

Different Packing Structures Observed in Copoly(γ -methyl, benzyl L-glutamate) Films

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ABSTRACT: The structural characteristics observed in copoly(γ -methyl, benzyl L-glutamate)s as a result of a systematic change in the side-chain composition have been classified for films cast from different solvents. The packing structures were seen to vary significantly as a function of the casting solvent, as well as the benzyl content in the copolymer. With the side-chain composition near the two extremes, the packing structures observed were similar to those of the corresponding homopolymers. However, in the intermediate region, characteristically different packings were discovered. For films cast from the *N,N*-dimethylformamide type of solvents, a well defined packing distorted from tetragonal packing, and in the case of the chloroform type of solvents a tetragonal-like molecular packing, were observed. These packings are discussed in the light of various factors influencing the molecular structures of solid films.

KEY WORDS Cast Film / Copoly(γ -methyl, benzyl L-glutamate) / Molecular Packing / Rod-like Polymers / Casting Solvent /

Detailed studies on the influence of structural changes induced by different casting techniques, on the dynamic mechanical, dielectric, and dilatometric properties of poly(γ -benzyl L-glutamate), poly(γ -benzyl D-glutamate) and of their mixtures have already been reported.¹⁻¹⁰ Similarly, in the case of poly(γ -methyl glutamate)s the influence of casting solvents on packing structures in solid films and their properties have also been investigated.¹⁰⁻¹⁴ In the present study, attention is directed to the effect of systematic changes in the side-chain composition of copoly(γ -methyl, benzyl L-glutamate)s with respect to their structural characteristics. Some new characteristics very different from those of the constituent homopolymers have been discovered, and are discussed hereunder with respect to their structural features.

EXPERIMENTAL

Materials

Poly(γ -methyl L-glutamate) (PMLG) having a molecular weight of about 100,000 was kindly supplied by Ajinomoto Co., Japan (AJICOAT Type

A2000) as a solution in perchloroethane and 1,2-dichloroethane. A film was cast from this polymeric solution at room temperature on a glass plate. The residual solvent in the film so cast was exchanged with methanol for about 24 hours. This film was then dried at room temperature *in vacuo* until all traces of solvent were removed. This film was used as the starting material for subsequent studies of structural characteristics.

Poly(γ -benzyl L-glutamate) (PBLG) was synthesized by the *N*-carboxyanhydride (NCA) method, using triethylamine as the initiator in dioxane. The polymer fibres were purified by precipitating the reaction solution in methyl alcohol. Solid films of homopolymers PMLG and PBLG were prepared by dissolving the polymers in various solvents, and then casting the films on glass plates, as noted below.

Synthesis

The synthesis of copoly(γ -methyl, benzyl L-glutamate)s (PMBLG) by NCA method has been reported earlier.¹⁵ In this study, a series of PMBLG copolymers were synthesized by ester-exchange

reaction between PMLG and benzyl alcohol. However, since the concentration of the reactants, type of catalyst and also the time and temperature of the reaction were reported to affect the molecular weight, its distribution, and other characteristics of the copolymers,¹⁶ certain details of the synthesis employed are specified here.

As a catalyst, *p*-toluenesulfonic acid was preferred over stronger sulfuric acid, because the latter is prone to attack the main chain and cause cleavage. After carrying out the preliminary experimentation at a fixed catalyst content and varying the reaction time (3 h, 12 h, 24 h, and 48 h) it was noted that after about 24 h, the substitution reaction almost stabilized at a constant benzyl content whose value predominantly depended on the catalyst content, as shown in Figure 1. Furthermore, considering the possibility that variation in the reaction time may also affect the molecular-weight distribution, the reaction time was fixed at 24 h, and copolymers with different benzyl contents were synthesized using different polymer to catalyst ratios, with the other factors kept constant. The copolymers so obtained, after filtering, were dissolved in dimethylformamide (DMF) and films were prepared by solvent casting at 70°C on glass plates. In order to cast films from other solvents such as chloroform etc., the DMF cast film was used as the starting material.

Characterization

The composition of side-chain residues in different copolymers was estimated from high-resolution NMR spectra in trifluoroacetic acid,

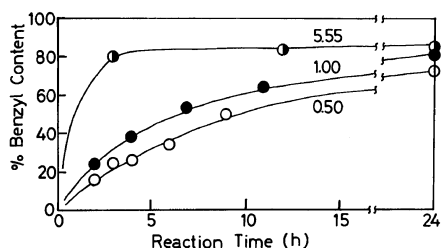


Figure 1. The variation in molar benzyl content of copoly(γ -methyl, benzyl L-glutamate)s with increasing reaction time, at different catalyst to poly(γ -methyl L-glutamate) ratios, such as 5.55 g g⁻¹, 1.00 g g⁻¹, and 0.50 g g⁻¹. The relative quantities of ethylene dichloride and benzyl alcohol, per gram weight of polymer were kept constant at 25.2 ml and 14.6 ml respectively.

using a 60 MHz JEOL JNM-PMX60 spectrometer. The molar percent benzyl content in PMLG copolymers was determined by comparing areas of the signals from the terminal phenyl groups of benzyl ester residues with those from the $-\text{CH}_3$ groups of methyl ester residues in the side chains.

The infrared spectra of thin films were measured by a JASCO DS-701G Diffraction Grating Spectrophotometer in the entire range from 400 to 4000 cm⁻¹. Density measurements were performed using the buoyant weight of a sample immersed in potassium bromide-water mixture at 25°C.

X-ray measurements with Ni-filtered Cu-K α radiation were carried out using a flat plate camera. The cast-film samples were cut into fine strips with dimensions 10 \times 0.3 \times 0.3 mm and mounted on a sample holder with the film surface parallel (called Edge View or EV) to the incident X-ray beam. The reflection spacings were calibrated using the 111 reflection of silicon powder applied over each specimen. Oriented films were prepared by stroking the concentrated solutions (over 40 wt%) on a glass plate with hot stage.

RESULTS

In the IR spectra of thin films of the series of PMLG copolymers and those of the homopolypeptides PMLG and PBLG, the Amide I, II, V bands as well as the NH-stretching and CO bands strongly suggested that the chain conformation is α -helical. Apparently, for the copolypeptides under study here, the loss of side-chain repetition does not strongly affect the conformationally sensitive vibrations. Frushour and Koenig¹⁷ have also proposed that the spectrum of an α -helical random copolypeptide appears to be a simple superposition of the two homopolypeptide spectra, and this is in conformity with our results. Similar results were reported earlier by Kanamori *et al.*¹⁵

Furthermore, as described in detail below, the X-ray photographs of the oriented films of PMLG copolymers also show several reflections on the fifth layer line at 5.4 Å, corresponding to the pitch of the helix, and a 1.5 Å reflection on the meridian, corresponding to the height of one residue along the major axis (designated here as *c* axis). These observations strongly confirm the formation of α -helix in spite of the substitution of different terminal groups in the side chains.

On the other hand, the packing characteristics of the above-mentioned α -helices were seen to be remarkably sensitive not only to the kind of solvent from which the copolymeric films were cast, but also to the extent of substitution of the side-chain groups as well. Such effects are discussed in detail below.

Solvent Effect

Just as with the PBLG molecules, the PMBLG copolymer films in the solid state, as a result of the

influence of different solvents during the casting process, showed two distinctly different packing systems. These films cast from different helicogenic solvents are classified, in general, as:

Type I Films: Copolymer films cast from different solvents such as *N,N*-dimethylformamide (DMF), dioxane, benzyl alcohol etc., showing sharp X-ray patterns characteristic of highly crystalline materials.

Type II Films: Copolymer films cast from sol-

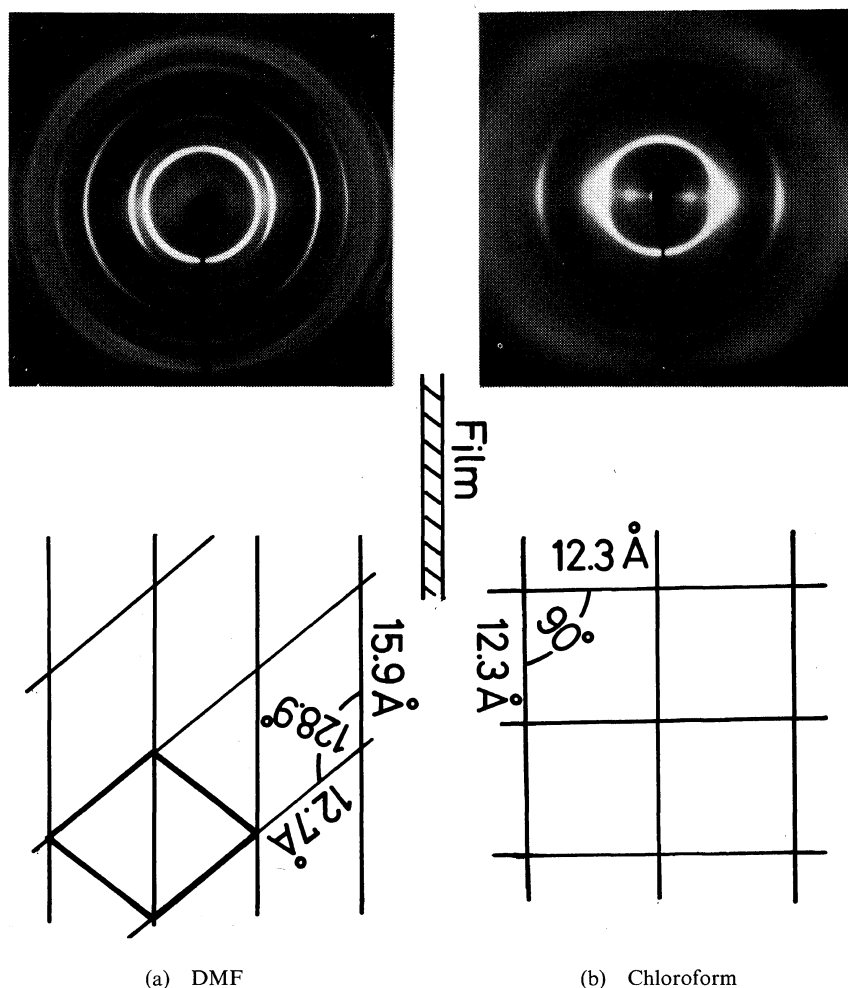


Figure 2. The molecular packings and X-ray EV photographs of copoly(γ -methyl, benzyl L-glutamate) films with 49% benzyl content and cast from different solvents. In the molecular packings of DMF cast films, the oblique net was conveniently selected as the basic unit cell in order to compare the structures observed in copolymers with that of poly(γ -benzyl L-glutamate) of Form B, as reported earlier.^{5,19} Alternately, taking the monoclinic unit cell ($a' = b' = 12.7$ Å, $\gamma' = 102.2^\circ$) as shown by thick line, the lattice is nearly tetragonal.

vents such as chloroform, dichloromethane (DCM), *m*-cresol etc., showing diffuse X-ray patterns characteristic of poorly crystalline materials.

On comparing the typical copolymers having about the same number of methyl and benzyl ester groups in the side chains, the Type I films cast from dioxane, DMF-type solvents, showed packings distorted from tetragonal array and which had good crystallinity. On the other hand, in the Type II films cast from chloroform, *m*-cresol-type solvents, the typical quadratic position of reflections with strong intensity, indicate a tetragonal-like packing structure having uniplanar orientation and rather poor crystallinity. The typical EV photographs and the corresponding molecular packings are shown in Figure 2. In order to investigate further the reasons for such marked differences in the packing arrangements, the effect of a systematic increase in the benzyl content of the copolymers was studied.

Composition Effect

Packing Characteristics in Type-I Films: As the benzyl content in the copolymers increased, three distinct regions (termed as regions A, B, and C), with different packing characteristics were identified. Figure 3 shows the typical X-ray photographs in these three regions. The spacings of X-ray reflections for the PMBLG films cast from DMF solutions for these different regions, are given in Table I. The copolymer films with benzyl contents less than 30% (Region A) showed characteristic X-ray patterns of low crystallinity. But with higher benzyl content, the X-ray reflections become much sharper, showing relatively a much higher crystallinity. This higher crystallinity region was further

demarcated into B and C regions, with the C region showing a structure similar to that of PBLG, starting from a benzyl content of 80% and upwards. The molecular packings in the B and C regions are indicated in Figure 4.

Figure 5 shows the variations in the unit cell dimensions a , b , and the intermediate angle γ , as a function of the benzyl content % in the DMF cast copolymer films. The above-mentioned three regions are clearly marked by the discontinuities in the variation of the lattice dimensions with the benzyl content. For very low-benzyl-content films cast from DMF, a tendency for gelation was observed during the casting process. In this region, the X-ray pattern shows only a diffuse ring with a spacing corresponding to the average intermolecular distance. Due to this inability to form a well defined structure, the lattice dimensions in this region could not be established precisely.

Packing Characteristics in Type II Films: Figure 6 shows three typical X-ray EV photographs of copolymer films cast from chloroform, and with different benzyl contents covering the entire span of the copolymerization process. Figure 7 indicates the variation in the characteristic lattice dimension ' a ', plotted against the corresponding benzyl content in the copolymer films. Again, just as in the case of the Type I films, as a result of variation in benzyl content, three regions with different packings and distinct changes in their lattice dimensions were observed. Homopolymer PMLG film showed a well defined hexagonal packing with a two dimensional net of 12 Å sides. Region A with a hexagonal packing very similar to the molecular packing in PMLG cast film, was observed upto around a 30%

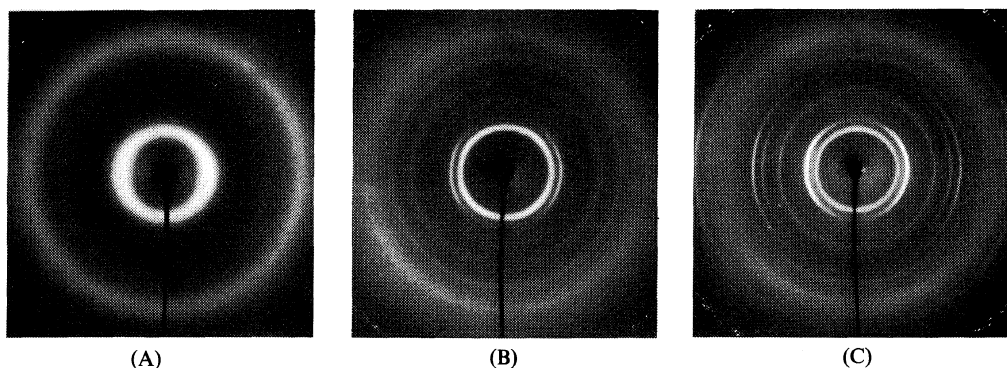


Figure 3. The typical X-ray EV photographs of copoly(γ -methyl, benzyl L-glutamate) films cast from DMF, each having molar benzyl content in three different regions, such as (A), 20%; (B), 69%; (C), 80%.

Table I. Spacings in X-Ray diffraction patterns of PMBLG films cast from DMF solutions

Region A		Region B								Region C							
PMLG		B-31 ^a				B-49 ^a				B-69 ^a				PBLG			
d_0^b	Intensity ^c	d_0	d_c^b	hkl	Intensi- ty	d_0	d_c	hkl	Intensi- ty	d_0	d_c	hkl	Intensi- ty	d_0	d_c	hkl	Intensi- ty
~11	d	11.9	11.8	100	vs	12.3	12.4	100	vs	13.3	13.3	100	s	14.5	14.5	100	s
										12.2	12.4	1 $\bar{1}$ 0	s	12.1	12.0	010	vs
		9.90	9.82	010	s	9.90	9.88	010	s	10.5	10.5	010	vs	7.76	7.78	110	m
		7.41	7.40	2 $\bar{1}$ 0	m	8.01	7.95	2 $\bar{1}$ 0	m	8.01	8.07	2 $\bar{1}$ 0	m	7.23	7.23	200	w
		5.91	5.91	200	s	6.13	6.19	200	s	6.62	6.65	200	w	6.60	6.60	1 $\bar{2}$ 0	m
										6.20	6.18	2 $\bar{2}$ 0	w	6.00	6.00	020	m
						5.12	5.11	3 $\bar{1}$ 0	w					5.30	5.30	210	w
		5.00	4.91	020	w	4.92	4.94	020	w	5.22	5.26	020	m	4.88	4.87	120	w
		4.01	3.94	300	vw	4.10	4.12	300	vw	4.58	4.43	300	vw	4.00	4.00	030	m
										4.28	4.26	2 $\bar{3}$ 0	vw	3.93	3.94	310	w
						3.78	3.68	4 $\bar{1}$ 0	vw								

^a B-31, B-49, and B-69 represent the benzyl content percent in the copolymers.

^b d_0 , and d_c represent the observed and calculated interplanar spacings in Å. d_c and indices are based on corresponding unit cells. B-31, $a=14.8$ Å, $b=12.3$ Å, $\gamma=127.0^\circ$; B-49, $a=15.9$ Å, $b=12.7$ Å, $\gamma=128.9^\circ$; B-69, $a=16.2$ Å, $b=12.8$ Å, $\gamma=124.8^\circ$; PBLG, $a=15.9$ Å, $b=13.2$ Å, $\gamma=114.6^\circ$.

^c Intensity distribution pertains to the Edge View X-Ray photographs. The reflection intensities: d, diffused; s, strong; m, moderate; w, weak; vs, very strong; vw, very weak.

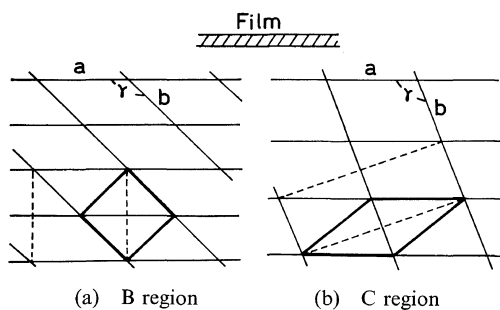


Figure 4. Typical molecular packings observed in copoly(γ -methyl, benzyl L-glutamate) films cast from DMF, in regions B and C. Possible alternate unit cells are indicated by a thick line and a dashed line, respectively. When the monoclinic unit cells in the two regions were compared, the molecular packing in region B was found to be nearly tetragonal, while that in region C is nearly hexagonal.

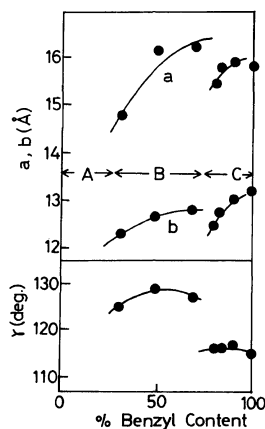


Figure 5. Variation in unit-cell dimensions a (Å), b (Å), and γ (degree), as a function of % molar benzyl content in the copoly(γ -methyl, benzyl L-glutamate) films cast from DMF.

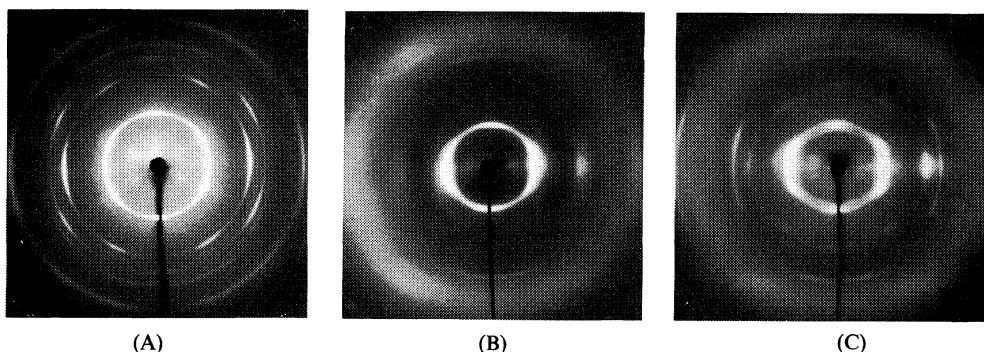


Figure 6. Typical X-ray EV photographs of copoly(γ -methyl, benzyl L-glutamate) films cast from chloroform solutions, each having a different benzyl content in three regions, such as (A), 20%; (B), 69%; (C), 80%.

molar benzyl content.

Region B giving rather less defined X-ray reflections, spanned from about 30% to about 70% benzyl content. The typical X-ray reflections and the lattice dimensions in different regions are given in Table II. In region B, the 100 reflections and 200 reflections were rather distinctly visible throughout this range of benzyl content. However, 110 reflections could not be distinguished clearly for the copolymer film with 31% benzyl content, although it could be faintly observed as a diffuse streak in the case of the copolymer films with 49% benzyl content, and as moderate reflection for copolymer with 69% benzyl content. Thus, for chloroform cast copolymer films in the range of 30% to 70% benzyl

content, a precise determination of crystal cell was rather difficult from X-ray analysis alone. Hence, we compared the densities observed by the buoyant weight method, with the densities calculated assuming hexagonal and tetragonal packings. Table III shows the variation in measured densities of films in B region cast from DMF and chloroform, and the densities calculated for the chloroform cast films. Thus for example, for copolymer film with 31% benzyl content, if we take the 100 reflection as corresponding to a hexagonal packing, the calculated density is 1.108, which is inconsistent with the observed density of 1.28₁. On the other hand, calculating the density assuming a tetragonal packing gives a plausible value of 1.28₁. Consequently,

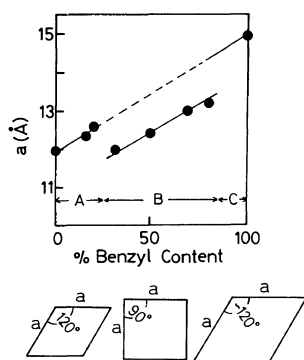


Figure 7. Variation in the unit-cell dimension of copoly(γ -methyl, benzyl L-glutamate) films cast from chloroform solutions, with variation in benzyl content. The typical packings observed in the different regions are also indicated. In region C, the unit cell is not precisely hexagonal, and the lattice dimensions cannot be determined uniquely because of fluctuations in the observed dimensions.

the molecules in this region can be taken to have a tetragonal-like packing. In case of DMF cast copolymer films, the densities calculated from the

X-ray data matched satisfactorily with the observed densities over the whole range of benzyl content.

DISCUSSION

The PMBLG copolymer molecules, with a changing side-chain composition, show some marked changes in their molecular packings, while preserving their secondary structure with α -helical conformation. Hikichi *et al.*¹⁸ also suggested that in chloroform cast films, the transformation from the hexagonal form of PMLG to another crystal form takes place at a 30% benzyl content. The above-mentioned results show that the structures typical for the different copolymer-solvent systems considered here, are visible in the intermediate region of 30% to 70% benzyl content, and consequently, particular attention is directed to the structures attained in this region.

Figure 8 shows the X-ray EV photographs of the oriented copolymer films with 49% benzyl content, and cast from DMF and chloroform solutions. Type-I film in the B region gives several reflections on the fifth layer line with spacings of 5.23 Å, 4.55 Å,

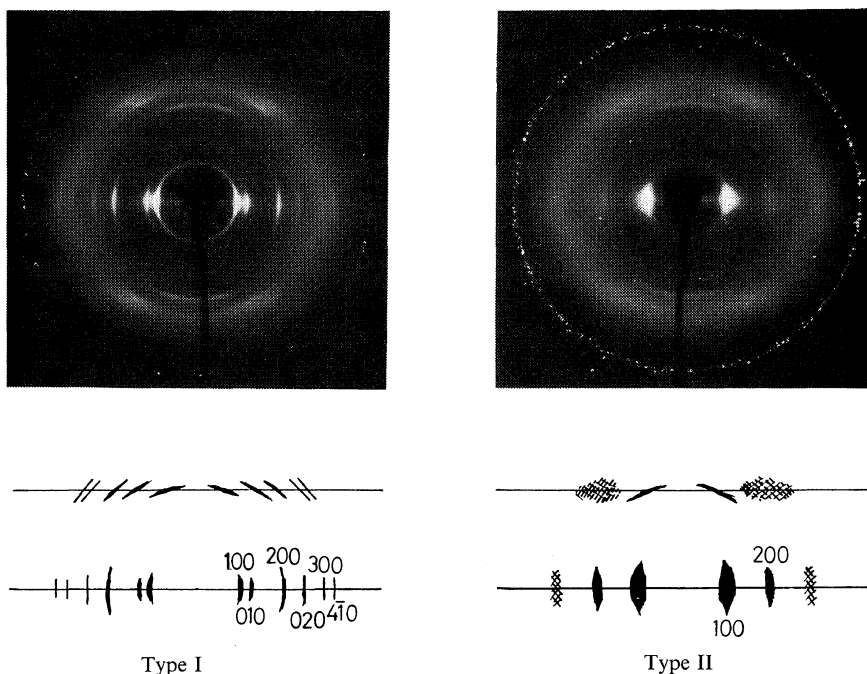


Figure 8. The X-ray EV photographs of two types of oriented films of copoly(γ -methyl, benzyl L-glutamate)s cast from different solvents, and having 49% benzyl content.

Table II. Spacings in X-Ray diffraction patterns of PMBLG films cast from chloroform solutions

Region A			Region B									Region C		
PMLG			B-31 ^a			B-49 ^a			B-69 ^a			PBLG		
d_0^b	hkl^b	Intensity ^c	d_0	hkl	Intensity	d_0	hkl	Intensity	d_0	hkl	Intensity	d_0	hkl	Intensity
10.4	100	s	12.0	100	s	12.4	100	s	13.1	100	s	12.8 ~ 13.4 ^d	100	s
6.0	110	m				~ 9	110	ds	9.3	110	m	12.6 ~ 12.8	010	s
5.2	200	w										7.4 ~ 7.6	110	w
3.9	210	w	6.0	200	w	6.2	200	s	6.5	200	m	7.3 ~ 7.4	$\bar{1}20$	w
3.5	300	w							4.3	220	vw	~ 6.5	200	vwv
												6.3 ~ 6.4	020	vw

^a B-31, B-49, and B-69 represent the benzyl content percent in the copolymers.

^b d_0 represents the observed interplanar spacings in Å. Indices are based on corresponding unit cells. PMLG, $a=b=11.96$ Å, $\gamma=120^\circ$; B-31, $a=b=12.0$ Å, $\gamma=90^\circ$; B-49, $a=b=12.4$ Å, $\gamma=90^\circ$; B-69, $a=b=13.1$ Å, $\gamma=90^\circ$; PBLG, $a=14.8 \sim 15.2$ Å, $b=14.3 \sim 14.8$ Å, $\gamma=118 \sim 120^\circ$.

^c Intensity distribution pertains to the Edge View X-Ray photographs. The reflection intensities: s, strong; m, moderate; w, weak; vw, very weak; vwv, very very weak; ds, diffused streak.

^d In region C, the reflections show fluctuations depending on the casting conditions.

Table III. Observed density for different films and calculated density for chloroform cast PMBLG copolymer films in region B

% Benzyl content	Observed density		Calculated density (chloroform cast)					Remarks
	DMF cast g cc ⁻¹	Chloroform cast g cc ⁻¹	X-Ray structure					
			Lattice type ^a	<i>d</i> ₁₀₀ Å	Unit cell		Density g cc ⁻¹	
					<i>a</i> = <i>b</i> Å	<i>γ</i> degree		
31	1.28 ₀	1.28 ₁	HEXA	12.0	13.86	120°	1.108	Inconsistent
			TETRA	12.0	12.0	90°	1.281	Consistent
49	1.27 ₆	1.27 ₀	HEXA	12.4	14.32	120°	1.123	Inconsistent
			TETRA	12.4	12.4	90°	1.298	Consistent
69	1.26 ₉	1.27 ₀	HEXA	13.0	15.01	120°	1.109	Inconsistent
			TETRA	13.0	13.0	90°	1.280	Consistent

^a Lattice types considered are hexagonal (HEXA) and tetragonal (TETRA).

4.18 Å, 3.69 Å, and 3.55 Å. Not all of these reflections correspond satisfactorily to the observed equatorial reflections when projected on the equator in different possible manner. For example, the innermost reflection of 5.23 Å should correspond to an equatorial reflection of 20.4 Å when projected perpendicularly on the equator, but the observed innermost equatorial reflection as indicated in Table I is of 12.3 Å. Such a structural characteristic is similar to that observed in the case of the Form B structure of the oriented PBLG film (corresponding to region C of the copolymer), where, in order to explain the 5th layer line reflections together with reflections on the other layer lines, it was quite necessary to consider a large unit cell containing two kinds of chains per unit cell with up and down orientations of the main-chain chemical sequence ($-\text{NH}-\text{CO}-\text{CHR}-$, where R: side chain), as the basic three-dimensional unit cell.¹⁹ In other words, with respect to the projection along the chain axis (lateral packing), the two chained, centered orthogonal unit cell was necessary to be considered, as shown in Figure 4b by the dashed line. In copolymers of region C, although the layer-line reflections, other than those on the fifth layer line, are actually not clearly visible, it is suggested that the two different kinds of chains with up and down orientation, are contained in the orthogonal unit cell for the Type I films in region B as well as in region C, as shown by the dashed lines in Figures 4a and b. Thus, it is noteworthy that with an increase in the benzyl content of the copolymers, discontinuity can also be observed with respect to the unit-cell dimensions of the orthogonal unit cells in regions B and C.

In case of oriented Type II films, only one innermost reflection on the fifth layer line is visible and no other outer reflections are so well defined. This indicates that the structure in Type II films is nematic-like, having a relative displacement of the helices in the c -axis direction, in comparison with the structure in Type-I films. In order to explain the overall poor crystallinity of the structure of Type-II films, we are at present considering a structural model containing dislocation, as shown by the dotted line in Figure 9. The broad equatorial reflections in the X-ray diffraction patterns indicate that the lateral packing contains some sort of disorder. Thus the structure may have two domains mutually displaced across a stacking fault, which may have got incorporated in the structure during

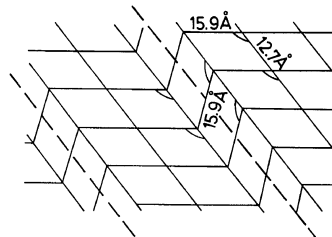


Figure 9. Structural model containing dislocation of planes across a stacking fault, for explaining the disorder observed in the structure of chloroform cast copoly(γ -methyl, benzyl L-glutamate) films. The structural model for copolymer film with 49% benzyl content is illustrated, with the dotted line indicating the axis of dislocation. The basic unit cell is the same as that of the DMF cast film, and does not change with stacking fault.

the casting process. The diffraction-intensity calculations are at present being made under the assumption that occurrence of the stacking fault in chloroform cast films is random. By incorporating such dislocation in the structure obtained for the films cast from DMF, the characteristic tetragonal packing structure observed for chloroform cast films can be explained.²⁰ Figure 9 indicates a probable model for the structure having stacking fault, and the unit-cell dimensions of Type I film.

Another distinguishing feature observed in copolymers, in contrast to homopolymers, is the absence of the formation of the so-called "complex phase." For instance, the PBLG films cast from DMF at low temperature show⁵ poorly ordered structure and hexagonal packing with four chains per unit cell, and the lattice dimensions of the order of 30 Å. In the case of PMBLG copolymers when cast from DMF at a low temperature, upto about 90% benzyl content, the Form-A structure⁵ (corresponding to the "complex phase"⁴) characterized by such a big unit cell was not observed. Since the formation of the "complex phase" and therefore that of Form A, was attributed to a significant role of stacking of benzene rings,⁴ as indicated by the near meridional reflection and the meridional reflection of 5.18 Å and 5.06 Å respectively, it may be proposed that the long-term order of the side chains may be essential for the formation of the "complex phase" and the Form A structure.

On the other hand, with respect to the influence of the copolymer composition for the different solvents considered, the copolymers with less than 30% benzyl content, *i.e.*, the copolymers with the number

of side chains containing methyl groups more than double of the side chains containing benzyl groups, packing structures similar to the one observed with the methyl glutamate homopolymer were observed. Similarly, in the copolymers with more than 70% benzyl content, *i.e.*, with the number of side chains containing benzyl groups more than double of the number of side chains with methyl groups, packing structures similar to that of the benzyl glutamate homopolymer were observed. The molecular packings with structures characteristic of the copolymer-solvent systems were observed in the intermediate region of 30% to 70% benzyl content, *i.e.*, for those copolymers having a comparable number of side chains containing methyl and benzyl groups. In this intermediate region of benzyl content, a well-defined but distorted tetragonal packing was observed in the case of the copolymer films cast from DMF-type solvents (Type I), and a tetragonal-like packing was observed when chloroform-type solvents (Type II) were used. These packing structures are essentially different from those observed in homopolymers, or in copolymers having a high methyl content (showing hexagonal structure), or having a high benzyl content (showing a near hexagonal structure).

In general, the packing of polypeptide macromolecules in bulk may be considered to be mainly determined by their main-chain conformations, intermolecular side-chain-side-chain interactions, and dipole-dipole interactions between large dipoles by virtue of the main chains. In the present study, since the main-chain conformation was seen to be unaffected by the changes in the side-chain composition as well as the casting solvents, the balance between the remaining two likely governing factors may have determined the formation of hexagonal-like or tetragonal-like packing structures. In the typical copolymeric films in the intermediate benzyl content region, with the random ordering of the side-chain terminal groups, there is likely to be less significant intermolecular side-chain-side-chain interactions. As a consequence, the dipole-dipole interactions may dominate, thus possibly causing upward directed chains tetragonally surrounded by downward directed chains. To confirm the universal occurrence of similar structural changes with varying side-chain composition, we are at present investigating other copolymers of alkyl glutamates having different

side-chain combinations. In copolymers with methyl glutamate residues in combination with butyl glutamate residues and hexyl glutamate residues, similar tetragonal-like molecular packings were observed in the intermediate ranges of the side-chain compositions. Thus, it is possible that the observed tetragonal-like molecular packing is characteristic of copolyglutamates in general, when cast from helicogenic solvents.

CONCLUSION

The terminal groups in the side chains of an ester of glutamic acid were gradually changed from all methyl groups in PMLG, to all benzyl groups as in PBLG, and the influence of this on the solid-state structures so obtained was characterized.

Considering that the α -helical conformation of PMLG as well as that of PBLG cast from helicogenic solvents, is the stable conformation, for PMBLG in the solid state also, apparently this conformation is not affected significantly by incorporation of the irregularity into the side chains. Furthermore, with the randomization of the side-chain terminal groups, the copolymer films in the solid state show characteristic structures in the intermediate range of 30% to 70% benzyl content, and these are distinctly different from those observed for the constituent homopolymers, or any intermediate structure thereof. These characteristic structures show close to tetragonal packing whereas, the homopolymers and the copolymers with less than 30% or more than 70% benzyl content, show structures with close to hexagonal packings. This may result from the breakdown of the regularity of the side-chain terminal groups in the copolymers in the intermediate region.

The characteristic copolymeric structures vary significantly, depending on the solvent from which the solid films of PMBLG are cast. The solvent may influence the packing arrangement of molecules during the casting process, causing poor crystallinity in the films cast from chloroform-type solvents, but a more ordered packing in films cast from DMF, dioxane-type solvents.

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