Using NMR spectroscopy, Ferretti and Paolillo[9] and Ferretti and Ninham[10] have reported a relaxation time associated with the helix–coil transition of $\tau \geq 10^{-1}$ s. These authors have attributed this slow relaxation time to long lived pure random coil chains in the sample. This interpretation means that a significant concentration of pure random coil chains must survive as pure random coils for at least 10^{-1} s. A second interpretation[11,12] has suggested that doublet peaks in the NMR spectra are caused by polydisperse samples. We resolve the apparent conflict using our Monte Carlo kinetics simulation. At chain length 85, we used one molecule which we allowed to make normal transitions. When the molecule contained a helix segment, the helical segment would grow and shrink according to the probability scheme discussed previously. Occasionally the molecule would make the transition to the pure random coil. When this occurred we counted the number of fundamental time units which passed before the molecule nucleated. Averaged over 2×10^8 time units, the equilibrium value of θ was 0.5 and the molecule made the transition to the pure random coil 3818 times. The average lifetime of the pure random coil was 12 260 fundamental time units. Using the value of p^{-1} calculated previously, the pure random coil survived for 5×10^{-4} s on the average. The longest time period that any random coil survived was 4.3×10^{-3} s. Since the value of p^{-1} used is considered to be an upper bound of the correct value, our estimate of the survival time of the pure random coil must also be considered an upper bound. These calculations show that the pure random coil does not survive long enough to be measured by NMR spectroscopy. Therefore according to the stochastic model of the kinetics of the helix–coil transition the doublet peaks which appear in NMR spectra do not represent long lived helix and random coil species.

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Block Copolypeptides. 1. Synthesis and Solid State Conformational Studies

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ABSTRACT: Triblock copolypeptides of γ-benzyl L-glutamate (G) and L-leucine or L-valine of high molecular weight have been prepared. The solubilities and solution conformation were determined and compared with random copolymers of similar composition as well as the appropriate homopolypeptides. Characterization of the secondary structure in the solid state was undertaken as part of an investigation into the solid state properties of this new class of materials. Infrared and solid state measurements indicate that the G and L-leucine blocks assume an α-helical conformation and L-valine blocks a β-sheet structure. Polarized infrared measurements showed the chain axis in oriented films to be parallel to the orientation direction. Further solid state characterization of the tertiary structure and mechanical properties of the block copolypeptides will be reported in succeeding papers.

It is well known that copolymer properties can be profoundly influenced by the presence of blocks, i.e., long sequences of one of the comonomers, especially if these are long and numerous enough to segregate into separate phases of glasslike or crystalline domains. Among copolymers with such long blocks, it is possible to distinguish several types, namely block copolymers made by sequential homopolymerization (for example, A–B–A type triblock copolymers) and statistically random copolymers made by conventional copolymerization with monomer concentrations and reactivity ratios which lead to block structures. Many copolymers are of interest in which the molecules consist of long blocks capable of precipitating in glasslike or crystalline domains separated by amorphous chain segments. The glasslike or crystalline domains form tie points, i.e., quasi-cross-links, which bind the amorphous chains into a network structure similar to that of conventionally cross-linked elastomers. The reversible nature of such tie points bestows upon these materials the special properties which permit their use as thermoplastic elastomers.

Of the synthetic polypeptides which have been used as materials at one time or another (synthetic silk fiber analogues, surface coatings, microphone piezoelectric membranes, biocompatible materials), all have been either derivatives of

polyamino acids (particularly polyglutamic acid esters) or random copolypeptides. Relatively few block copolypeptides have been reported in the literature. Exceptions have been alanine/glutamic acid,[1] alanine/lysine,[2] phenylalanine, leucine, and tryptophan with glutamates.[3-5] In most cases these were "half-sandwich" blocks of relatively low molecular weight. Very little structural data were reported and no information regarding mechanical properties or solid state morphology is available.

We have now succeeded in synthesizing and characterizing a substantial number of ABA type block copolymers of reasonably high molecular weight. For the convenience of comparison with our earlier characterization studies of random copolypeptides,[6-9] our initial efforts involved synthesis and characterization of block copolymers of γ-benzyl L-glutamate with L-leucine or L-valine. As is well known, both G and L-leucine are α-helix directing amino acids.[10] Block copolypeptides were also synthesized from G and L-valine in which the two components are α-helix and β-sheet directing, respectively.[10] In this manner we expected to form biconformational block copolypeptides and thus could expect to study the role of conformation in block behavior.

The chain structure and conformation of the block copolypeptides were characterized by viscosity measurements, solubilities, infrared spectroscopy, and circular dichroism (CD) measurements, and the results were compared with data for random copolypeptides having the same amino acid components as well as the homopolypeptides, poly(γ-benzyl L-glutamate) (PBLG), poly-L-leucine (PPL), and poly-L-valine (PLV). The results of mechanical property and solid state morphology studies will be reported in the following papers.

Experimental Section

Synthesis and Purification of Materials. *N*-Carboxyanhydride (NCA) of γ-Benzyl L-Glutamate (G), L-Leucine (L), and L-Valine (V). Phosgene was bubbled into a suspension of 50 g of amino acid in 750 ml of purified tetrahydrofuran (THF) at 50 °C. A clear solution was obtained within 10 to 15 min. Nitrogen gas was then passed through the solution for 120 min and the solution condensed to an oil at 40 °C using a rotatory evaporator. The oil was dissolved in purified ethyl acetate and rotatory evaporated, causing crystallization of the NCA. This process was repeated two or three times to remove the excess phosgene. The resulting crude crystals were dissolved in approximately 150 ml of purified hot ethyl acetate (about 60 °C), and about 400 ml of *n*-hexane was added. The solution was kept at −5 °C for 24 h and the crystals obtained were filtered. After drying in vacuo at room temperature, the *N*-carboxyanhydride was recrystallized from ethyl acetate–*n*-hexane, giving 80 to 85% yields. γ-Benzyl L-glutamate–NCA, mp 93.5 °C; L-leucine–NCA, mp 76 °C; and L-valine–NCA, mp 67 °C.[11]

Block Copolymer Polymerization. (a) (γ-Benzyl L-Glutamate)$_m$-(L-Leucine)$_n$-(γ-Benzyl L-glutamate)$_0$, (GLG). Polymerization of the first γ-benzyl L-glutamate (G) block was achieved by initiation of the G-NCA in a dioxane–benzene mixture (1:1) using *n*-hexylamine as the initiator. The initiator to NCA ratio, [A]/[I], was between 50 and 100. The polymerization reaction was monitored by the carbon dioxide evolved and between 6 to 24 h the reaction reached more than 90% conversion. The time required was dependent on the ratio of anhydride to initiator. On completion of the G polymerization, a small sample was removed for molecular weight determination of the first block and L-leucine–NCA (L-NCA) in the same solvent mixture as the polymerization was added through a filter. The polymerization time to more than 80% conversion varied from 12 to 36 h. A total polymerization time of 4 to 7 days was therefore allowed for the L-leucine polymerization. It was found that when the L-leucine block reached a length much in excess of the first G block, the solution turned turbid and the copolymer precipitated from solution. Such material was removed by filtration in an atmosphere of nitrogen gas. A small sample was again taken for molecular weight determination and amino acid analysis. Finally, the G-NCA was added and completion of the third block was achieved in 7 to 14 days. All polymerizations were carried out at a concentration of 20 mg/ml at room temperature. The copolymer was precipitated by addition of methanol and washed several times with methanol. The product was then dried under vacuum for 3 days. To remove co-existing homopolymers, poly(γ-benzyl L-glutamate) (PBLG) and poly-L-leucine (PLL), a fractional precipitation technique was employed using mixtures of chloroform and trifluoroacetic acid (TFA).

(b) (L-Leucine)$_m$-(γ-Benzyl L-Glutamate)$_{2n}$-(L-Leucine)$_m$, (LG–GL). The above procedure does not produce block copolymers with end blocks of equal length. To make a symmetrical triblock copolypeptide the center block was initially prepared with the use of a diamine initiator, followed by simultaneous polymerization of the end blocks. A typical example of this synthesis is as follows: G-NCA, 0.01 mol, was dissolved in 100 ml of dioxane–benzene (1:1), and 1,6-hexamethylenediamine, 0.0002 mol, in benzene was added to initiate polymerization. The appropriate amount of L-leucine–NCA was then added as previously described. The techniques used in determination of conversion and purification of the product were identical with those of the previous case. The total polymerization time was from 4 to 7 days.

(c) (L-Leucine)$_m$-(γ-Benzyl L-Glutamate)$_n$-(L-Leucine)$_0$, (LGL); (γ-Benzyl L-Glutamate)$_m$-(L-Leucine)$_{2n}$-(γ-Benzyl L-Glutamate)$_m$, (GL–LG): (γ-Benzyl L-Glutamate)$_m$-(L-Valine)$_n$-(γ-Benzyl L-Glutamate)$_0$, (GVG); (L-Valine)$_m$-(γ-Benzyl L-Glutamate)$_{2n}$-(L-Valine)$_m$, (VG–GV). These triblock copolypeptides were prepared in the same manner as above, except that in these cases a mixture of benzene–dioxane (19:1) was used for the polymerization solvent mixture because of solubility problems.

The results of all the copolymerizations are summarized in Table I. The polymers prepared by method (a), asymmetric polymerization from one end, are labeled GLG, LGL, and GVG and those symmetrically polymerized from the center outwards, method (b), are designated GL–LG, LG–GL, and VG–GV. The random copolymers are labeled by the monomers and their respective ratios in the polymerization feed.

Preparation of Related Random Copolymers. A typical polymerization for copoly(γ-benzyl -glutamate/L-valine) GV11 is as follows: 0.01 mol of G-NCA and 0.01 mol of L-valine–NCA were dissolved in dioxane (100 ml). The polymerization was initiated by addition of triethylamine in the ratio [A]/[I] equal to 50. The polymerization reaction was followed by titration of the carbon dioxide evolved and the reaction stopped within 40% conversion. The polymer solution was poured into cold methanol (500 ml) with vigorous stirring. The white fibrous copolymer was collected by filtration and dried in vacuo at 50 °C for 24 h.[9]

Pertinent data for the random copolypeptides and homopolypeptides, poly(γ-benzyl L-glutamate), poly-L-leucine, and poly-L-valine, are also summarized in Table I.

Molecular Weights. For the triblock copolypeptides, the molecular weight of the first block was determined from the viscosity number of a dichloroacetic acid (DCA) solution, using an Ubbelohde type viscometer, and applying the molecular weight calibration of Doty et al.[12] The average size of the second block as well as the third block was estimated from the result of the amino acid analysis combined with the viscosity measurement.

Amino Acid Analysis. Amino acid analysis was made with a Durrum D-500 Amino Acid Analyzer by the method of Spachman et al.[13] The hydrolysis of the copolymers was carried out at 110 °C in 12 N HCl for several days.

Infrared Spectra. The spectra were obtained with a Perkin-Elmer Model 521 infrared spectrometer. Spectra of block copolypeptides and related random copolymers were measured on films that were cast from chloroform or TFA solution. These films were removed from the glass plate and held in the film holder.

Infrared dichroism measurements were made on a Digilab Fourier transform spectrometer with a Perkin-Elmer wire grid polarizer. Oriented films were obtained by stroking a solution of the polymer in TFA or chloroform as it dried on a KBr crystalline plate.

Circular Dichroism Spectroscopy. Optical measurements were recorded at 25 °C in the 200–250 nm wavelength range using a JASCO J-20 recording spectrophotometer. Ellipticities for materials in solution were calculated in the normal manner. For purposes of comparison with other methods CD spectra of films on polyethylene and also in Nujol mulls were investigated. Such methodology is often subject to experimental artifacts arising from orientation, light scattering, etc. These effects seem to be minimal in the present case since rotation of the film in a plane normal to the beam produced no discernable differences in the recorded spectrum. Similarly the use of Nujol to minimize the refractive index change at the interface and thus minimize light scattering did not noticeably affect the spectra. Although quantitative interpretation of the solid state CD spectra is not possible because of uncertainties in precise film thickness, el-

Table I
Preparation and Analysis of Polypeptide Materials

A. Triblock Copolypeptides, $A_xB_yA_z$

Sample	Initiator	Polymerization solvent	$[\eta]$, dL/g[a]	x[b]	y	z
GLG	*n*-HA[c]	Bz–DO (1:1)[d]	0.44	130 (G)	120 (L)	50 (G)
GL–LG	HMDA[e]	Bz–DO (19:1)	0.53	130 (G)	250 (L)	130 (G)
LGL	*n*-HA	Bz–DO (19:1)	0.52	300 (L)	150 (G)	60 (L)
LG–GL	HMDA	Bz–DO (1:1)	0.52	115 (L)	270 (G)	115 (L)
GVG	*n*-HA	Bz–DO (19:1)	0.33[f]	120 (G)	100 (V)	30 (G)
VG–GV	HMDA	Bz–DO (19:1)	0.34[f]	100 (V)	80 (G)	100 (V)

B. Random Copolypeptides and Homopolypeptides

Sample	Initiator	A/I	Polymerization solvent	$[\eta]$, dL/g	G, mol %[g]
PBLG	*n*-HA	50	Bz–DO (1:1)	1.07	100
PPL	TEA[h]	50	DO	1.55[f]	
PLV	*n*-HA	50	Bz–DO (19:1)	0.55[f]	
GV-41[i]	TEA	50	DO	1.10	93
GV-11	TEA	50	DO	1.66	73
GV-14	TEA	50	DO	2.49	44
GV-19	TEA	50	DO	4.25	29
GL-11	TEA	25	DO		55
GL-14	TEA	25	DO		28

[a] The viscosity number was determined in DCA at 25 °C unless otherwise indicated. [b] Average degree of polymerization of individual blocks: $A_xB_yA_z$. [c] *n*-Hexylamine. [d] Volume ratio, benzene–dioxane. [e] 1,6-Hexamethylenediamine. [f] In TFA at 25 °C. [g] From amino acid analysis. [h] Triethylamine. [i] Indicates mole ratio of G–NCA and V–NCA in polymerization feed.

liptical amplitudes, etc., nevertheless good correlation was found with IR and x-ray data.

Results and Discussion

Materials. There is evidence that the polymerization of NCA's can proceed by one of two mechanisms, nucleophilic attack or proton abstraction from the nitrogen of the NCA.[14] In the former case, the polymer contains the initiator fragment, and block copolymers would be formed by sequential addition of monomers. In the latter case, significant amounts of the homopolymers can result as the initiator is not incorporated in the propagating chain. Primary amine initiated NCA polymerization has been shown to proceed via nucleophilic attack with the degree of polymerization being equal to the initiator to anhydride ratio. Although primary amine initiated polymerization in dioxane and benzene is thought to involve primarily nucleophilic attack, there is evidence that the second mechanism may also be active and for this reason our block copolymers were carefully purified by differential solubility to remove homopolymers.

Furthermore, the low solubility of L-leucine and L-valine polymers in conventional polymerization solvents increases the difficulty of incorporating them into block copolymers. Oya et al.[15] found that when the NCA polymerization is initiated with *n*-butylamine in acetonitrile, the amino end group in the polymer produced, although insoluble, remains active. Thus he was able to synthesize block copolypeptides consisting of various types of α-amino acids and of various chain lengths. Unfortunately, the degree of polymerization of the block copolypeptides synthesized by this method is not necessarily high enough to our purpose. We found that high molecular weight block copolymers of γ-benzyl L-glutamate and L-leucine or L-valine could be synthesized successfully by the method of Ingwall and Scheraga[16] if the appropriate solvent mixture was used (Table I).

The block copolymers prepared by this method were purified by using solubility differences in mixtures of chloroform and TFA or DCA. The solubility of the block copolypeptides was different in several solvents compared with that of the homopolypeptides as well as random copolypeptides consisting of the same amino acids in the block copolypeptides. For example, the block copolypeptide of G and L-valine was insoluble in chloroform in spite of the solubility of PBLG in this solvent. Furthermore, the block copolypeptide of G and L-leucine was soluble in chloroform–DCA (9:1) in spite of the insolubility of poly-L-leucine in this solvent mixture. The solubilities of the block copolypeptides were also different from those of the corresponding random copolypeptides obtained by polymerization of mixtures of two NCA's. For example, GVG was insoluble in DCA, while the corresponding random copolypeptides GV-11 and GV-14 were soluble in DCA, even though their molecular weights are much higher than that of GVG. Solubilities of all the polymers prepared are summarized in Table II.

Infrared Spectra of Films of Block Copolypeptides Cast from TFA Solution. The infrared spectra in the amide I and II regions for the unoriented films of block copolypeptides, random copolypeptides, and homopolypeptides cast from TFA solution are seen in Figures 1 and 2. The correlation of the amide I and II bands with chain conformation, such as α and β, is now fairly well established.[17] The amide I band, due to C=O stretching vibration, and amide II band associated with C–N stretching and N–H deformation of the α-helix conformation are expected to appear at 1650 and 1550 cm^{-1}, respectively. This is observed to be the case for the block copolypeptides, GLG, GL–LG, LGL, and LG–GL.

On the other hand, for the infrared spectrum of the β-conformation, the amide I and II bands appear approximately at 1632 and 1530 cm^{-1}, respectively. The infrared spectrum in the amide I and II regions for the poly-L-valine film is seen in Figure 2. The spectrum shows a small shoulder at about 1650 cm^{-1}, indicating the presence of a small amount of random (or α-helix) structure. The same behavior was reported by Itoh and Fasman[18] for poly-L-valine having a high molecular weight.

Infrared spectra for block copolypeptides VG–GV and GVG

Table II
Solubility of Polypeptides in Organic Solvents at 25 °C

Sample	Solvents[a]	Nonsolvents
GLG	CF, DCA, TFA	DMF, DO–ethanol (19:1, 1:1)
GL–LG	CF–DCA (9:1), DCA, TFA	CF–ether (19:1)
LGL	CF–DCA (9:1), DCA, TFA	CF–ether (19:1)
LG–GL	CF–DCA (9:1), DCA, TFA	CF–ether (19:1)
GVG	CF–TFA (19:1), TFA	CF, DCA
VG–GV	CF–TFA (19:1), TFA	CF, DCA
PBLG	DMF, DO, CF, DCA, TFA	
PLL	CF–TFA (1:1), TFA	CF–DCA (9:1), DCA
PLV	TFA	CF–TFA (19:1), DCA
GV-41	CF, DCA, TFA	
GV-11	CF, DCA, TFA	
GV-14	CF–DCA (9:1), DCA, TFA	CF, DO
GV-19	CF–TFA (19:1), DCA, TFA	CF, DO
GL-11	CF, DCA, TFA	
GL-14	CF, DCA, TFA	

[a] CF = chloroform; TFA = trifluoroacetic acid; DMF = dimethylformamide; DO = dioxane; DCA = dichloracetic acid.

are seen in Figure 2. The amide I and II bands corresponding to both α-helix and β-sheet structures are clearly seen with the relative intensities being dependent on the comonomer composition ratio of G and L-valine.

Infrared spectra for the blended film of PBLG and poly-L-valine (PBLG, 25 mol %) and for the GV-14 random copolypeptide (G, 43 mol %) cast from TFA solution are also shown in Figure 2. In the case of the blended film, the amide I bands appear at 1650 (α) and 1633 (β) cm^{-1} and the amide II bands at 1550 (α) and 1533 (β) cm^{-1}. The 1633-cm^{-1} value for the β conformation of L-valine in these block copolypeptides is the same as that of the homopolymer, but the band frequency (1633 cm^{-1}) does not coincide exactly with that (1638 cm^{-1}) found in the film of the corresponding random copolypeptide (GV-14). The 1638-cm^{-1} value for L-valine residue in the GV random copolymer is similar to that for the β structure in many globular proteins.[18]

Blout et al.[19] have reported the amide I frequency of poly-L-valine to be about 1638 cm^{-1}, which is higher than that found by Fraser et al.[20] (1630 cm^{-1}) and Itoh et al.[21] (1635 cm^{-1}). Further, Kubota et al.[22] have reported a value of 1638 cm^{-1} for the amide I frequency of copoly(DL-Lys-HCl)$_{10}$(L-Val)$_{20}$(DL-Lys-HCl)$_{10}$. Itoh and Fasman[18] reported that the peak of the amide I for poly-L-valine films was dependent on the molecular weight and shifted from 1635 to 1633 cm^{-1} on increasing the molecular weight. It seems clear, therefore, that the shorter β-sheet segments in GV random copolypeptides and globular proteins give the slightly higher frequency amide I band than the longer L-valine residues of block copolypeptides and high molecular weight poly-L-valine.

Infrared Dichroism Spectra of the Block Copolypeptides. The use of polarized infrared radiation in the examination of the spectra of oriented polypeptides has proven to be of great value. The dichroism measurements allow the vector of the vibrational transition moment to be determined. In particular the chain orientation of the α-helix and β-sheet conformations may be readily identified.

The first polypeptide in which the stroking method of orientation was used, and the one in which the highest dichroism has been produced so far, was PBLG by Ambrose and Elliott.[23] The infrared dichroism spectra for poly-L-valine film cast from TFA solution has been measured by Itoh et al.[18] They reported that the dichroic nature and frequency of each

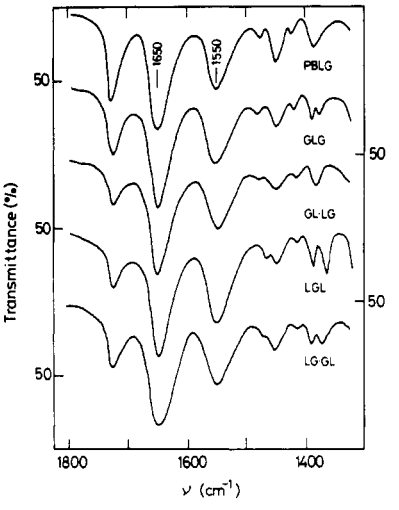

Figure 1. Solid state infrared spectra of the amide I and II regions for block copolypeptides cast from TFA.

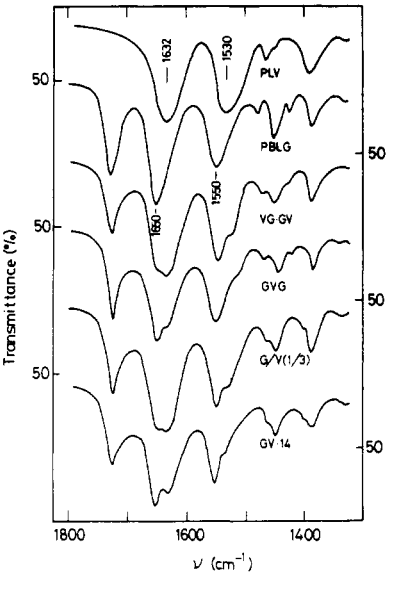

Figure 2. Solid state infrared spectra of the amide I and II regions for copolypeptides containing L-valine cast from TFA.

component of the amide I and II bands corresponded well to those expected for the antiparallel pleated sheet structure.[24,25]

Figures 3 and 4 show spectra in the amide I and II regions of oriented films of block copolypeptides, GVG and GV–VG, obtained with polarized radiation. As may be seen, the dichroic ratio in the C=O band at 1658 cm^{-1} for G residues is notable, and the **E** vector parallel to the direction of orientation is much higher than that perpendicular to the direction of orientation for both polymers. Further, a band of uncertain origin associated with N–H deformation (1545 cm^{-1}) also shows a high dichroic ratio, and as in Nylon 66,[26] its transition moment is normal to that of the N–H stretching mode. From the preceeding data it is clear that the α-helix identified with the G block is parallel to the direction of orientation.

For the β-sheet conformation containing L-valine residues, the major C=O deformation band appears at 1635 cm^{-1} with the **E** vector perpendicular to the direction of orientation while the N–H deformation band (1530 cm^{-1}) appears with the **E** vector parallel to the direction of orientation. These results are analogous to those for Nylon 66 in which the fiber axis is parallel to the orientation direction.[24,27]

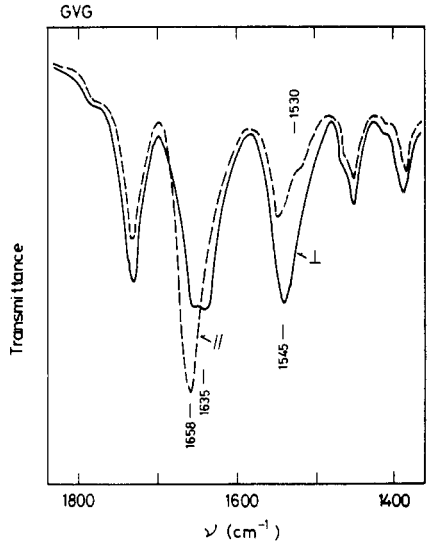

Figure 3. Polarized infrared spectra of the amide I and II regions of GVG: (—) **E** vector perpendicular to direction of orientation, (- - -) **E** vector parallel to direction of orientation.

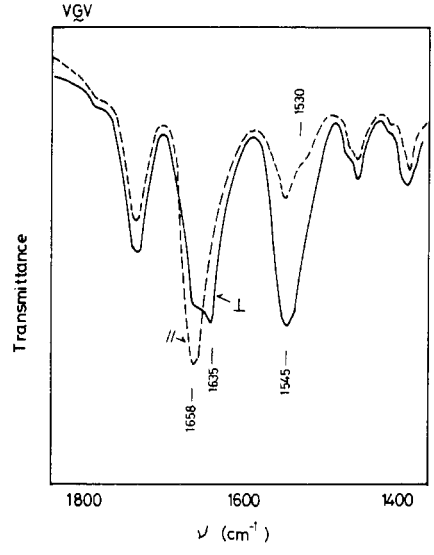

Figure 4. Polarized infrared spectra of the amide I and II regions of VG–GV: (—) **E** vector perpendicular to direction of orientation, (- - -) **E** vector parallel to direction of orientation.

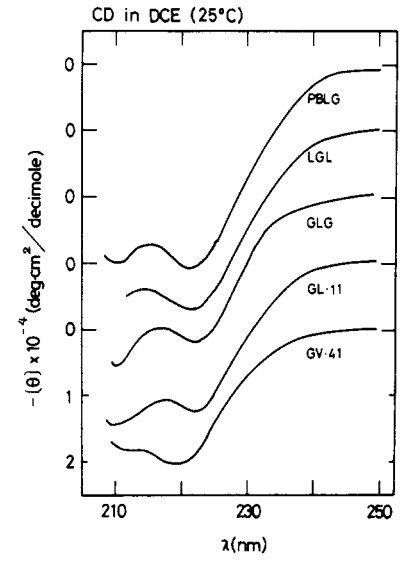

Figure 5. Circular dichroism spectra of some copolypeptides in DCE solution at 25 °C.

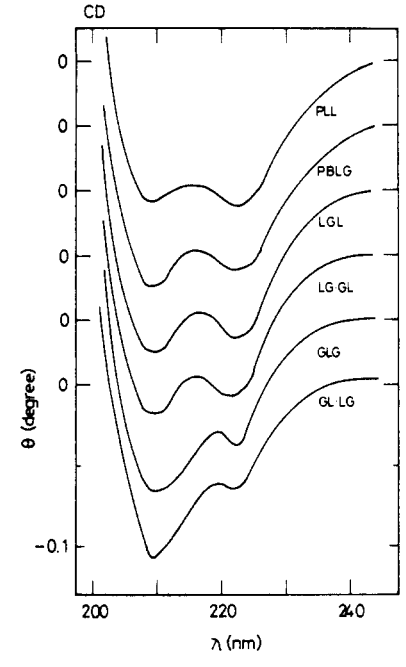

Figure 6. Circular dichroism spectra of block copolypeptides in the solid state. Films were cast from TFA on a thin film of polyethylene.

Finally, we can conclude from our oriented film studies of GVG and VG–GV block copolypeptides that the chain axis of the α-helical G blocks and of the β-sheet conformation of the L-valine block are parallel to the direction of orientation, even if the degree of orientation is not high. Often, the presence of a weak vibrational mode at 1680–1700 cm^{-1} can be seen and is indicative of antiparallel β-sheet structure.

Circular Dichroism Properties. The circular dichroism (CD) spectra of samples in 1,2-dichloroethane (DCE) are shown in Figure 5. PBLG, LGL, GLG, and the GL-11 random copolymer have two negative peaks characteristic of an α-helix conformation. The n–π* transition appears as a broad peak centered around 222 nm, and the second peak, due to the π–π* transition, appears at 209 nm.[28] The GV-41 random copolypeptide has a broad negative peak (due to the n–π* transition) centered around 220 nm. Schellman and Lowe[29] have pointed out that a decrease in helix size or a distortion of the helix conformation can cause a shift of the n–π* transition peak to shorter wavelengths. However, it seems reasonable to conclude that in this case the downward shift of the 222-nm band is caused by an increase in the random content (or β structure) of the film.

Figures 6, 7, and 8 show CD spectra of block copolypeptides, as well as those of random copolypeptides and homopolypeptides, in the solid state cast from TFA solutions on a thin film of polyethylene. In general one notes the deepening low wavelength trough expected when β or random structures are present. The CD spectra measured in the solid state gave almost the same peaks as in solution. For example, the CD spectrum of PBLG in the solid state (Figure 6) gave peaks at exactly the same positions (222 and 209 nm) as well as in the same intensity ratio as in the DCE solution (Figure 5). The CD spectra of GLG, GL–LG, LGL, and LG–GL block copolypeptides in the solid state (Figure 6) are basically similar to that of PBLG. These peaks appear at 222 nm (n–π* transition) and 209 nm (π–π* transition), respectively.

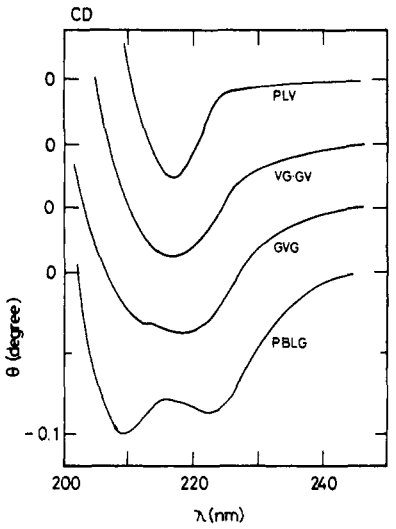

Figure 7. Circular dichroism spectra of block copolypeptides containing L-valine in the solid state. Films were cast from TFA on a thin film of polyethylene.

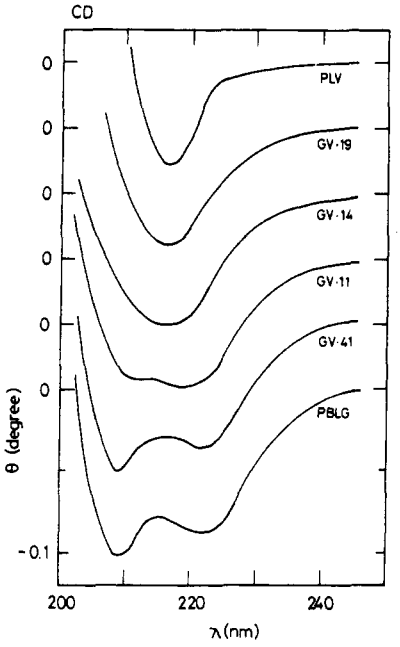

Figure 8. Circular dichroism spectra of random copolypeptides containing L-valine in the solid state. Films were cast from TFA on a thin film of polyethylene.

The CD spectrum of poly-L-valine (Figure 7) in the solid state is also the same as that in solution.[21,30,31] The solid state CD spectrum of poly-L-valine has a negative trough (due to the n–π^* transition) at 215–216 nm, the same wavelength as in the solution.[31] The optical rotatory dispersion (ORD) of solid films of poly-L-valine cast from TFA solution have been reported previously[32] and the trough, peak, and crossover point were located at 230, 205, and 215 nm, respectively, with the trough also being very broad. These characteristics agree well with those found in CD for poly-L-valine in water solution.[31]

The CD spectra of GVG and VG–GV block copolypeptides in the solid state are shown in Figure 7. Both polymers have a rather broad negative trough (n–π^* transition) around 216–222 nm, suggesting a mixture of α-helix conformation (222 nm) and β structure (216 nm). Similar behavior is seen in GV random copolymers with the negative trough (n–π^* transition) being broad and shifting to shorter wavelengths with increasing proportions of L-valyl residues (Figure 8).

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