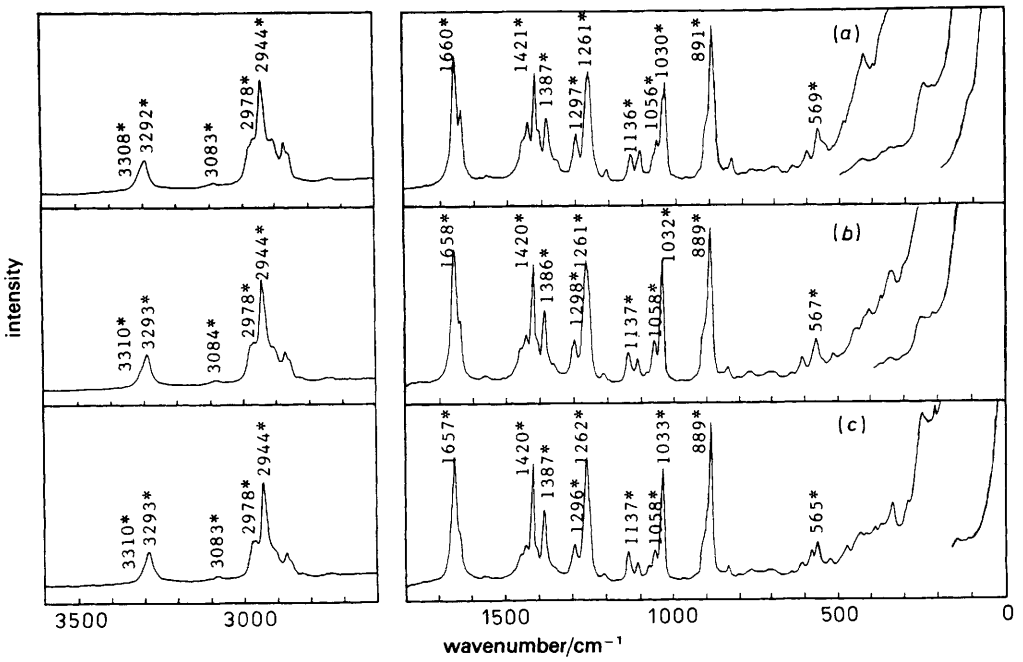

Fig. 1. Raman spectra of PeGH oligomers: (*a*) PeG3H, (*b*) PeG4H and (*c*) PeG5H in the solid state at room temperature. Asterisks denote the bands characteristic of PGII.

cm^{-1} are assigned to the peptide skeletal stretching modes and those at 1029–1033 cm^{-1} to the coupled modes between the ND in-plane angle bending and the CH_2 rocking modes.

The characteristic modes of glycine CH_2 group and peptide skeleton stretching are independent of the residue number and acyl chain length in frequency. On the other hand, the spectral features of NH and ND stretching, amide I and II, and low-frequency regions are markedly dependent on both the residue number and acyl chain length, and are discussed in detail.

NH *and* ND *Stretching Regions*

Fig. 3A shows the *N*-acyl chain length dependence of the Raman bands in the NH stretching region of the acid types. The NH stretching mode features (amide A) of *N*-acylglycine oligomers depend upon the residue number. Two broad Raman bands at 3307 and 3270 cm^{-1} appear for AcG3H-A. With an increase in the residue number, these bands broaden and shift to lower frequency. The spectral patterns of the NH stretching for PrGH and BuGH oligomers are different from those of AcGH oligomers. In addition to the bands at 3297–3310 cm^{-1}, broad bands appear at 3271–3278 cm^{-1} with increasing intensities for increase in residue number. For AcGH-A, PrGH and BuGH oligomers, the spectral feature of the NH stretching spreads over into the 3300–3250 cm^{-1} region, showing that each NH group participates in a different hydrogen-bonding environment and that strong hydrogen bonds are formed on increasing the residue number.

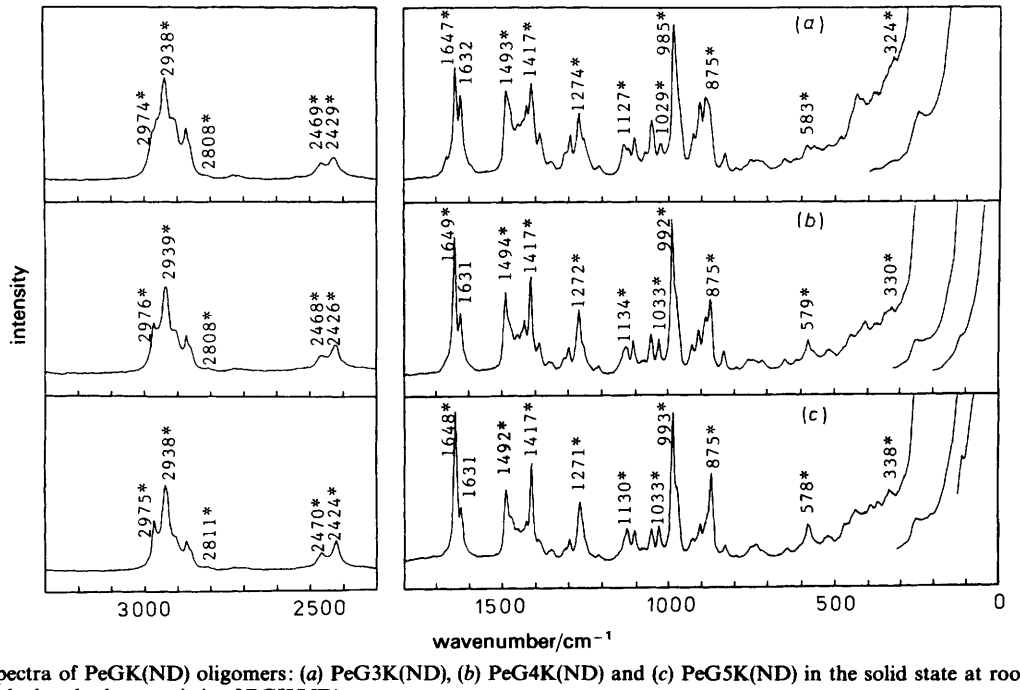

Fig. 2. Raman spectra of PeGK(ND) oligomers: (*a*) PeG3K(ND), (*b*) PeG4K(ND) and (*c*) PeG5K(ND) in the solid state at room temperature. Asterisks denote the bands characteristic of PGII(ND).

For PeGH, HeGH and OcGH oligomers the spectral feature of the NH stretching is completely different from that of the shorter species. These longer acyl chain derivatives have weak shoulders at 3305–3310 cm^{-1} and medium ones at 3291–3296 cm^{-1}. The latter become sharper and stronger in intensity than those of the shorter acyl chain derivatives. The environment of the NH group of the longer acyl chain derivatives resembles a PGII-like hydrogen-bonding environment; the formation of so-called typical and bifurcated hydrogen bonds similar to that of PGII[15] may be promoted by the long acyl chain.

Fig. 3B shows the NH stretching Raman bands for the *N*-acylglycine tetramer salts. Very broad Raman bands are observed at 3292 and 3296 cm^{-1} for AcG4K and PrG4K. Unlike the acid types, the BuGK oligomers are similar to the longer acyl chain derivatives in a spectral pattern of the NH stretching region. For BuG4K and the longer acyl chain derivatives, the shoulders at 3308–3314 cm^{-1} and the bands at 3297–3298 cm^{-1} are observed and the spectral patterns become sharper and stronger than those of AcG4K and PrG4K. Similar observations were also made for the trimer and pentamer salts.

The ND stretching Raman bands for the teramer salts are shown in fig. 3C. Raman bands are observed at 2462–2468 and 2417–2427 cm^{-1}, and correspond to the Raman bands at 2472 and 2419 cm^{-1} for PGII(ND), respectively. The ND stretching bands for the long acyl chain derivatives become sharper and stronger compared with those of the shorter species. These bands are caused by Fermi resonance between the ND stretching modes and combination bands.[15] The bands at 2469 and 2429 cm^{-1} for PeG3K(ND) are almost equal in intensity, while for PeG4K(ND) and PeG5K(ND) the bands at 2424–2426 cm^{-1} increase in intensity compared with those bands at 2468–2470 cm^{-1} (fig. 2). The band at 2419 cm^{-1} for PGII(ND) is associated with the typical N—D···O=C hydrogen bond. Thus, the intensity increase of the bands at 2424–2429 cm^{-1} for PeGK(ND) oligomers may imply the dependence of the typical hydrogen-bond formation on the residue number. Similar observations were made for all the series of *N*-deuterated *N*-acylglycine salts.

The relative intensity (I_B/I_A) of the amide B (3080–3090 cm^{-1}) and amide A (3310–3250 cm^{-1}) bands was measured for these oligomers (table 3). I_B/I_A values of PeGH, HeGH and OcGH oligomers are found to be smaller than those of AcGH, PrGH and BuGH oligomers. This indicates that the Raman intensity of amide A band relative to that of amide B increase with increasing acyl chain length. The mechanism of the relative intensity increase is due to the Fermi resonance between the amide A and amide B modes, which has been used to explain the NH stretching modes of PGI[19] and PGII.[15] The NH stretching modes of the longer acyl chain oligomers definitely gain Raman intensity from the overtone modes of amide II. The unperturbed frequencies of the NH stretching bands for all these oligomers and their salts were calculated by a Fermi resonance analysis[15,19] and those of the pentamers are listed in table 2. The unperturbed frequencies (ν_A^0 and ν_B^0) are dependent on the acyl chain length and are close to those of PGII.[15]

Table 3. Acyl chain dependence of I_B/I_A[a] and unperturbed frequencies[b] of NH stretch modes for pentamer acid-types

	trimer	tetramer	pentamer				
	observed		observed			calculated[c]	
	I_B/I_A		I_B/I_A	ν_A	ν_B	ν_A^0	ν_B^0
Ac	0.24	0.18	0.19	3300 3254	3082	3265 3227	3117 3109
Pr	0.22	0.18	0.18	3310 3276	3085	3276 3247	3119 3114
Bu	0.20	0.23	0.15	3302 3278	3084	3273 3252	3113 3110
Pe	0.12	0.11	0.11	3310 3293	3083	3287 3272	3106 3104
He	0.12	0.12	0.11	3310 3294	3080	3287 3273	3103 3101
Oc	0.12	0.12	0.12	3308 3292	3084	3284 3270	3108 3106

[a] Observed relative intensity (overall area intensity ratio) of amide B to amide A; the maximum errors are *ca.* ±0.02. [b] ν_A and ν_B: observed frequencies (cm^{-1}) of amide A and amide B ν_A^0 and ν_B^0: unperturbed frequencies (cm^{-1}) of amide A and amide B calculated by a Fermi resonance analysis. [c] Ref. (15) and (19).

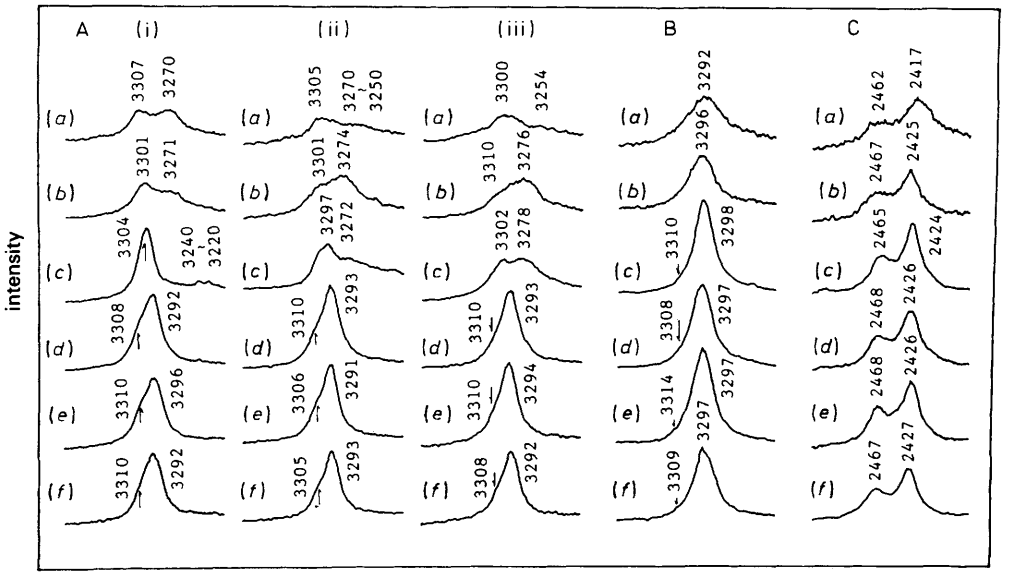

Fig. 3. *N*-Acyl chain length dependence of the Raman bands in the NH and ND stretch regions: A, for acid-types; (i) trimers; (ii) tetramers and (iii) pentamers; B, for their *N*-undeuterated tetramer salts, and C for their *N*-deuterated tetramer salts; (*a*) Ac, (*b*) Pr, (*c*) Bu, (*d*) Pe, (*e*) He and (*f*) Oc series of oligomers.

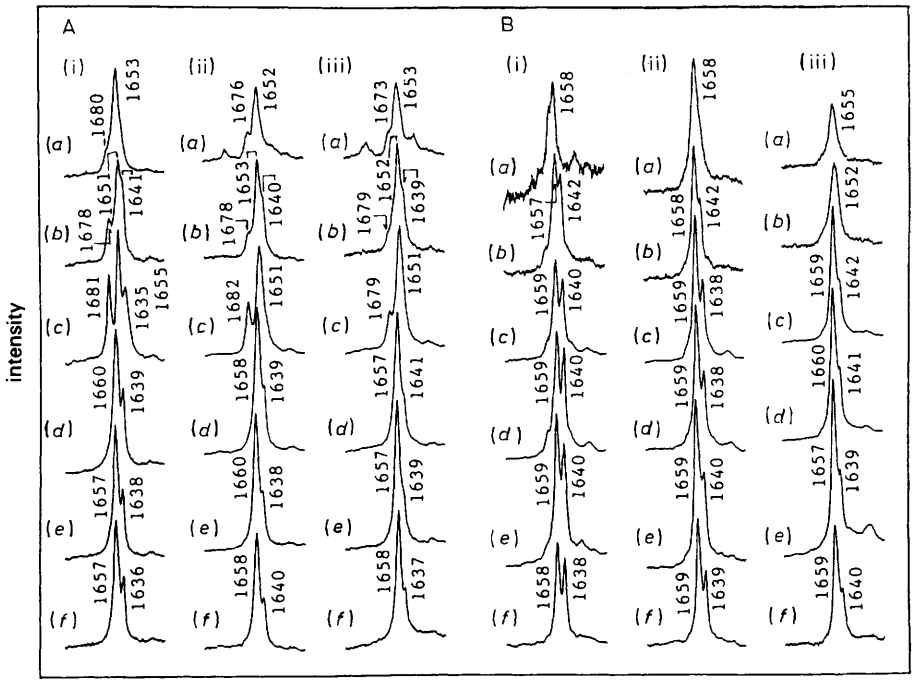

Fig. 4. Effect of *N*-acyl chain length on the Raman bands in the amide I region for acid types (A) and their *N*-undeuterated salts (B): (i) for trimers, (ii) for tetramers and (iii) for pentamers; (*a*) Ac; (*b*) Pr; (*c*) Bu; (*d*) Pe; (*e*) He; and (*f*) Oc series of oligomers.

Amide I and II Regions

The *N*-acyl chain length affects the Raman spectral patterns in the amide I region (fig. 4). Shoulders at 1678 and 1640 cm^{-1} for PrG4H are observed in addition to the strong amide I band at 1653 cm^{-1}, while the band at 1682 cm^{-1} for BuG4H appears beside the amide I band at 1651 cm^{-1} and increases in intensity (fig. 4A). The bands at 1678 cm^{-1} for PrG4H and at 1682 cm^{-1} for BuG4H are assigned to the C=O symmetric stretching mode of the end CO_2H group, since these bands disappear in the K salts. For PeG4H, HeG4H and OcG4H, however, two bands at 1658–1660 and 1638–1640 cm^{-1} are observed; the former bands correspond to the band at 1654 cm^{-1} for PGII. The latter bands may be due to the amide I bands characteristic of the peptide group at the *N*-acyl chain side, since the latter are not observed for PGII and their intensities decrease with increasing residue number. Similar observations were found for the trimer and pentamer acid types.

Fig. 4B shows the Raman bands of *N*-acyglycine K and Na salts in the amide I region. The bands at 1655–1658 cm^{-1} for AcGK oligomers are assigned to the amide I band, while for PrG3K and PrG4K the bands at 1642 cm^{-1} appear beside the bands at 1657–1658 cm^{-1}. Unlike the acid types, BuGK oligomers have a spectral pattern similar to the longer acyl chain derivatives. Similar observations were made for the salts of the *N*-deuterated derivatives.

For the IR spectra of the *N*-acetylglycine oligomer K salts, broad and strong amide I bands are observed at 1648–1654 cm^{-1} (fig. 5A–C). However, for PrG3K, BuG3K and HeG3Na, four IR bands at 1680, 1655, 1639–1643 and 1620 cm^{-1} appear in the amide I region (fig. 5A). As the residue number increases, the intensity of the bands at 1680, 1639–1643 and 1620 cm^{-1} decreases, while the bands at 1655 cm^{-1} increase in intensity. The former three bands may arise from both end groups of the *N*-acyl and carboxylate. In particular, with an increase in the acyl chain length the bands at 1680 and 1620 cm^{-1} become weak in intensity.

Similar splittings of the amide I mode is found for the acid types (fig. 5D). The bands at 1649–1651 cm^{-1} are the characteristic amide I band of the PGII-type, and the bands at 1680–1681, 1640–1645 and 1610 cm^{-1}, corresponding to those of the K and Na salts at 1680, 1639–1643 and 1620–1621 cm^{-1}, may be also due to both end groups. Thus, long acyl chains markedly induce an amide I splitting. The splitting mechanism should be due to transition dipole interaction.[20,21] The splitting patterns reflect the steric

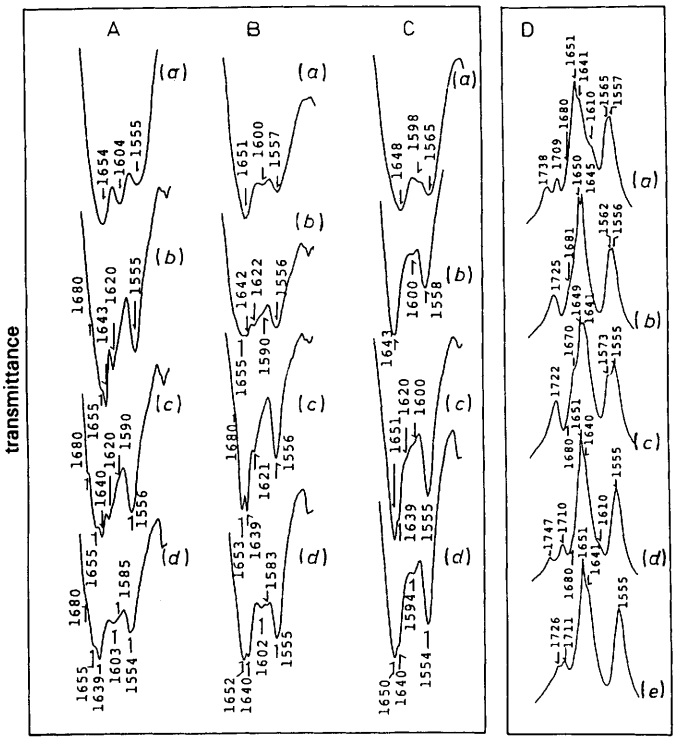

Fig. 5. Effect of *N*-acyl chain length on the IR bands in the amide I and amide II region: A (*a*) AcG3K, (*b*) PrG3K, (*c*) BuG3K and (*d*) HeG3Na; B (*a*) AcG4K, (*b*) PrG4K, (*c*) BuG4K and (*d*) HeG4Na; C (*a*) AcG5K, (*b*) PrG5K, (*c*) BuG5K and (*d*) HeG5Na; D (*a*) AcG5H, (*b*) PrG5H, (*c*) BuG5H, (*d*) PeG5H and (*e*) HeG5H.

configuration of peptide groups in these oligomers.[22–24] Probably, the close packing of the long acyl chain in the solid state brings about a peptide configuration similar to that of PGII.

For AcGK, PrGK and BuGK oligomer salts, no distinct splitting of IR amide II band at 1554–1565 cm^{-1} occurs. However, for HeG3Na and HeG4Na, the bands at 1583–1585 cm^{-1} are observed in addition to the bands at 1554–1555 cm^{-1} (fig. 5A and B). For the pentamer acid types, the amide II modes depend upon the acyl chain length (fig. 5D). For AcG5H, PrG5H and BuG5H, two IR bands of amide II are observed at 1562–1573 and 1555–1557 cm^{-1}, while for PeG5H and HeG5H only the band at 1555 cm^{-1} appears. Two amide II bands of the shorter acyl chain derivatives may be caused by the different hydrogen-bonding environment with the peptide groups of neighbouring chain as well as the NH stretch band features of these derivatives (fig. 3A). Evidently, long acyl chain induces the PGII-like amide II modes.

IR bands of the C=O asymmetric stretch of the CO_2H group depend upon the *N*-acyl chain length in frequency; 1720–1725 cm^{-1} for PrGH oligomers, 1722–1727 cm^{-1} for BuGH oligomers and 1701–1711 cm^{-1} for PeGH, HeGH and OcGH oligomers. Evidently, the long acyl chain brings about the shift of the C=O asymmetric stretching to lower frequencies, implying the formation of strongly hydrogen-bonded CO_2H cyclic dimers.[25] However, for PeGH, HeGH and OcGH oligomers, bands also appear at 1725–1747 cm^{-1}, which arise from the weakly hydrogen-bonded CO_2H groups (fig. 5D).[25] Thus, in the long acyl chain oligomer acid types strongly hydrogen-bonded CO_2H cyclic dimers and the weakly hydrogen-bonded CO_2H groups coexist.

Low-frequency Region

Fig. 6 shows the Raman and IR spectra of the oligomer acid types in the low-frequency region. For HeG4H and OcG4H the Raman bands at 563 cm^{-1} closely correspond to the 566 cm^{-1} band of PGII, and are assigned to the mixed modes of C=O and NH out-of-plane angle bend.[15] In the shorter acyl chain oligomers, the corresponding Raman bands are observed at higher frequencies (for AcG4H, PrG4H, and BuG4H the modes appear at 571–573 cm^{-1}, while for PeG4H they are observed at 567 cm^{-1}). The intensity of the Raman bands at 563–571 cm^{-1}, relative to the other bands, increases with acyl chain length.

The IR band at 361 cm^{-1} for OcG5H is very close to the band at 363 cm^{-1} (IR) for PGII,[12] which is assigned to the $NC^{\alpha}C$ and $C^{\alpha}CN$ skeletal deformation vibration. For the shorter acyl chain oligomers, the corresponding IR bands appear at lower frequency.

The Raman and IR bands at 115 cm^{-1} for OcG5H are also characteristic of PGII, and arise from the mixed modes of the C—N torsion, N=H···O in-plane bend and H···O stretch.[15] As the acyl chain length becomes shorter, the corresponding bands shift to higher frequency; namely, for PrG5H to 121 (IR) and 119 (Raman) cm^{-1} and for AcG5H to 131 (IR) and 124 (Raman) cm^{-1}. The intensity of the IR bands at 115–131 cm^{-1}, relative to that of the other bands, also increase with acyl chain length.

The Raman bands of OcG5H at 81 cm^{-1} may be assigned to the mixed modes of NH out-of-plane angle bend, $NC^{\alpha}C$ deformation, H^{α}···O stretch and NC^{α} torsion of the peptide skeleton, since it corresponds to the Raman band at 83 cm^{-1} for PGII.[14] The corresponding Raman bands are observed at 96 cm^{-1} for AcG5H and at 86 cm^{-1} for PrG5H. Similar observations in the low-frequency region were made for the other acyl chain oligomers. The vibrational bands in low-frequency region directly reflect the structures in hydrogen bonding and peptide skeleton. Thus, it is concluded that the longer acyl chain group in these oligomers strongly induces PGII-like structure in the NH···O=C and peptide skeleton.

Conclusions

The X-ray diffraction powder patterns show that the longer *N*-acyl chain glycine oligomer acid types and the salts take the PGII-like structures.

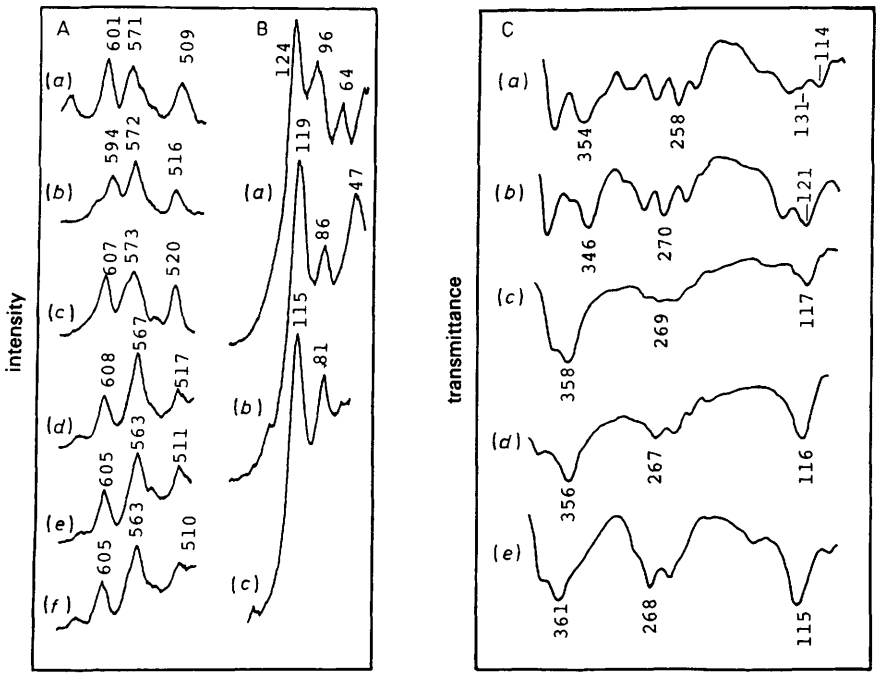

Fig. 6. Low-frequency regions of Raman spectra (A and B) and far-IR spectra (C) for *N*-acylglycine oligomer acid types: A (*a*) AcG4H-A, (*b*) PrG4H, (*c*) BuG4H, (*d*) PeG4H, (*e*) HeG4H and (*f*) OcG4H; B (*a*) AcG5H-A, (*b*) PrG5H and (*c*) OcG5H; C (*a*) AcG5H-A, (*b*) BuG5H, (*c*) PeG5H, (*d*) HeG5H and (*e*) OcG5H.

A PGII-like hydrogen-bonding environment of *N*-acylglycine oligomers is promoted by the long acyl chain. I_B/I_A decreases with increasing acyl chain length. This indicates that the NH stretching modes of the longer acyl chain oligomers have a smaller degree of Fermi resonance with the amide II overtones than the short-chain oligomers.

The long acyl chain affects the spectral features in the amide I and amide II regions. In particular, long acyl chains markedly induce an amide I and II splitting. This observation may be caused by the promotion of a PGII-like peptide configuration due to the close packing of the long acyl chain in the solid.

The low-frequency region in the vibrational spectra provides ample evidence that the PGII-like structures of the peptide skeleton in the *N*-acylglycine oligomers are promoted by the long acyl chains.

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Paper 9/04094C; *Received* 25*th September*, 1989