

Table IV
Methylene Carbon Spectra of Poly(vinyl acetate)^a

Chemical shift, ppm, from HMDS	Tetrad assign	Peak intensities			
		Atactic sample		Isotactic sample	
		Calcd ^b	Obsd	Calcd ^b	Obsd
38.2	rrr	0.17	0.20	0.04	0
37.8	rrm	0.25	0.25	0.06	0.1
37.7	rmr + mrm	0.28	0.25	0.08	0.1
37.6	mmr	0.19	0.17	0.25	0.2
37.3	mmm	0.11	0.13	0.57	0.6

^a Methylene carbon spectra were obtained in CDCl₃ at 120°. ^b The tetrads were obtained from the starting PVA (ref 8).

tral resolution was also achieved by examining PVAc dissolved in orthodichlorobenzene at about 140° in nitromethane at 100°, and in DMSO-*d*₆ at 100°. Therefore, the above-mentioned specific solvent shielding in the proton resonance spectra of PVAc does not significantly contribute to the corresponding carbon-13 spectra. The effect of raising solution temperature appears to impart increased mobilities to the polymer backbone carbons and the pendant groups, which, in turn, lead to improved spectral resolution.

In Figure 5 are shown the horizontal expansion of Figure 4 and the corresponding scan of the isotactic PVAc. The atactic samples give five methylene carbon lines centered at 37.7 ppm. Unlike the spectrum of its precursor PVA, neither the relative positions nor the intensities of these lines exhibit any regularities. They cannot, therefore, be unambiguously assigned to the two stereochemical dyads. However, by using the known tetrad distributions of the starting PVA samples, we have analyzed the methylene carbon resonances of the derived PVAc polymers as presented in Table IV. For such analyses, we have invoked the assumption, in accordance with the work of Schaefer and Natusch¹¹ and our previous studies on PVA,⁸ that the integrated peak intensity of each methylene carbon line can be used to count the number of carbons contributing to that

resonance. The nearly quantitative agreements between the observed intensities and the calculated values for both the atactic and isotactic samples indicate that our assignments are consistent. Thus, it follows that the methylene carbon spectra can be used for quantitative tacticity measurements of PVAc. In this work, we have also calculated the triad distributions by using the following relationships of tetrads and triads: $mm = mmm + \frac{1}{2}mmr$, $rr = rr + \frac{1}{2}rrm$, and $mr = \frac{1}{2}mmr + \frac{1}{2}rrm + rmr + mrm$.¹⁰ The results are included in Table II to compare with the corresponding proton measurements.

The methine carbon region which ranged from 66.6 to 65.6 ppm consists of two main features. The lower field singlet was found to have relative intensities of 0.20 and 0.68 for the atactic and isotactic PVAc, respectively. Therefore, this peak must arise from the mm triads. On the other hand, the upfield feature with additional fine structures cannot be readily assigned to the mr and rr triads. For the atactic sample, it is conceivable that these lines could be attributed to the combinations of various pentads. However, fitting seven pentads into the three partially resolved peaks of the upfield feature is of rather questionable validity.

Acknowledgment. The authors would like to acknowledge F. W. Barney, Jr., G. Watunya, and J. M. White for technical assistance.

References and Notes

- (1) (a) Plastics Department; (b) Central Research Department.
- (2) (a) K. Fujii, *J. Polym. Sci., Part D*, **5**, 431 (1971), and references therein; (b) F. A. Bovey, E. W. Anderson, D. C. Douglass, and J. A. Manson, *J. Chem. Phys.*, **39**, 1199 (1963).
- (3) K. C. Ramey and J. Messick, *J. Polym. Sci., Part A-2*, **4**, 155 (1966).
- (4) K. Fujii, Y. Fujiwara, and S. Fujiwara, *Makromol. Chem.*, **89**, 278 (1965).
- (5) A. Abe and A. Nishioka, *Kobunshi Kagaku*, **29**, 448 (1972).
- (6) Y. Inoue, R. Chûjô, A. Nishioka, S. Nozakura, and H. Iimuro, *Polym. J.*, **4**, 244 (1973).
- (7) T. K. Wu, D. W. Ovenall, and G. S. Reddy, *J. Polym. Sci., Part A-2*, **12**, 901 (1974).
- (8) T. K. Wu and D. W. Ovenall, *Macromolecules*, **6**, 582 (1973).
- (9) A. Beresiewicz, *J. Polym. Sci.*, **35**, 321 (1959).
- (10) F. A. Bovey, "Polymer Conformation and Configuration," Academic Press, New York, N.Y., 1969, Chapters 1 and 2.
- (11) J. Schaefer and D. F. S. Natusch, *Macromolecules*, **5**, 416 (1972).

Conformational Studies of Poly[(S)- β -aminobutyric acid]

Fu Chen,^{1a} Giuseppina Lepore,^{1b} and Murray Goodman*

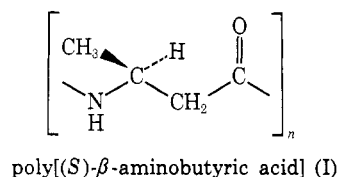
Department of Chemistry, University of California, San Diego, La Jolla, California 92037.
Received March 5, 1974

ABSTRACT: The conformation of high molecular weight and optically active poly[(S)- β -aminobutyric acid] in hexafluoroacetone sesquihydrate (HFA · 1.5(H₂O)), hexafluoroisopropyl alcohol (HFIP), methanesulfonic acid, and their mixtures were examined by using circular dichroism, ultraviolet, and infrared spectroscopy. The results suggest that the polymer exhibits a β -associated conformation in HFIP. The addition of a trace amount of water to a solution of the polymer in HFIP enhances the association phenomenon. Circular dichroism spectra of the polymer films which were cast from HFA and HFIP solutions also show the same β structure. In methanesulfonic acid the poly[(S)- β -aminobutyric acid] assumes a disordered structure.

High molecular weight poly(β -amides) which have β -amino acids as the repeating units are similar to polypeptides and to silk fibroin. They have high melting points and also low solubility in typical organic solvents. The synthesis and fiber properties of various poly(β -amides) have been extensively studied in recent years.²⁻⁴ Optically active poly(β -amides) have also been synthesized.⁵

The structure of poly[(S)- β -aminobutyric acid] (I) is similar to that of poly(L-alanine). The latter polymer exhibits an α -helical form both in solution and as a film.⁶⁻¹⁰ With the additional α -methylene group, poly[(S)- β -aminobutyric acid] would be expected to have different conformational properties from poly(L-alanine).

Studies with X-ray and polarized infrared dichroism of



poly[(S)-β-aminobutyric acid] films have been carried out by Schmidt.⁵ He concluded that in the solid state this polymer exists in a β conformation constructed from antiparallel chains. Since the polymer (mol wt = 200,000) is insoluble in most of the nonacidic solvents, it is difficult to perform studies in solution.

However, the polyamide is soluble in hexafluoroacetone sesquihydrate (HFA · 1.5(H₂O)) and in hexafluoroisopropyl alcohol (HFIP). Both solvents are transparent in the spectral regions critical for the conformational diagnoses. In this paper, we report the conformational analysis of poly[(S)-β-aminobutyric acid] in solution by using circular dichroism (CD), ultraviolet (uv), and infrared (ir) spectroscopy.

Experimental Section

Materials. Hexafluoroacetone sesquihydrate and hexafluoroisopropyl alcohol were purchased from Aldrich Chemical Co. Hexafluoroacetone deuterate was obtained from Wilmad Glass Co., Inc. Methanesulfonic acid was purchased from Eastman Kodak Co. All solvents were used without further purification. Elementary analysis was carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

Poly[(S)-β-aminobutyric acid] and the monomer (S)(-)-4-methylazetidinone were generous gifts from Drs. J. Brandrup and E. Schmidt at Farbwerke Hoechst, Inc., in Frankfurt, Germany. Light scattering measurements in dichloroacetic acid indicated that the molecular weight of poly[(S)-β-aminobutyric acid] was 200,000. The synthesis and properties of the above compounds have been reported earlier.⁵

(S)-β-Aminobutyric Acid Hydrochloride. The compound, (S)(-)-4-methylazetidinone (2 g, 0.023 mol), was dissolved in 6 N hydrochloric acid (8 ml) and the solution was refluxed at 110° for 20 min. After cooling the solution, the solvent was removed by lyophilization. The hydrolyzed product (S)-β-aminobutyric acid hydrochloride was obtained: 3 g (95% yield); mp 131°; [α]_D²⁵ +21.18° (c 0.7, H₂O); nmr (D₂O) δ 1.38 (d, 3); 2.75 (d, 2), 3.73 (q, 1). *Anal.* Calcd for C₄H₁₀NO₂Cl: C, 34.42; H, 7.17; N, 10.04. Found: C, 34.41; H, 7.31; N, 10.09.

N-Acetyl-(S)-β-aminobutyric Acid Benzyl Ester. The compound, (S)-β-aminobutyric acid benzyl ester, was synthesized from (S)-β-aminobutyric acid hydrochloride according to the method of Greenstein and Winitz.¹¹ An oily product was obtained which was used without further purification.

(S)-β-Aminobutyric acid benzyl ester (2.3 g, 0.01 mol) was dissolved in pyridine (3.5 ml, 0.04 mol). Acetyl chloride (2.4 g, 0.032 mol) was added dropwise to the ice-cooled solution. Ether (50 ml) was added to this mixture. The ether layer was washed successively by the following sequence: water, 5% aqueous citric acid, water, 10% aqueous sodium bicarbonate, and water. After drying over sodium sulfate, the ether was removed under reduced pressure. The remaining oily residue was further lyophilized. The product was crystallized from ethyl acetate–n-hexane to yield 0.9 g (38%) of product: mp 58°; [α]_D²⁵ –14.83° (c 0.4, EtOAc); tlc *R_f* 0.83 (silica gel, BuOH:HAc:H₂O = 4:1:5). *Anal.* Calcd for C₁₃H₁₇NO₃: C, 66.38; H, 7.23; N, 5.95. Found: C, 66.10; H, 7.15; N, 5.93.

N-Acetyl-(S)-β-aminobutyric Acid. The compound N-acetyl-(S)-β-aminobutyric acid benzyl ester (0.8 g, 0.003 mol) was dissolved in anhydrous methanol (100 ml) and 0.1 g of a 5% palladium-charcoal catalyst was added. A few drops of glacial acetic acid were also added. The mixture was hydrogenated for 3 hrs at room temperature in a Parr hydrogenation apparatus. The catalyst was removed by filtration and the solvents were removed by reduced pressure to yield a clear oil. No resonance for the benzyl group was found on the nmr spectrum. The compound was used without further purification.

N-Acetyl-(S)-β-aminobutyric Acid N'-Methylamide. The compound, N-acetyl-(S)-β-aminobutyric acid (0.45 g, 0.004 mol) was dissolved in 25 ml of dry tetrahydrofuran. The solution was

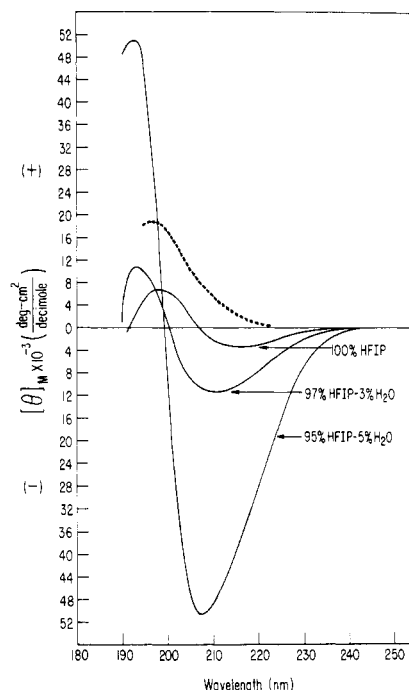


Figure 1. Circular dichroism of poly[(S)-β-aminobutyric acid] in hexafluoroisopropyl alcohol–water mixtures (—) and of N-acetyl-(S)-β-aminobutyric acid N'-methylamide in hexafluoroisopropyl alcohol (---).

cooled with stirring to –20° in a Dry Ice–carbon tetrachloride bath; N-methylmorpholine (0.44 g, 0.004 mol) was added. Isobutyl chloroformate (0.58 g, 0.004 mol) was then added and a white precipitate formed. After stirring for 5 min, monomethylamine gas was passed through the mixture for 5 min., after which it was stirred at –20° for 30 min and then slowly warmed to room temperature. The solution was filtered through a sintered glass filter to remove the precipitate. The filtrate was concentrated and dried *in vacuo* to give a solid residue. The white product thus obtained was recrystallized from chloroform–hexane and yielded 0.25 g (36% yield): mp 181° dec; nmr (CDCl₃) δ 1.21 (d, 3, *J* = 6.7 Hz), 1.93 (s, 3), 2.38 (m, 2), 2.77 (d, 3, *J* = 5 Hz), 4.24 (m, 1), 6.30 (d, 1), and 6.75 (d, 1); [α]_D²⁵ –13.08° (c 0.4, trifluoroethanol); *R_f* 0.55 (silica gel, BuOH:HAc:H₂O = 4:1:5). *Anal.* Calcd for C₇H₁₄N₂O₂ · ½(H₂O): C, 50.29; H, 8.98; N, 16.76. Found: C, 50.34; H, 8.56; N, 16.75.

Apparatus and Measurements. In the CD, uv, and ir measurements, dry, prepurified nitrogen was employed to purge each instrument at a rate of 40 ft³/min before and during the experiments. All spectra were recorded at ambient temperature.

Circular dichroism studies were carried out by using a Cary 61 spectropolarimeter with a 450 W Osram Xenon lamp as the light source. The reliabilities of the molar ellipticity values are as follows: at 203 nm, ±5%; at 213 nm, ±2%; at 238 nm, ±1.5%. The experimental solutions were prepared by weighing the desired sample into a volumetric flask and adding the solvent to the appropriate concentration. The studies performed in HFIP–water, HFA–water, and HFIP–methanesulfonic acid mixtures were conducted by first dissolving the polymer in HFIP or HFA. Water or methanesulfonic acid (on a volume basis) was then added and the resulting solution was stirred for 15–20 min to ensure equilibration. Cells with path lengths from 0.01 to 1.0 cm were used. The preparation of solid films for the CD studies was according to the method of Fasman.¹² Films were cast by evaporation of the appropriate polymer solutions layered on quartz disks. The films were dried in a vacuum desiccator before use. Each disk with the film on it was mounted as a window on a Teflon sample holder designed in our laboratory for alignment in the instrument.¹³ The optical rotations were measured on a Perkin-Elmer Model 141 polarimeter.

Ultraviolet solution spectra were measured on a Cary 14 spectrophotometer. A cell with a path length of 0.1 mm was used.

Infrared spectra were recorded with a Perkin-Elmer Model 180 grating infrared spectrophotometer. For solution spectra, the polymers were measured as 0.2–0.4% solution by weight in an Irtan-2 cell with a path length of 0.2 mm. A matched cell containing the solvent was used as the reference. For solid film studies, the prepa-

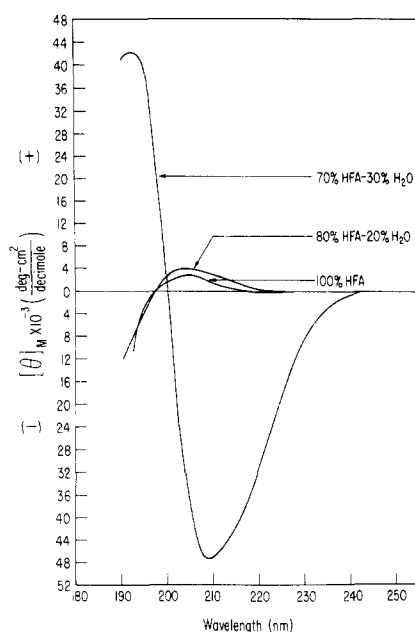


Figure 2. Circular dichroism of poly[(S)- β -aminobutyric acid] in hexafluoroacetone sesquihydrate–water mixtures.

ration was the same as that described for circular dichroism studies. Films were cast directly on the potassium bromide pellets followed by immediate evaporation of the polymer solutions. Films were also prepared by casting the polymer solutions on glass plates. After drying in a vacuum desiccator, the plates were soaked in water. Transparent films were obtained and separated from the plates. The films were dried again before measurements were made.

Results

Circular Dichroism Studies in HFIP and HFA · 1.5(H₂O). The CD spectrum of poly[(S)- β -aminobutyric acid] in HFIP shows a trough at 216 nm and a positive peak at 197 nm with molar ellipticities of -3.2×10^3 and 6.6×10^3 deg cm²/dmol, respectively (Figure 1). The crossover occurs at 207 nm. The CD pattern remains the same as the concentration of the polymer in solution is varied from 2.0 to 0.06 mg/ml. The model compound, *N*-acetyl-(S)- β -aminobutyric acid *N'*-methylamide, shows only an intense positive band near 197 nm. No negative band is observed. The spectral differences between the polymer and the model compound can be interpreted to indicate a conformational difference for a residue in the polymer as compared to the model compound.

Since it has been reported that HFA · 1.5(H₂O) can disrupt the β conformation of isoleucine oligomers,¹⁴ the CD spectrum of the polymer in HFA · 1.5(H₂O) was also examined (Figure 2). The CD pattern is similar to that obtained in HFIP but is shifted to a higher wavelength. The spectrum has a negative band centered at 223 nm with a molar ellipticity of only -1.5×10^2 deg cm²/dmol and a positive band below 218 nm. The circular dichroism of the polymer in HFA · 1.5(H₂O) is much smaller than that reported for polypeptides in a β conformation.^{12,15,16}

In order to study how water affects the conformation of the polymer in HFIP and HFA · 1.5(H₂O) solutions, a small amount of water was added to both solutions. Figure 1 shows that the intensity of the trough and the peak are increased by the addition of water to the HFIP solution. At 3% water concentration based on HFIP, the spectrum shifts toward the blue. At 5% water concentration, the CD shows a large negative band centered at 208 nm and an intense positive peak at 192 nm.

Spectral changes are also observed in HFA–water

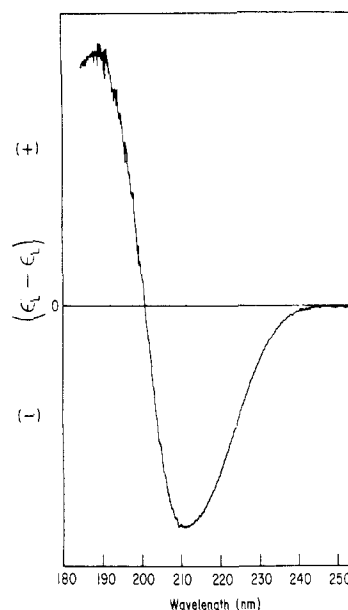


Figure 3. Circular dichroism of poly[(S)- β -aminobutyric acid] film cast from hexafluoroisopropyl alcohol.

mixtures. Below 20% water concentration in HFA · 1.5(H₂O), the spectrum is similar to that in 100% HFA · 1.5(H₂O) solution. A substantial change, however, occurs between 20 and 30% water concentration. Above 30% water concentration, the solution becomes cloudy; further addition of water causes the precipitation of the polymer.

To ascertain the solvent effect of poly[(S)- β -aminobutyric acid] in solution, films were cast from HFIP and HFA · 1.5(H₂O) solutions. The CD spectra of these films show a trough centered at 212 nm and a positive peak near 190 nm (Figure 3). Compared to the solution spectra, these spectra are shifted 6–7 nm toward the blue; the spectral patterns are similar, however.

Methanesulfonic acid has been found to be a good and transparent solvent for polypeptides.¹⁷ In this solvent, polypeptides are usually in a disordered conformation before degradation occurs.¹⁸ A titration study of poly[(S)- β -aminobutyric acid] in HFIP–methanesulfonic acid mixtures clearly indicates that the spectra change as the amount of acid is increased. The results are shown in Figure 4. At 0.1% concentration of acid in HFIP, a strong positive peak is observed at 215 nm. As the concentration of the acid is increased up to 1%, the intensity of the peak increases. Above 1% the intensity gradually decreases. At 100% acid, a positive band is visible at 212 nm with molar ellipticity 3.6×10^3 deg cm²/dmol.

Infrared Studies. Infrared spectra of poly[(S)- β -aminobutyric acid] were measured in HFIP (Figure 5). A decreased absorbance relative to the reference (“negative absorption”) appears between 3380 and 3120 cm⁻¹. This absorption masks the amide A band (N–H stretching) of the polymer. An amide I band is observed at 1640 cm⁻¹ and an amide II band appears at 1525 cm⁻¹, with a small shoulder at 1515 cm⁻¹. Absorption of the solvent prevents infrared measurements below 1450 cm⁻¹.

Due to solvent absorption the ir spectrum of the polymer in HFA is unavailable. However, a deuterium exchange can be obtained in hexafluoroacetone deuterate. The *N*-deuterated amide I' band has a peak at 1615 cm⁻¹ and a shoulder at 1625 cm⁻¹. The amide II' band is observed at 1460 cm⁻¹. The large shift of the amide II' is associated with the N–D bending mode and C–N stretching mode.

Films cast from HFA and HFIP solutions were also examined by infrared spectroscopy. The spectra of these

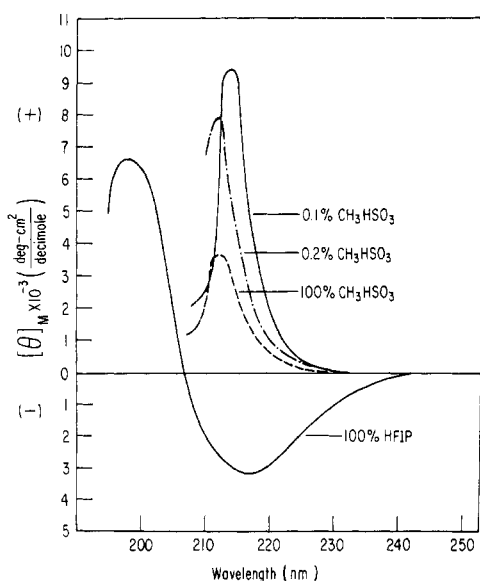


Figure 4. Circular dichroism of poly[(*S*)- β -aminobutyric acid] in hexafluoroisopropyl alcohol-methanesulfonic acid mixtures.

films can be clearly observed from 4000 to 250 cm^{-1} . The results are similar to those reported by Schmidt.⁵

Ultraviolet Studies. The ultraviolet spectrum of poly[(*S*)- β -aminobutyric acid] in HFIP shows an absorption maximum at 192 nm [$\epsilon_{\text{max}} = 9180 \pm 5\% \text{ M}^{-1} \text{ cm}^{-1}$] (Figure 6). On the addition of water, the maximum shifts to a longer wavelength, *i.e.*, near 197 nm. The overall spectrum is similar to that of the β structure of poly(L-serine),¹⁹ which has a λ_{max} at $191 \pm 3 \text{ nm}$ and ϵ_{max} of 7550 ± 50 . A λ_{max} is observed in HFA $\cdot 1.5(\text{H}_2\text{O})$ at 191 nm. A similar red shift is noted on the addition of water.

Discussion

As can be seen from Figure 1, the overall shape of the CD spectrum of poly[(*S*)- β -aminobutyric acid] in HFIP is very similar to that reported for several polypeptides in a β conformation.^{12,15,16} Poly(L-lysine)¹² in aqueous solution shows a negative band at 217–218 nm and a strong positive band at 195–198 nm. Poly(L-serine)¹⁹ in the same β conformation also exhibits positive and negative extrema at 222 and 197 nm, respectively. Since poly[(*S*)- β -aminobutyric acid] lacks side chains which absorb over the wavelength range studied (260–190 nm), the bands in the CD spectrum of this polymer may be characterized in terms of rotational strengths and oscillatory strengths. The positive peak at 197 nm is assumed to arise from excited resonance interactions of the π - π^* transition, while the 217-nm band is associated with a n - π^* electronic transition. The relatively small magnitudes for the molar ellipticities of this polymer in HFA $\cdot 1.5(\text{H}_2\text{O})$ may be attributed to the decreased stability of the β conformation. Goodman, *et al.*,¹⁴ have found that isoleucine oligomers can be partially disrupted by HFA $\cdot 1.5(\text{H}_2\text{O})$ but not by HFIP. This solvent effect is probably due to the increased acidity of HFA $\cdot 1.5(\text{H}_2\text{O})$ compared with HFIP.²⁰

The increasing absolute values for the ellipticity of the CD spectra in HFIP-water and HFA-water mixtures clearly represent the increase of the π - π^* and the n - π^* transitions. The observed blue shift is due to the increasing dielectric constants of the solvent media. The addition of water to the solutions apparently enhances the formation of the β -associated structure; the polymer becomes less solvated when water is introduced into the solution. This tends to favor the attractions between the polymer backbone and the hydrophobic side chains, which will stabilize

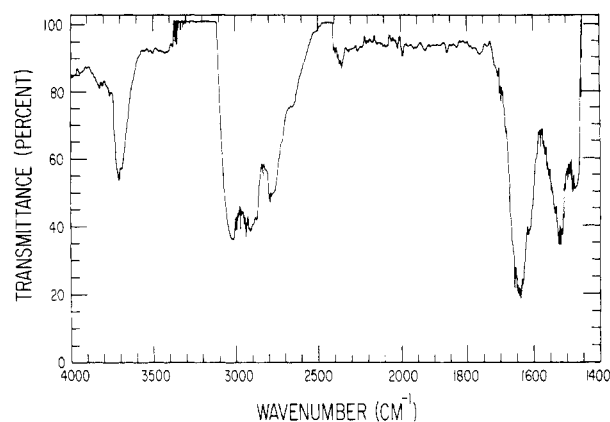


Figure 5. Infrared spectrum of poly[(*S*)- β -aminobutyric acid] in hexafluoroisopropyl alcohol vs. hexafluoroisopropyl alcohol as a reference solvent.

β -like structures. Similar phenomena have been reported by Goodman, *et al.*,¹⁴ in the study of isoleucine oligomers, which showed a sharply increasing dichroism at 217 nm when the water concentration in HFA is between 20 and 40%. Their results suggest that the addition of water causes the oligomer to assume a β conformation. The magnitudes of the CD bands observed in HFIP-H₂O and HFA-H₂O mixtures are about twice as large as those observed for other β structures and those calculated theoretically.^{21–24} However, the presence of an additional group in the main chain of poly(β -amino acids) may appreciably alter the interpeptide coupling which gives rise to the observed CD bands.

The CD spectrum of the poly[(*S*)- β -aminobutyric acid] film is similar in shape, wavelength of extrema, and zero crossover point to that observed in HFA with 30% water and in HFIP with 5% water present in the solution, respectively (Figures 1 and 2). The β conformation with the antiparallel chains for the polymer film has been confirmed by Schmidt⁵ by using X-ray and polarized infrared dichroism. This evidence strongly supports our CD assignments.

Figure 4 shows the spectral changes on the addition of methanesulfonic acid. It is well known that a strong acid can induce a helix-coil or an order-disorder transformation in polypeptide systems.^{25,26} The spectral changes on the addition of acid indicate a conformational change. The CD pattern which we attribute to the β structure disappears on addition of methanesulfonic acid. Only a positive band is observed. The intensity of the peak is decreased by adding more acid; this has been attributed to protonation of the amide chromophores.²⁷ In pure methanesulfonic acid, the CD spectrum of this polymer is similar to that of poly(L-phenylalanine) and poly(γ -ethyl-L-glutamate).^{16,17} The observed positive band is shifted 4–5 nm toward the red and the intensity is several times higher than the polypeptides in the “random coil” state. Similarly, Goodman, *et al.*,²⁸ reported that the addition of 1% sulfuric acid to the alanine nonamer in trifluoroethanol solution completely destroys the CD pattern for the β structure. Montaudo and Overberger²⁹ recently investigated the effect of methanesulfonic acid on the CD spectra of some asymmetric polyamides. From their studies, they concluded that protonation of amide units by methanesulfonic acid creates enough charge repulsion to cause the observed conformational change.

In the infrared studies, a “negative absorption” was observed between 3400 and 3100 cm^{-1} for poly[(*S*)- β -aminobutyric acid] in HFIP. In the same solvent poly(L-alanine)⁶ shows a “negative absorption” near 3600 cm^{-1} . Middleton and Lindsey²⁰ reported that HFIP has a nonbonded hy-

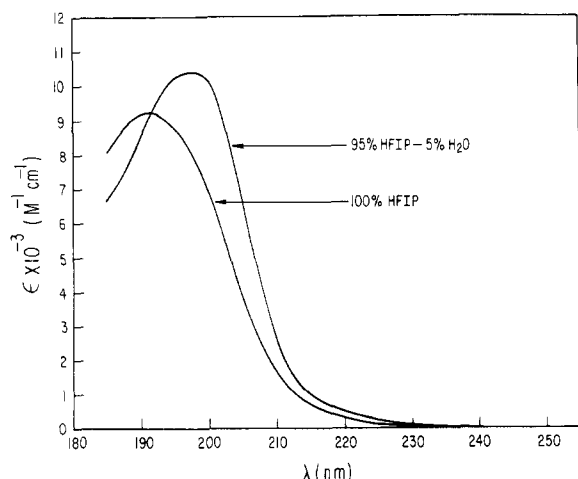


Figure 6. Ultraviolet absorption spectrum of poly[(S)- β -aminobutyric acid] in hexafluoroisopropyl alcohol and in hexafluoroisopropyl alcohol–5% water.

droxyl stretching band at 3610 cm^{-1} carbon tetrachloride solution and a hydrogen-bonded hydroxyl stretching band at 3205 cm^{-1} in tetrahydrofuran. Therefore, these “negative absorptions” may arise from specific solvent-solute hydrogen bonds which give less intense infrared bands than those hydrogen bonds present in the HFIP solvent alone. The amide II band centered at 1525 cm^{-1} is very close to that of the antiparallel β structure for poly(γ -benzyl-L-glutamate) at 1524 cm^{-1} . Strong N–H bands located at 3284 and 3082 cm^{-1} were observed in the spectra of polymer films. This shows strong hydrogen bonding in the polymer. The amide I band of the polymer film is at the same position as in HFIP at 1640 cm^{-1} . This value is usually observed in polyamides.³⁰ Polarized infrared studies on stretched films of poly[(S)- β -aminobutyric acid] were carried out by Schmidt.⁵ In the amide I region, more intense absorption bands were observed in the direction perpendicular to the stretching direction than those in the parallel direction. This indicates that a strong hydrogen bond is perpendicular to the chain axis and is strong evidence for the β -associated structure.

Lastly, the ultraviolet spectrum of poly[(S)- β -aminobutyric acid] with a λ_{max} at 192 nm in HFIP is very close to the β structures for poly(L-lysine)³¹ and poly(L-serine).¹⁹ Our polymer shows a higher extinction coefficient than polypeptides in the similar structure. When water is added to the HFIP solution, the absorption maximum of the polymer shifts to the red. The same phenomenon is also observed for the β structure of poly(L-serine).

Conclusion

The β conformation of poly[(S)- β -aminobutyric acid] in HFIP has been determined using the uv, ir, and CD studies described above. When a trace amount of water is added to a solution of the polymer in HFIP, the amount of β structure is enhanced. Poly(L-alanine) in HFIP with a trace of water forms a distorted α helix.⁶ The additional α -methylene group in poly[(S)- β -aminobutyric acid] leads to a preference for a β conformation in solution and in the solid state. In the presence of methanesulfonic acid, the β conformation is disrupted.

We intend to synthesize the N-methylated poly[(S)- β -aminobutyric acid] to compare its conformation with that of our previously reported poly(N-methyl-L-alanine),³² which exhibits an ordered helical structure in helix-supporting solvents but a disordered structure in the presence of trifluoroacetic acid. We expect these studies will add to our understanding of the conformational properties of polypeptides as well as poly(β -amides).

Acknowledgment. We gratefully acknowledge financial support of this work by grants from the National Science Foundation (GP 35810) and the National Institutes of Health (GM 18694). We wish to thank Drs. J. Brandrup and E. Schmidt of Farbwerke Hoechst, Inc., for providing the material studied. We also thank Drs. R. T. Ingwall, U. Lepore, and N. Ueyama for helpful discussion and suggestions. Technical assistance from Mrs. M. M. Chen is also appreciated.

References and Notes

- (1) (a) This work was carried out by F.C. in as partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of California, San Diego, Calif. (b) Postdoctoral fellow at the University of California, San Diego, Calif., 1971–1972.
- (2) R. Graff, G. Lohaus, K. Borner, E. Schmidt, and H. Bestian, *Angew. Chem., Int. Ed. Engl.*, **1**, 481 (1962).
- (3) R. Graf, *Angew. Chem.*, **80**, 179 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 172 (1968).
- (4) H. Bestian, *Angew. Chem., Int. Ed. Engl.*, **7**, 278 (1968), and references cited.
- (5) E. Schmidt, *Angew. Makromol. Chem.*, **14**, 185 (1970).
- (6) J. R. Parrish and E. R. Blout, *Biopolymers*, **11**, 1001 (1972).
- (7) F. Quadrioglio and D. W. Urry, *J. Amer. Chem. Soc.*, **90**, 2755 (1968).
- (8) G. D. Fasman in “Polyamino Acids, Polypeptides, and Proteins,” M. Stahmann, Ed., University of Wisconsin Press, Madison, Wis., 1962, p 221.
- (9) R. T. Ingwall, H. A. Scheraga, N. Lotan, A. Berger, and E. Katchalski, *Biopolymers*, **6**, 331 (1968).
- (10) N. Lotan, F. Th. Hesselink, H. Benderly, J. F. Yan, I. Schechter, A. Berger, and H. A. Scheraga, *Macromolecules*, **6**, 447 (1973).
- (11) J. G. Greenstein and M. Winitz in “Chemistry of Amino Acids,” Wiley, New York, N.Y., 1961, p 939.
- (12) L. Stevens, R. Townend, S. N. Timasheff, G. D. Fasman, and J. Potter, *Biochemistry*, **7**, 3717 (1968).
- (13) M. Goodman and N. Ueyama, in press.
- (14) M. Goodman, F. Naider, and C. Toniolo, *Biopolymers*, **10**, 1719 (1971).
- (15) For a review, see M. Goodman, A. S. Verdini, N. S. Choi, and Y. Masuda, *Top. Stereochem.*, **2**, 69 (1970); A. J. Adler, N. J. Greenfield, and G. D. Fasman, *Methods Enzymol.*, **27**, 675 (1973).
- (16) S. Beychok in “Poly- α -Amino Acids,” G. D. Fasman, Ed., Marcel Dekker, New York, N.Y. 1967, p 293.
- (17) J. Steigman, E. Peggion, and A. Cosani, *J. Amer. Chem. Soc.*, **91**, 1822 (1969).
- (18) E. Peggion, L. Strassorier, and A. Cosani, *J. Amer. Chem. Soc.*, **92**, 381 (1970).
- (19) F. Quadrioglio and D. W. Urry, *J. Amer. Chem. Soc.*, **90**, 2760 (1968).
- (20) W. J. Middleton and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **86**, 4948 (1964).
- (21) D. W. Urry, *Proc. Nat. Acad. Sci. U. S.*, **60**, 394 (1968).
- (22) E. S. Pysh, *Proc. Nat. Acad. Sci. U. S.*, **56**, 825 (1966).
- (23) R. W. Woody, *Biopolymers*, **8**, 669 (1969).
- (24) V. Madison and J. Schellman, *Biopolymers*, **11**, 1041 (1972).
- (25) For reviews, see G. D. Fasman in ref 16, p 499, and F. A. Bovey in “High Resolution NMR of Macromolecules,” Academic Press, New York, N.Y., 1972, p 286.
- (26) A. Cosani, E. Peggion, M. Terbojevich, and M. Acampora, *Macromolecules*, **4**, 390 (1971).
- (27) J. Steigman, A. S. Verdini, C. Montagner, and L. Strassorier, *J. Amer. Chem. Soc.*, **91**, 1829 (1969).
- (28) M. Goodman, F. Naider, and R. Rupp, *Bioorg. Chem.*, **1**, 310 (1971).
- (29) G. Montaudo and C. G. Overberger, *J. Polym. Sci., Part A-1*, **11**, 2739 (1973).
- (30) C. G. Cannon, *Spectrochim. Acta*, **16**, 302 (1960).
- (31) K. Rosenheck and P. Doty, *Proc. Nat. Acad. Sci. U. S.*, **47**, 1775 (1961).
- (32) M. Goodman, F. Chen, and F. R. Prince, *Biopolymers*, **12**, 2549 (1973).