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Vibrational spectra of *N*-acetylglycine oligomers

Part 2.†—Raman scattering study of selectively C-deuteriated oligomers with polyglycine I- and II-type structures

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Selectively C-deuteriated *N*-acetylglycine trimer and tetramer acid types have been synthesized, and their two crystalline modifications, solid-A and solid-B [which correspond in structure to polyglycine (PG) II and I, respectively] have been prepared. Raman scattering spectra have been measured for a series of these glycine oligomers, and the CH_2- and CD_2-characteristic modes have been investigated in detail. Assignment of the CH_2-characteristic bands to each CH_2 group in the oligomers has been carried out successfully. In particular, the results obtained from the CD_2 stretch region show that N- and C-terminal glycine residues for the PGI- and PGII-type trimers and tetramers are all in very similar environments and that the glycine residues which are sandwiched between the two terminal residues are also in a similar environment for both the trimers and the tetramers.

Polyglycine (PG) exists in two crystalline forms known as the I- (PGI) and II-types (PGII).[1] According to X-ray and electron diffraction studies, PGI takes up an antiparallel-chain rippled sheet structure[2–6] while PGII takes up an antiparallel chain structure with a 3_1-helix.[7–10]

Suzuki *et al.*[11] have prepared five isotopic polyglycines, (undeuteriated, N-deuteriated, C-deuteriated, completely deuteriated and ^{15}N-substituted PG), and made a detailed investigation of the IR spectra of these samples. Their results provided an almost complete data set of IR absorption spectra of PGI and PGII. The vibrational spectra of PGI, PGII and their deuteriated derivatives have also been investigated in detail.[12,13] Most of the observed frequencies have been successfully assigned by normal coordinate analysis using force constants associated with the intermolecular hydrogen bonds.[14,15]

Conformational studies of the glycine oligomers have been made in order to determine the critical size for formation of the secondary structure of polypeptides.[16–19] In our previous study,[20] we demonstrated, by the use of X-ray powder diffraction patterns and vibrational spectra, that two crystalline modifications (solid-A and solid-B) are obtained for the *N*-acetylglycine trimer, tetramer and pentamer acid types and that a solid-A ⇔ solid-B conversion which is similar to the PGII ⇔ PGI conversion is possible for these oligomers.

However, for *N*-acylglycine oligomers with long acyl chains,[21] it has been shown that the chains induce formation of a further PGII-like structure in the solid state. The reason why such a PGII-like conformation shows preferential stabilization by the long acyl chain derivatives remains unresolved. The solution may be linked with the reason why the PGI ⇔ PGII type conversion is possible for very simple *N*-acetylglycine oligomers. Probably, both C- and N-terminal groups play an important role in the mechanism of such an interconversion.

In order to understand the role of the C- and N-terminal residues, selectively C-deuteriated *N*-acetylglycine trimer and tetramer acid types were prepared. X-Ray powder diffraction patterns and vibrational spectra of these oligomers were measured and compared with those for PGI[2–6,11,13,14] and PGII.[7–11,15] In particular, the effects of N- and C-terminal glycine residues on the vibrational spectra have been discussed. Vibrational bands characteristic of PGI[13,14] and PGII[15] have also been used as references for interpretation of the Raman scattering spectra of these oligomers.

† Part 1: ref. 20.

Experimental

Materials

Selectively C-deuteriated *N*-acetylglycine trimers [$AcG_1^*G_2G_3$, $AcG_1G_2^*G_3$ and $AcG_1G_2G_3^*$ (the asterisk shows the residue for location of CD_2-glycine)] and tetramers ($AcG_1^*G_2G_3G_4$, $AcG_1G_2^*G_3G_4$, $AcG_1G_2G_3^*G_4$ and $AcG_1G_2G_3G_4^*$) were prepared by acetylation of the corresponding C-deuteriated triglycines ($G_1^*G_2G_3$, $G_1G_2^*G_3$ and $G_1G_2G_3^*$) and tetraglycines ($G_1^*G_2G_3G_4$, $G_1G_2^*G_3G_4$, $G_1G_2G_3^*G_4$ and $G_1G_2G_3G_4^*$) with acetic anhydride, respectively.[22] The selectively C-deuteriated triglycines and tetraglycines were prepared by a stepwise procedure as follows. The glycine-2,2,d_2 (G*; 98 atom % D, Aldrich) was treated with carbobenzoxy chloride (Z—Cl) to protect the N-terminus.[23] The product, carbobenzoxy C-deuteriated glycine (Z—G*) was then condensed with glycine *p*-nitrobenzyl ester (G—ONb), which was prepared by esterification of glycine with *p*-nitrobenzyl alcohol in benzene,[24] to obtain Z—G*G—ONb using a method similar to that described by Anderson *et al.*[25] The Z-group of Z—G*G—ONb was removed in 25% HBr–acetic acid solution in order to obtain G*G—ONb. The G*G—ONb thus obtained was further condensed with Z—G to prepare Z—GG*G—ONb and GG*G was obtained by removing the Z— and —ONb groups by catalytic reduction with Pd. The other C-deuteriated trimers and tetramers were prepared similarly. G*—ONb was used for preparation of GGG* and GGGG*.

These oligomers were treated with an aqueous solution of LiBr or with dichloroacetic acid (DCA) as described previously.[20] The samples treated with an aqueous solution of LiBr and with DCA are termed the A-series and B-series samples, respectively. The abbreviations for the two crystalline modifications of these C-deuteriated *N*-acetylglycine trimer and tetramer acid types are listed in Table 1.

Table 1 Abbreviations for A- and B-series of selectively C-deuteriated *N*-acetylglycine trimer and tetramer acid types

N-acetylglycine oligomer acid type[a]		A-series	B-series
trimer	$AcG_1^*G_2G_3$	G1D3-A	G1D3-B
	$AcG_1G_2^*G_3$	G2D3-A	G2D3-B
	$AcG_1G_2G_3^*$	G3D3-A	G3D3-B
tetramer	$AcG_1^*G_2G_3G_4$	G1D4-A	G1D4-B
	$AcG_1G_2^*G_3G_4$	G2D4-A	G2D4-B
	$AcG_1G_2G_3^*G_4$	G3D4-A	G3D4-B
	$AcG_1G_2G_3G_4^*$	G4D4-A	G4D4-B

[a] An asterisk-marked G denotes a C-deuteriated glycine residue.

Samples were identified by elemental analysis and the agreement between the calculated and observed values was within 0.5%. Isotopic purity of each C-deuteriated oligomer, determined by ^{1}H NMR, was 98%.

Methods

Raman spectra below 3600 cm^{-1} were obtained with a Nicolet 950 Fourier transform Raman spectrometer using the Nd:YAG laser (excitation wavelength of 1064 nm) with a resolution of 4 cm^{-1} at room temperature. The Raman spectra of the solid samples were obtained from pressed solid samples using a laser power of 500 mW.

X-Ray powder diffraction patterns were obtained by use of an RAD-RC diffractometer with countermonochrometer (Cu-Kα ray; voltage, 60 kV, current, 200 mA).

Abbreviations

The following abbreviations for vibrational assignments are used: amide I, mainly C=O stretching vibration; amide II, NH in-plane bending vibration coupled with the amide CN stretching mode; amide III, amide CN stretching vibration coupled with NH in-plane bending and C^{α}—H bending modes.[26,27]

Results and Discussion

X-Ray powder diffraction patterns of *N*-acetylglycine oligomers

The X-ray powder diffraction patterns of selectively C-deuteriated *N*-acetylglycine trimer and tetramer acid types were measured and compared with those of PGI[1,5,6] and PGII.[1,7–10] For the C-deuteriated A-series, very intense reflections at 4.18–4.19 Å and weak reflections at 3.15–3.17 Å, which correspond well to the 4.14 and 3.09 Å reflections of PGII, were observed, while the diffraction patterns of the C-deuteriated B-series contained very intense reflections at 3.35–3.37 Å and medium reflections at 4.35–4.36 Å, corresponding to the reflections at 3.42 and 4.36 Å for PGI. The results indicate that the oligomers of the C-deuteriated A-series take up the PGII-like helical structure while those of the C-deuteriated B-series take up a structure similar to the β-sheet structure of PGI. Thus, the oligomers of the C-deuteriated A-series can be regarded as PGII-type oligomers and those of the C-deuteriated B-series as PGI-type oligomers.

Raman scattering spectra of PGII- and PGI-type glycine oligomers

The Raman scattering spectra of PGII- and PGI-type *N*-acetylglycine trimer and tetramer acid types and their selectively C-deuteriated derivatives were measured in the 100–3600 cm^{-1} region, and were compared with the data of isotopic polyglycines[11] and with the normal modes of PGI[13,14] and PGII.[15] It was also confirmed from the Raman spectra that the A-series samples take up a PGII-like structure while the B-series samples are in a PGI-like structure.

For these C-deuteriated oligomers, it has been found that the observed band frequencies of the NH stretch mode, the C=O stretch mode of the terminal CO_2H group, and the amide I and amide II modes are virtually invariant upon selective C-deuteriation. Therefore, discussion is focussed on the amide III, CH_2- and CD_2-characteristic modes.

Raman scattering spectra of selectively C-deuteriated PGII-type glycine oligomers

Amide III. Fig. 1 shows the Raman spectra of the A-series oligomers. For undeuteriated oligomers, the Raman bands at 1280–1284 and 1290–1294 cm^{-1} are assigned to amide III modes.[15] For C-deuteriated A-series oligomers, selective C-deuteriation affects the spectral features in this region, since amide III modes are heavily mixed with the C^{α}—H and CH_2 characteristic modes.[15] For the trimers, deuteriation of G1-CH_2 brings about the disappearance of the 1284 cm^{-1} band and on deuteriation of G2-CH_2 the 1290 cm^{-1} band disappears, indicating that the G1-CH_2 group contributes to the former band and the G2-CH_2 group to the latter. For the tetramers, the intensity of the 1280–1282 cm^{-1} band decreases on deuteriation of the G1- or G4-residue, while that of the 1292–1298 cm^{-1} band decreases upon deuteriation of the G2- or G3-CH_2 group. Thus, the G1- and G4-CH_2 groups contribute to the band at 1280–1282 cm^{-1} and the G2- and G3-CH_2 groups to those at 1292–1298 cm^{-1}.

CH_2 deformational bands. For the undeuteriated A-series oligomers, broad and strong bands at 1423–1424 cm^{-1} are assigned to the CH_2 bend modes. These bands are split by selective C-deuteriation. For the trimers, when the G1- or G2-CH_2 group is deuteriated, the intensity of the 1423 cm^{-1} band decreases and the 1408–1410 cm^{-1} band appears, while on deuteriation of the G3-CH_2 group this latter band disappears. Thus, we may assume that both the G1- and G2-CH_2 groups contribute to the 1423 cm^{-1} band but only the G3-CH_2 group contributes to the 1410 cm^{-1} band. For the A-series tetramers, the intensity of the 1422–1425 cm^{-1} band decreases on deuteriation of the G1- (or G2- or G3-) methylene, indicating that all three methylene groups contribute to the 1422–1425 cm^{-1} band. Furthermore, since the band at 1412–1415 cm^{-1} disappears on deuteriation of the G4-CH_2 group, we may assign this band to the G4-CH_2 group.

The CH_2 wag modes, which are coupled with an NH in-plane bend mode,[15] appear in the 1330–1390 cm^{-1} region. For the Raman spectra of undeuteriated A-series oligomers, the bands at 1350–1358 and 1385 cm^{-1} are assigned to the CH_2 wag modes.

For the C-deuteriated trimers, deuteriation of the G1- or G2-CH_2 group results in a decrease in intensity of the 1380–1381 cm^{-1} band while on deuteriation of the G3-CH_2 group the 1357–1358 cm^{-1} band disappears. Therefore, it may be assumed that the G1- and G2-CH_2 groups predominantly contribute to the 1380–1385 cm^{-1} band while the G3-CH_2 group contributes to the 1357–1358 cm^{-1} band. For the C-

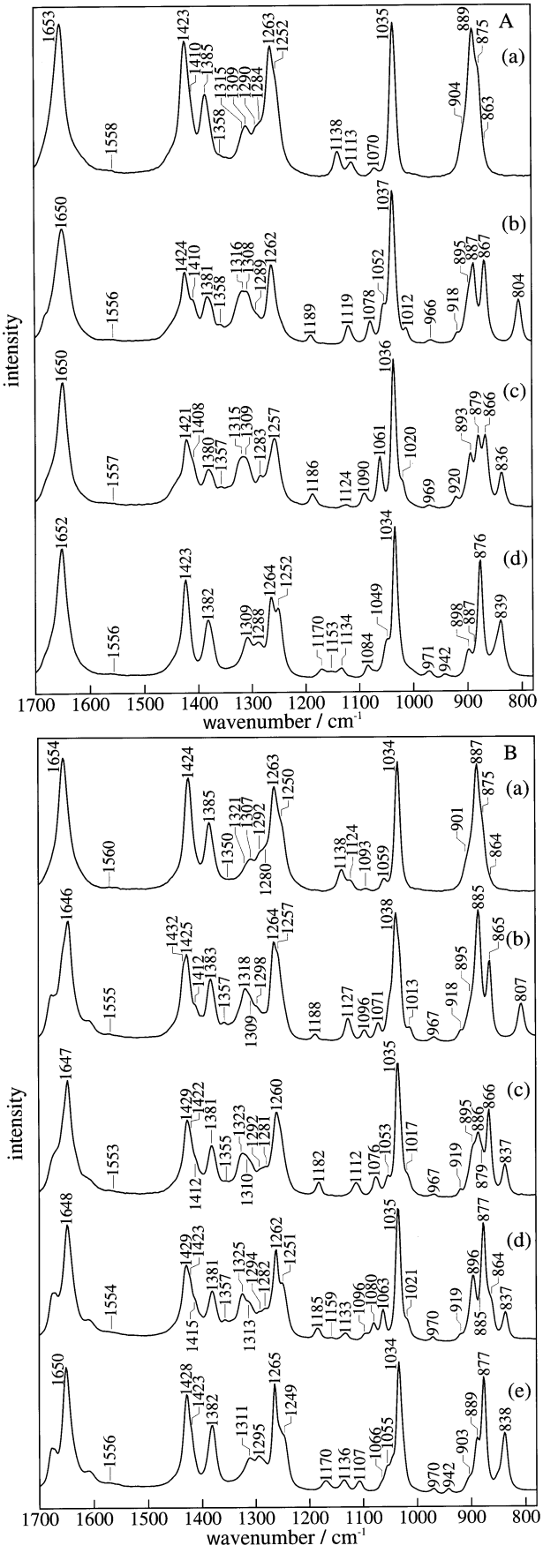

Fig. 1 Raman spectra of undeuteriated and selectively C-deuteriated PGII-type *N*-acetylglycine oligomers in the solid state in the 800–1700 cm^{-1} region. [A, Trimers: (a) undeuteriated; (b) G1D3-A; (c) G2D3-A; (d) G3D3-A. B Tetramers: (a) undeuteriated; (b) G1D4-A; (c) G2D4-A; (d) G3D4-A; (e) G4D4-A].

deuteriated tetramers, similar observations were made: on deuteriation of the G2- or G3-CH_2 group the intensity of the band at 1381–1385 cm^{-1} decreases, while on deuteriation of G4-CH_2 the 1350–1357 cm^{-1} band disappears. Thus, it is evident that both G2- and G3-CH_2 groups contribute to the 1381–1385 cm^{-1} band and the G4-CH_2 group contributes to the 1350–1357 cm^{-1} band.

For the Raman spectra of G1D3-A and G2D3-A, the bands at 1308–1309 and 1315–1316 cm^{-1} are observed in common, and may be assigned to the CH_2 wag modes coupled with the CH_2 twist modes. On deuteriation of the G3-CH_2 group the latter band disappears, indicating that the 1315–1316 cm^{-1} band arises from the G3-residue. For the C-deuteriated tetramers, the 1307–1313 cm^{-1} bands observed in common may arise from all CH_2 groups and the 1318–1325 cm^{-1} bands from the G4-CH_2 group.

For undeuteriated oligomers, the CH_2 twist modes, which are heavily mixed with CH_2 wag and NH in-plane bend modes,[15] appear at 1250–1252 and 1263 cm^{-1}. Selective C-deuteriation markedly affects the Raman band features in this region; for the trimers the intensity of the 1252 cm^{-1} band decreases upon deuteriation of the G1- or G2-CH_2 group, showing the contribution of G1- and G2-CH_2 groups to this band. Similar results were obtained for the tetramers.

The CH_2 rock modes, which are heavily mixed with skeletal C—C stretch and C—N stretch modes, are observed in the 800–1000 cm^{-1} region. For the undeuteriated trimer, a dominant Raman band at 889 cm^{-1} (in addition to shoulders at 863, 875 and 904 cm^{-1}) is observed, and is assigned to the CH_2 rock mode. For the C-deuteriated trimers, the 875 cm^{-1} band disappears on deuteriation of the G1-CH_2 group, indicating that the G1-CH_2 group contributes to this band. On deuteriation of the G2-CH_2 group the 889 cm^{-1} band disappears, while deuteriation of G3-CH_2 group results in a disappearance of the 863 cm^{-1} band. Therefore, the G2- and G3-CH_2 groups contribute to the 889 and 863 cm^{-1} bands, respectively. Since the 893–898 cm^{-1} bands (which corresponds to the 904 cm^{-1} band in the undeuteriated trimer) are observed in common for all these C-deuteriated trimers, all the CH_2 groups contribute to these bands.

For the undeuteriated tetramer, a predominant Raman band at 887 cm^{-1} is observed, in addition to very weak shoulder bands at 864, 875 and 901 cm^{-1}, and is assigned to the CH_2 rock mode. When the CH_2 group of the tetramer is selectively deuteriated, splitting of the rock mode also occurs, as shown in Fig. 1(B). On deuteriation of the G1-CH_2 group the 875 cm^{-1} band disappears while deuteriation of the G4-CH_2 group brings about disappearance of the 864 cm^{-1} band. These results are similar to those obtained for G1D3-A and G3D3-A. Thus, we may assume that the 875 cm^{-1} band arises from the CH_2 group of the N-terminal glycine residue, while the 864–866 cm^{-1} band arises from that of the C-terminal glycine. When the G2-CH_2 group is deuteriated, the intensities of the 879 and 886 cm^{-1} bands decrease, while deuteriation of the G3-CH_2 group results in a decrease in intensity of the 885 cm^{-1} band. Thus, for the tetramers, both the G2- and G3-CH_2 groups predominantly contribute to the 887 cm^{-1} band and the G2-CH_2 group also contributes to the 879 cm^{-1} band.

CD_2 deformational bands. For the G1D3-A and G1D4-A samples, in which each G1-CH_2 group was deuteriated, the band arising from the CD_2 rock modes appears at a lower frequency [804 (trimer) and 807 (tetramer) cm^{-1}], compared with those of the oligomers C-deuteriated at other positions, as seen in Table 2. For the G3D3-A and G4D4-A samples, in which the C-terminal CH_2 group was deuteriated, the CD_2 bend modes are clearly observed at a lower frequency and splitting of the bend and wag modes also occurs.

Table 2 CD_2 characteristic band frequencies (cm^{-1}) for selectively C-deuteriated PGII-type trimers and tetramers

trimer			tetramer				
G1D3-A	G2D3-A	G3D3-A	G1D4-A	G2D4-A	G3D4-A	G4D4-A	tentative assignment[a]
1189	1186		1188	1182	1185		
		1170			1159	1170	
		1153			1133	1136	CD_2 bend
		1134		1112			
1078	1090	1084	1071	1076	1080	1066	
1052	1061	1049					
966	969	971	967	967	970	970	CD_2 wag
		942				942	
918	920		918	919	919		CD_2 twist
	836	839		837	837	838	CD_2 rock
804			807				

[a] Ref. 11.

Skeletal stretch bands. For the undeuteriated trimer and tetramer, the Raman bands observed in the 1000–1150 cm^{-1} region are assigned to the skeletal stretch modes. In particular, C-deuteriation does not affect the frequency of the 1034–1038 cm^{-1} band which is characteristic of the PGII-type structure.[15]

CD_2 stretch bands. Fig. 2 shows the Raman spectra of selectively C-deuteriated A-series oligomers in the CD_2 stretch region. For the C-deuteriated PGII-type trimers, the Raman bands at 2110–2117, 2166–2169 and 2245–2248 cm^{-1} correspond closely to the IR bands at 2117, 2172 and 2244 cm^{-1} which were observed for C-deuteriated PGII.[11] The Raman spectral features in this region reflect the environment of the selectively C-deuteriated glycine residue. We may compare the Raman band features of the CD_2 stretch modes for the three selectively-C-deuteriated trimers with those of the four C-deuteriated tetramers. In this region the features of the G1- and G3-deuteriated trimers are very similar to those of the G1- and G4-deuteriated tetramers, respectively. This observation implies that the environments of the N- and C-terminal glycine residues in both the trimer and the tetramer are very similar. The spectral feature of the G2D3-A sample is approximately similar to those of the G2D4-A and G3D4-A samples. Therefore, we may assume that the glycine residues which are sandwiched between the two terminal residues are also in a similar environment for both the trimers and the tetramers.

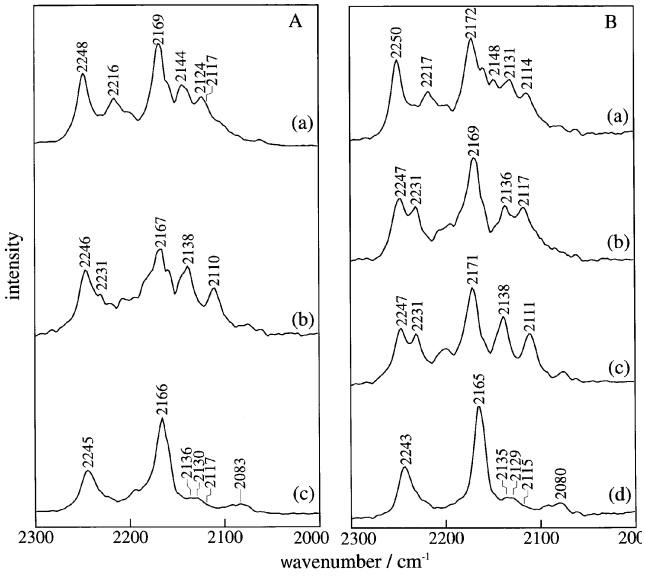

Fig. 2 Raman spectra of selectively C-deuteriated PGII-type *N*-acetylglycine oligomers in the solid state in the CD_2 stretch region. [A, Trimers (a) G1D3-A; (b) G2D3-A; (c) G3D3-A. B, Tetramers: (a) G1D4-A; (b) G2D4-A; (c) G3D4-A; (d) G4D4-A].

Raman scattering spectra of selectively C-deuteriated PGI-type glycine oligomers

Fig. 3 shows the Raman spectra of the B-series oligomers. For the undeuteriated trimer and tetramer, the Raman bands at 1014–1015 and 1154 cm^{-1} are assigned to the skeletal stretch modes, which are characteristic of a PGI-type structure.[13,14] For the C-deuteriated oligomers, selective C-deuteriation strongly affects the Raman bands in this region in both frequency and intensity. Indeed, from the results of normal mode analysis for isotopic PGI,[13,14] one may assume that bands coupled between the CD_2 wag and bend modes and those for the skeletal stretch modes appear in this region. In this study, detailed discussion of these spectral features is omitted, since it is difficult at present explicitly to interpret them.

CH_2 deformational bands. For the B-series samples, the Raman bands arising from the CH_2 bend, wag and rock modes are listed in Table 3 (A, trimers; B, tetramers). It is found that the Raman bands arising from these modes vary markedly both in frequency and intensity upon C-deuteriation.

The Raman bands in the 1430–1460 cm^{-1} region arise from the CH_2 bend modes. For the undeuteriated trimer, the CH_2 bend modes consist of the three bands at 1433, 1454 and 1459 cm^{-1}. We may note that selective deuteriation of G1- or G2- or G3-CH_2 groups cause the bands at 1450–1455, 1459–1460 and 1431–1438 cm^{-1} to disappear. Therefore, the G1-CH_2 group predominantly contributes to the 1450–1455 cm^{-1} band and the G2-CH_2 group to the 1459–1460 cm^{-1} band. Furthermore, the 1431–1438 cm^{-1} band contains the predominant contribution of the G3-CH_2 group, although the increased intensity found for the 1438 cm^{-1} band of G1D3-B cannot be explained.

The CH_2 wag modes are reflected in the 1300–1420 cm^{-1} region. For the undeuteriated trimer, the wag modes consist of four bands at 1337, 1373, 1389 and 1412 cm^{-1}. Deuteriation of the G1- or G2-CH_2 group causes the band at 1383–1389 or 1373–1378 cm^{-1} to disappear. Moreover, on deuteriation of the G3-CH_2 group the 1337–1344 and 1411–1414 cm^{-1} bands also disappear. These results indicate that the G1- and G2-CH_2 groups contribute mainly to the bands at 1383–1389 and 1373–1378 cm^{-1} while the G3-CH_2 group contributes to the bands at 1337–1346 and 1411–1414 cm^{-1}.

For these trimers, the Raman bands at 1240–1243 and 1268–1269 cm^{-1} may be assigned to the CH_2 twist modes.

For the undeuteriated trimer, we may assign the bands at 896, 961 and 985 cm^{-1} to the CH_2 rock modes. For the selectively C-deuteriated trimers, the very weak bands at 895–896,

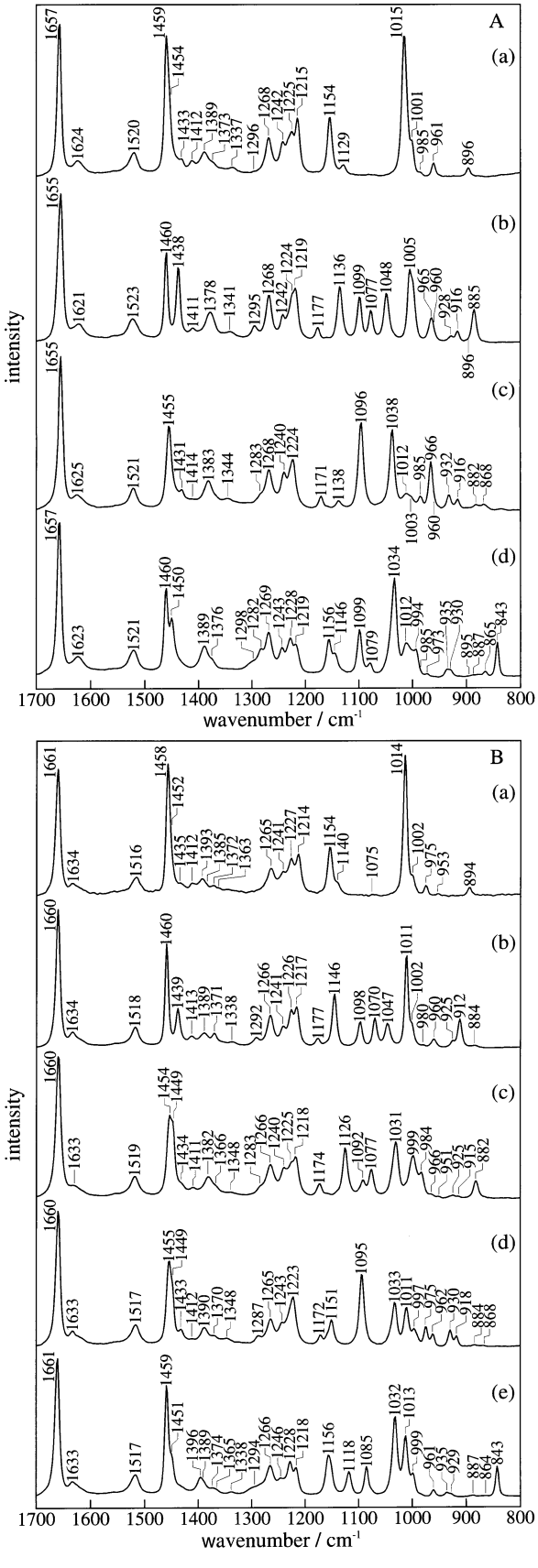

Fig. 3 Raman spectra of undeuteriated and selectively C-deuteriated PGI-type *N*-acetylglycine oligomers in the solid state in the 800–1700 cm^{-1} region. [A, Trimers: (a) undeuteriated; (b) G1D3-B; (c) G2D3-B; (d) G3D3-B. B, Tetramers: (a) undeuteriated; (b) G1D4-B; (c) G2D4-B; (d) G3D4-B; (e) G4D4-B].

960 and 985 cm^{-1} probably correspond to the 896, 961 and 985 cm^{-1} bands of the undeuteriated trimer. When the G1-CH_2 group is deuteriated, the 985 cm^{-1} band disappears,

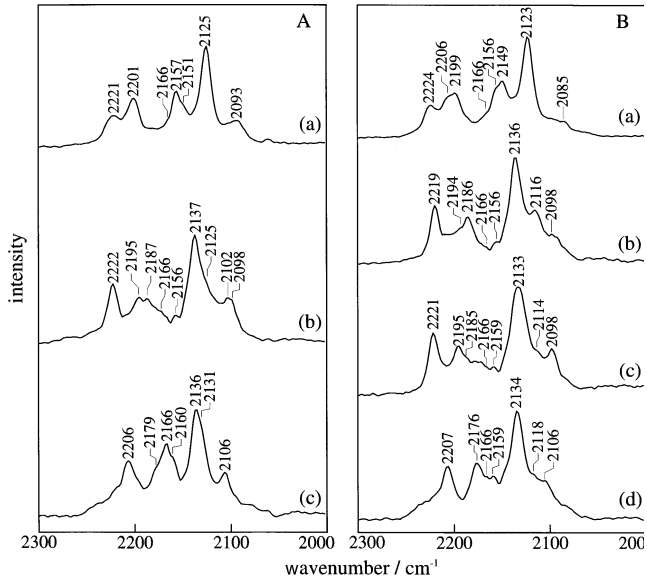

Fig. 4 Raman spectra of selectively C-deuteriated PGI-type *N*-acetylglycine oligomers in the solid state in the CD_2 stretch region. [A, Trimers: (a) G1D3-B; (b) G2D3-B; (c) G3D3-B. B, Tetramers (a) G1D4-B; (b) G2D4-B; (c) G3D4-B; (d) G4D4-B]

while upon deuteriation of the G2-CH_2 group, the 895–896 cm^{-1} band disappears, and upon deuteriation of the G3-CH_2 group the 960–961 cm^{-1} band disappears. Thus, the G1-CH_2 group predominantly contributes to the 985 cm^{-1} band and the 895–896 cm^{-1} band probably arises from the G2-CH_2 group. Furthermore, the G3-CH_2 group predominantly contributes to the 960–961 cm^{-1} band.

For selectively C-deuteriated tetramers similar observations were made, and tentative assignment of the CH_2 characteristic modes for these PGI-type tetramers is also summarized in Table 3(*a*).

CD_2 stretch bands. Fig. 4 shows the Raman spectra of selectively C-deuteriated PGI-type oligomers in the CD_2 stretch region.

The Raman spectral features of the C-deuteriated B-series oligomers in this region reflect the environment of the selectively C-deuteriated glycine residue in the PGI-type structure. For the trimers, the spectral features of G1D3-B and G3D3-B are very similar to those of G1D4-B and G4D4-B. Furthermore, the Raman spectral features of the CD_2 stretch modes for G2D3-B are similar to those of G2D4-B and G3D4-B. Thus, in the B-series oligomers, we may assume that N- and C-terminal glycine residues have similar residual environments and that the G2-glycine residue of the trimer also has a similar environment to those of the G2- and G3-residues of the tetramer.

CD_2 deformational bands. The bend, wag, twist and rock modes characteristic of the CD_2 group in the PGI-type structure are listed in Table 4. Note that the CD_2 rock modes of the G3D3-B and G4D4-B are observed at a lower frequency (843 cm^{-1}). This observation may indicate restriction of the C-terminal glycine residues of the trimer and the tetramer.

Conclusion

Selectively C-deuteriated *N*-acetylglycine trimer and tetramer acid types have been synthesized, and their two crystalline modifications, solid-A and solid-B, which correspond to PGII and PGI in secondary structure, have been prepared.

Table 3(*a*) CH_2 characteristic mode frequencies (cm^{-1}) for PGI-type trimers and their tentative assignment

undeuteriated trimer	G1D3-B	G2D3-B	G3D3-B	tentative assignment	
1459	1460	—	1460	G2-CH_2	bend
1454	—	1455	1450	G1-CH_2	
1433	1438	1431	—	G3-CH_2	
1412	1411	1414	—	G3-CH_2	wag
1389	—	1383	1389	G1-CH_2	
1373	1378	—	1376	G2-CH_2	
1337	1341	1344	—	G3-CH_2	
985	—	985	985	G1-CH_2	rock
961	960	960	—	G3-CH_2	
896	896	—	895	G2-CH_2	

(*b*) CH_2 characteristic mode frequencies (cm^{-1}) for PGI-type tetramers and their tentative assignment

undeuteriated tetramer	G1D4-B	G2D4-B	G3D4-B	G4D4-B	tentative assignment	
1458	1460	—	—	1459	G2-, G3-CH_2	bend
1452	—	1449	1449	1451	G1-CH_2	
1435	1439	1434	1433	—	G4-CH_2	
1412	1413	1411	1412	—	G4-CH_2	wag
1393	—	—	1390	1396	G1-, G2-CH_2	
1385	1389	1382	—	1389	G3-CH_2	
1372	1371	—	1370	1374	G2-CH_2	
1363	—	1366	—	1365	G1-, G3-CH_2	

Table 4 CD_2 characteristic band frequencies (cm^{-1}) of selectively C-deuteriated PGI-type trimers and tetramers

trimer			tetramer				
G1D3-B	G2D3-B	G3D3-B	G1D4-B	G2D4-B	G3D4-B	G4D4-B	tentative assignment[a]
1177	1177		1177	1174	1172		CD_2 wag + CD_2 bend
		1156	1146	1126	1151	1156	
1136	1138	1146				1118	
1099	1096	1099	1098	1092	1095	1085	CD_2 bend + CD_2 wag
1077		1079	1070	1077			
1048	1038	1034	1047	1031	1033	1032	
928	932	935	925	925	930	935	CD_2 twist + CD_2 wag
916	916	930	912	915	918	929	
855	882	887	884	882	884	887	CD_2 wag + CD_2 rock
	868	865			868	864	
		843				843	CD_2 rock

[a] Ref. 14.

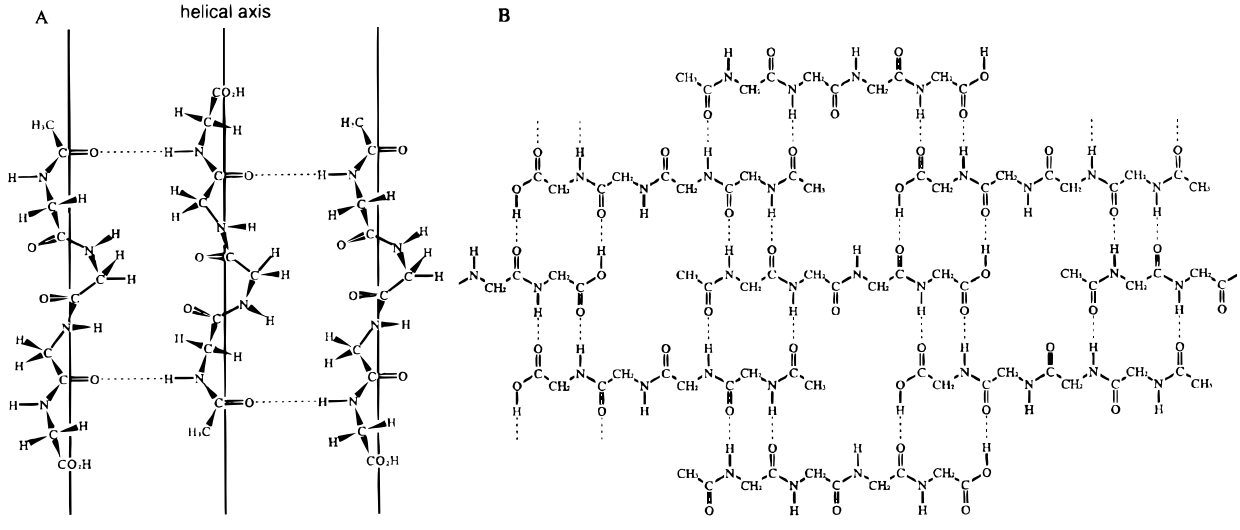

Fig. 5 PGII(helical)-type (A) and PGI(β-sheet)-type (B) structural models for the *N*-acetylglycine tetramer. The dotted lines represent hydrogen bonding.

X-Ray powder diffraction patterns of these oligomers have been measured and compared with those of PGII and PGI. The results indicate that the oligomers of the selectively C-deuteriated A-series take up the PGII-type helical structure while those of the C-deuteriated B-series adopt a β-sheet structure which is similar to that of PGI.

Raman scattering spectra were measured for these A- and B-series oligomers and, in particular, the CH_2- and CD_2-characteristic modes were examined. Selective C-deuteriation made it possible to assign the CH_2 deformational bands to each CH_2 group.

For the A- and B-series oligomers, in which the N- and C-terminal glycine CH_2 groups were deuteriated, the CD_2 bend, twist and rock modes appeared at a lower frequency than those of the oligomers C-deuteriated in other positions. From the Raman band features in the CD_2 stretch region, we may assume that the N- and C-terminal glycine residues of the A- and B-series oligomers are in very similar environments to one another and that the glycine residues which are sandwiched between the two terminal residues are also in a similar environment to each other.

We have recently studied the ^2H spin–lattice relaxation times for the samples of selectively C-deuteriated A- and B-series in the solid state,[28] in order to evaluate the mobility of each glycine residue in these oligomers. The results showed that for the two series of C-deuteriated oligomers segmental mobilities of the CH_2 groups of both the N- and C-terminal residues are more restricted than those of the methylenes sandwiched between the terminal residues.

Furthermore, in our previous studies,[20] we have shown that the mode of the hydrogen-bonding system is different between the A- and B-series samples.

Thus, we may assume that such behaviour of the two terminal residues depends on the mode of the hydrogen-bonding system. The two structural models are shown schematically in Fig. 5 for the representative tetramer case.

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