Crystalline complex between poly(γ-methyl L-glutamate) and dimethyl phthalate

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The crystalline complex between poly(γ-methyl L-glutamate) (PMLG) and dimethyl phthalate (DMP) has been formed in films cast from a solution in dichloroethane. It has the stoichiometry of 1 mol of DMP to three or four residues of PMLG and shows two definite characteristics in X-ray diffraction patterns; one is the large hexagonal unit cell with the edge of around 28 Å and another the 'extra' 5.07 Å meridional reflection which can not be interpreted by a PMLG α-helical conformation. The structural examination for the films with various DMP contents is carried out by X-ray, viscoelastic, and d.s.c. measurements and the following structure is proposed for the crystalline complex. Four PMLG are associated to form a group which is hexagonally packed and DMP molecules, located in the gaps between groups, form a specific favourable helical structure along PMLG chains in which the van der Waals stacking of benzene rings of DMP is significant.

(Keywords: Poly(γ-methyl L-glutamate); dimethyl phthalate; crystalline complex; X-ray measurement; van der Waals stacking of benzene rings)

INTRODUCTION

Poly(γ-methyl L-glutamate) (PMLG) offers two solid-state modifications consisting of α-helices, depending on the kind of solvents used for the casting of films from solutions[1,2]. The PMLG films prepared from chloroform, called here 'form I', is highly crystalline, with the α-helical molecules packed into a hexagonal lattice with dimensions of $a=b=11.95$ Å, $c=27$ Å and $\gamma=120°$. However, films prepared from 1,2-dichloroethane and *N*,*N*-dimethylformamide solutions, called 'form II', show a different X-ray pattern consisting of several broad reflections which cannot be explained by a simple hexagonal lattice. The structural differences between the two crystal modifications have been described according to the mechanical[1,2] and dielectric properties[3] and the overall morphology[2,4].

Recently, it has been established that the PMLG molecules has a good compatibility with low molecular dimethyl phthalate (DMP) when films are prepared from solutions only in the latter type of solvents. The films containing DMP of ≈30 wt% result in a markedly improved X-ray pattern in comparison with the pattern of form II. Interestingly, the X-ray data shows that four α-helices of PMLG are located in a unit cell and another structural order in addition to α-helix of PMLG exists along the chain axis. These structural characteristics are interpreted here as a type of crystalline complex of PMLG molecules with DMP molecules.

EXPERIMENTAL

Materials

A sample of PMLG (Ajicoat A-2000) with viscosity-average molecular weight $M_v=110000$ was kindly supplied by Ajinomoto Co. Ltd., Japan. PMLG samples were dissolved in 1,2-dichloroethane (DCE) and then the desired quantity of DMP was added to these solutions. The films with thickness ≈0.1 mm were cast onto a glass plate and the oriented films were prepared by stroking the concentrated solutions. All the films were dried *in vacuo* for two days to remove the residual traces of solvent. The loss of DMP was limited to within 2% of the original weight of DMP. Throughout this paper, the DMP content is expressed in weight per cent, except where indicated otherwise. The volume fractions were calculated from weight fractions and specific volumes of pure components (0.77 ml g^{-1} for PMLG and 0.836 ml g^{-1} for DMP).

Measurements

The samples for X-ray diffraction were cut into fine strips with dimensions of 10 × 0.3 × 0.1 mm^3. Wide-angle patterns were recorded on a flat-plate camera or cylindrical camera, using a Rigaku-Denki X-ray generator with Ni-filtered CuKα radiation. The cast films have a uniplanar orientation, in which the PMLG α-helical molecules tend to lie parallel to the film surface. To ascertain the orientation, two types of photographs were taken, either with the film surface parallel (referred to here as edge view, EV) or with it perpendicular (through view, TV) to the incident beam. The interplanar spacings were calibrated against the (111) reflection of silicon powder sprinkled over the specimen. The dynamic mechanical measurements of the as-cast films were carried out with a rheovibron viscoelastometer, model DDV-II-C (Toyo Baldwin Co. Ltd., Japan), at the frequencies of 110, 35, 11 and 3.5 Hz. The differential scanning calorimeter (d.s.c.) measurements were carried out using a Perkin Elmer DSC model II at a heating and cooling rate of 10°C min^{-1}. The ultraviolet absorption

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(u.v.) and circular dichroic (c.d.) spectra were measured by a Hitachi 556 double wavelength spectrophotometer and a JASCO automatic recording spectropolarimeter Model J-20, respectively. The densities were determined by measuring the buoyant weight of sample immersed in potassium bromide–water mixtures.

RESULTS AND DISCUSSION

Characteristics in a typical X-ray pattern of PMLG film containing DMP

X-ray patterns varied with DMP content and a well-defined pattern was observed for the films containing DMP of 25–30%. *Figures 1a* and *1b* show typical EV X-ray photographs of the as-cast and oriented films with a DMP content of 25%, respectively. In *Table 1*, the spacings of nine reflections discernible from these photographs are presented with their intensities and classified into the equatorial and non-equatorial groups. X-ray observation leads to the following structural characteristics for this material.

Five equatorial reflections (24.0, 13.7, 12.0, 9.02 and 7.86 Å) could be assigned to a two-dimensional hexagonal unit cell siwth an edge of 27.6 Å, as shown in *Table 1*.

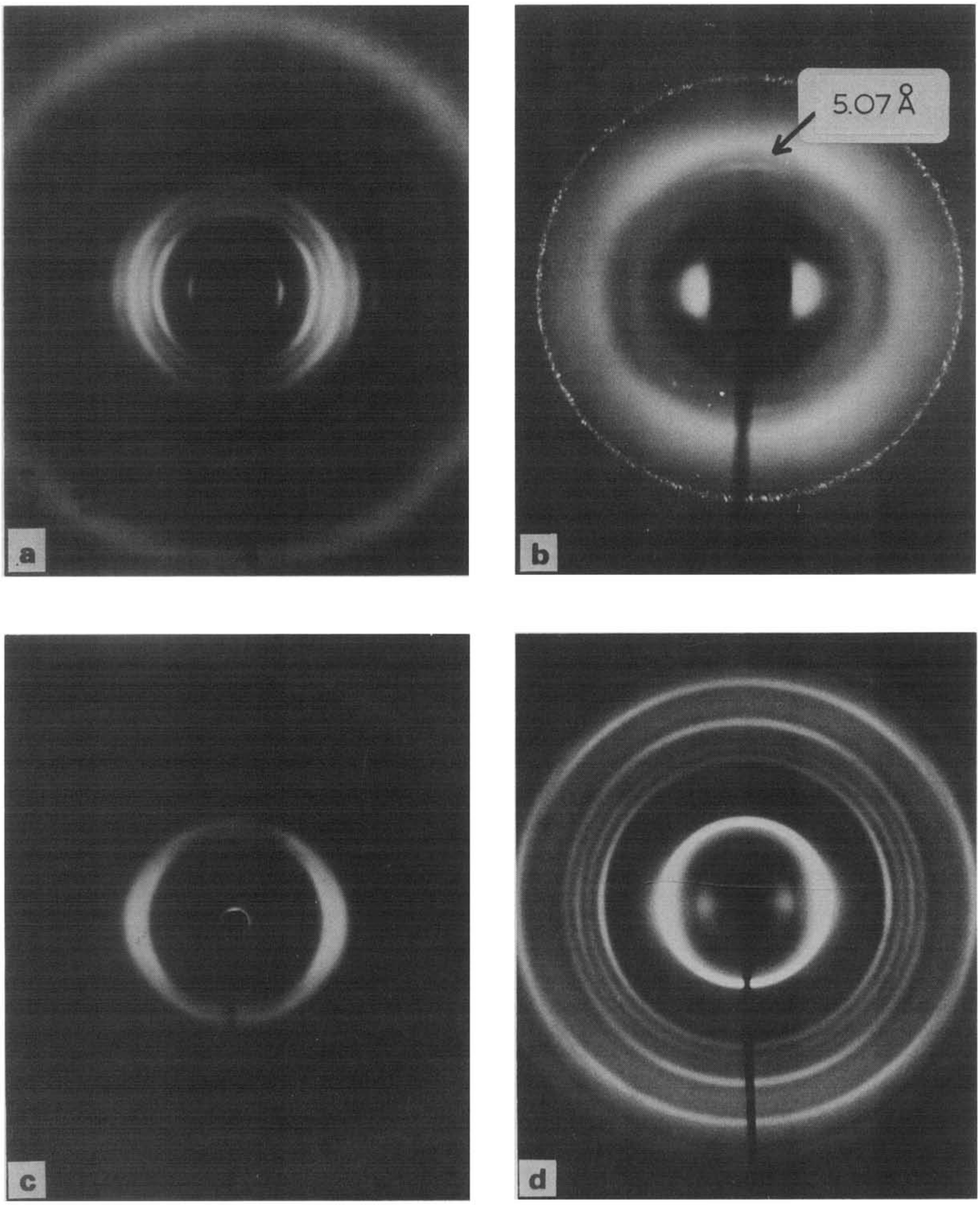


Figure 1 X-Ray EV patterns taken for: (a) crystalline complex in as-cast film with DMP content of 25%; (b) crystalline complex in oriented film with DMP content of 25%; (c) form II prepared by extracting DMP from crystalline complex; (d) form I prepared by heating crystalline complex at 120°C. The sample to camera distance was 11 cm for 1a and 1c, 6 cm for 1b and 8.5 cm for 1d. The film surface and the orientation direction were vertical

Table 1 X-Ray data of crystalline complex, form II and form I

[Crystalline complex with DMP content of 25%]

$d_{obs.}$(A)	Intensity[a]	Position[b]	$d_{calc.}$(A)[c]	*h k l*[c]
24.0	s	0°	23.92	1 0 0
	m	60°		0 1 0
13.7	vs	30°	13.81	1 1 0
	m	90°		$\bar{1}$ 2 0
12.0	s	0°	11.96	2 0 0
	m	60°		0 2 0
10.4	s		layer line (?)	
9.02	w	30°	9.04	2 1 0
	vw	90°		$\bar{1}$ 3 0
7.86	w	0°	7.97	3 0 0
	vw	60°		0 3 0
5.07	s		meridional	
2.54	w		meridional	
~5.4	streak		5th layer line	
~3.4	streak		8th layer line	
~2.1	streak		13th layer line	
1.5	s		meridional	

[Form II prepared by extracting DMP from crystalline complex]

d_{obs} (A)	Intensity[a]	Position[b]	d_{calc} (A)[c]	*h k l*[c]
~21	vvw		21.2	0 1 0
			20.4	1 0 0
12.6	w	90°	12.4	$\bar{1}$ 2 0
11.9	s	30°	11.9	1 1 0
10.6	m	60°	10.6	0 2 0
10.2	s	0°	10.2	2 0 0
8.2	vvw	~90°	8.12	$\bar{1}$ 3 0
7.9	vw	~30°	7.88	1 2 0
7.7	vw	~30°	7.74	2 1 0
~5.4	streak		5th layer line	
~3.4	streak		8th layer line	
~2.1	streak		13th layer line	
1.5	s		meridional	

[Form I prepared by heating crystalline complex]

d_{obs} (A)	d_{calc} (A)[c]	*h k l*[c]
10.40	10.36	1 0 0
6.00	5.98	1 1 0
5.48	5.47	1 1 2
5.19	5.18	2 0 0
4.81	4.79	1 0 5
4.01	4.01	1 1 5
3.92	3.91	2 1 0
3.74	3.74	2 0 5
3.46	3.45	3 0 0

[a] Abbreviations: v, very; w, weak; m, medium; s, strong

[b] Positions of equatorial reflections, estimated for the films exhibiting uniplanar orientation, are presented by the angle from an equator

[c] Calculated spacings and indices are based on the unit cells cited in text

This edge is relatively larger than the diameter of PMLG corresponding to 12 Å. The observed density of 1.28 g ml^{-1} requires that four chains of PMLG are located in a unit cell and all of the DMP is contained in crystals. As shown in the EV X-ray photograph in *Figure 1a*, the arcs of equatorial reflections have maximum intensities at certain angular positions, whereas in photographs taken in the TV position, equatorial reflections appear as Debye–Scherrer rings. Therefore, films display uniplanar orientation, with the helical molecules lying in the plane of the film and the helix axes randomly oriented in this plane. The uniplanar orientation becomes prominent with decrease in sample thickness and with an increase in casting temperature. The positions of maximum intensities are also presented by the angle from an equator in *Table 1*. In consideration of reciprocal–lattice diffraction geometry, the positions of reflections were well explained by this hexagonal lattice having a uniplanar orientation with the (100) planes parallel to the film surface.

The layer line pattern, characterized by the intense 1.5 Å meridional reflection and the intense streak on the layer line of 5.4 Å, indicates undoubtedly that the PMLG main chain assumes an α-helical conformation[5]. I.r. spectra also confirmed this. However, the layer line pattern contains the intense 'extra' reflections of 5.07 Å and 2.54 Å, the latter may be the second order of the 5.07 Å reflection. The spacing and sharpness for these reflections vary little with DMP content as shown later, suggesting that they can be attributed to a repeating unit along chain axis. In fact, the X-ray photograph of *Figure 1b* for the oriented film confirmed that they are on a meridian. As the repeating unit attributable to these reflections cannot be expected for a normal α-helix[5] or slightly distorted α-helix[6], another type of helix must coexist with the PMLG helix in this film. No other reflections of layer line indicate the irregular mutual levels of chains along their long axes.

A reflection of 10.4 Å (*Table 1*), was discernible only in as-cast film. Probably, this may be attributed to a near equatorial streak with the height of 1/50 Å^{-1} from the equator in the photograph of oriented film, for its maximum intensity is located at the position corresponding to the spacing of ≈10 Å.

When DMP molecules were extracted from the film by immersing it into boiling methanol, an appreciable change was observed in the X-ray pattern; the 5.07 Å and 2.54 Å meridional reflections disappeared, only the several broad equatorial ones remained (see *Figure 1c* and *Table 1*). As a result, the same X-ray pattern as that of form II[1] was obtained. Although the pattern is relatively poor for this form II, the positions and spacings of equatorial reflections were estimated from the photograph of *Figure 1c* exhibiting uniplanar orientation. As cited in *Table 1*, they are due to a slightly distorted hexagonal lattice with dimensions of $a = 23.9$ Å, $b = 24.9$ Å and $\gamma = 121.4°$. The lateral packing structure with a four-chain unit cell, thus, resembles that of a film containing DMP.

Initially, an attempt was made to interpret the characteristics in the X-ray patterns of *Figures 1a* and *1b*, according to the coiled-coil structure proposed in α-kelatin in which α-helices strand to each other[7–9]. However, it is likely that they are attributed to a crystalline complex formed between PMLG α-helices and DMP molecules, because the most predominant feature, the 5.07 Å meridional reflection, was easily lost by removal of DMP. Further structural examination of the crystalline complex was carried out from the observation of variation in the structure and properties of films with DMP content.

Variation of structure and mechanical properties with DMP content

Figure 2 shows the X-ray diffraction profiles of films with various DMP contents. The Figure shows that equatorial reflections became sharper with an increase in DMP content and the most clearly defined hexagonal pattern was obtained for the films with DMP contents from 25 to 30%. With further increase of DMP content, the hexagonal pattern again became obscure and thus,

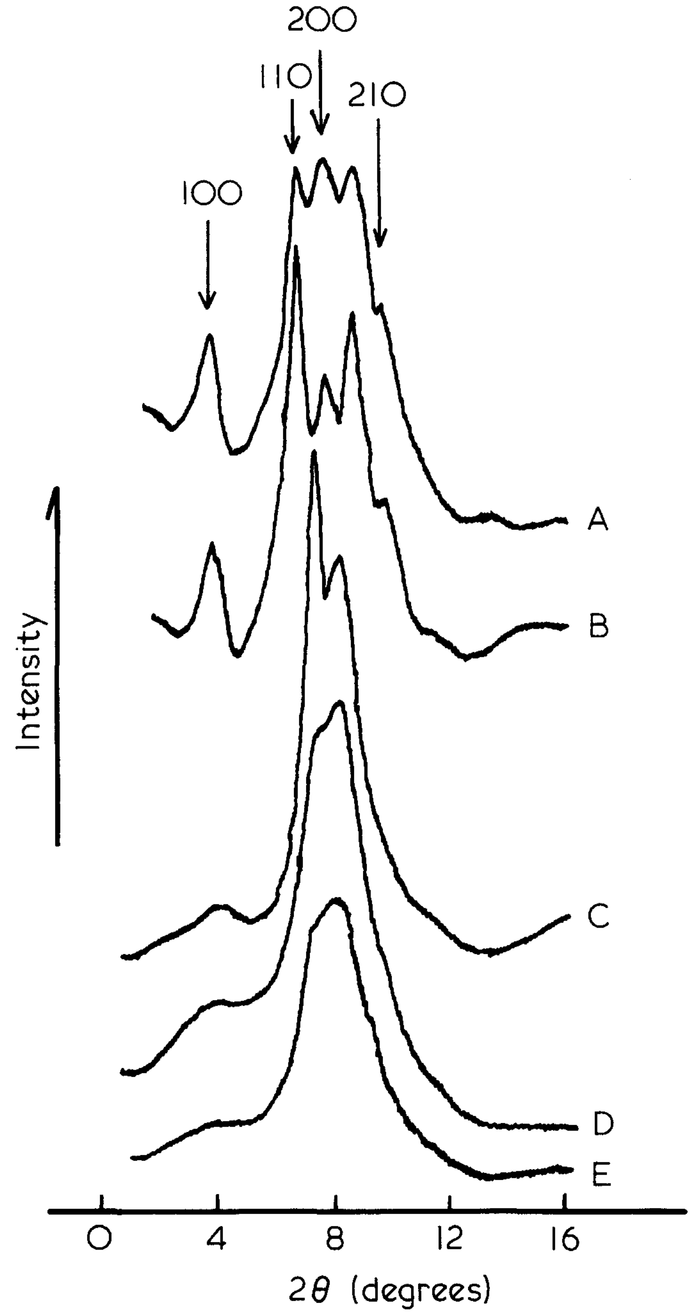


Figure 2 X-Ray diffraction profiles of the films with various contents. A, 29.8; B, 24.5; C, 10.0; D, 5.0; E, 0 wt%

in the region >60%, only the (100) reflection was retained. The disappearance of higher-order reflections in these films may be attributed to poor crystallization caused by the gelation which occurred in the evaporation process of DCE solvent which contained a large quantity of DMP. However, the 5.07 Å meridional reflection appeared at ≈20% and its sharpness and intensity were maintained throughout the region of DMP contents greater than this.

In addition to the variation of crystallinity, appreciable expansion of the hexagonal net was also observed with increase in DMP content. In a polypeptide with a high axis ratio, it is reasonable to assume that DMP molecules cause no dilution in a direction parallel to the helix axis, i.e., only the net lateral to α-helices expands with the addition of DMP. This assumption makes it possible to calculate how the distance between (100) planes in the large hexagonal net, d_{100}, should change as the volume fraction of PMLG, C, is changed. The derived relation between d_{100} and C is given by:

$$(d_{100})^2 = \frac{nW3^{1/2} \times 10^{24}}{2Nh\rho C}$$

where $n = 4$ is the number of chains located in a unit cell; $W = 143$, the residue weight of PMLG; N, the Avogadro's number; $h = 1.5$ Å, the residue height along PMLG chain axis and $\rho = 1.29\ \mathrm{g\,ml^{-1}}$, the density of PMLG. The experimental values of d_{100} *versus* C are compared with the theoretical line in *Figure 3*, where double logarithmic plots are given. In the region from 100 to 70 vol%, log d_{100} varies rectilinearly with the logarithm of PMLG concentration so that the data are on the theoretical line. In the region <70 vol% PMLG, the variation becomes negligible; the slight increase of spacings is considered to be caused by the deviation of molecular packing from hexagonal symmetry. The result indicates that the confined quantity of DMP corresponding to ≈30% is compatible with PMLG.

To expand the hexagonal net, DMP should penetrate into the side-chain domain. Thus, confirmation for the confined compatibility can be also obtained from dynamic mechanical measurements with respect to the side-chain motion. The mechanical loss due to the side-chain motion has been observed at ≈0°C for PMLG film at a frequency of 110 Hz[1,2]. The variation of the dynamic mechanical data with the DMP content is shown in *Figure 4*. In *Figure 5* are plotted the loss-peak temperatures against DMP content. These figures show that the peak temperature shifts from 0°C to ≈20°C in the first stage of dilution below 10%. In the next stage of 10–30%, the peak temperature is lowered markedly, and finally at >30%, it becomes constant at ≈ −20°C. Although the variation of peak temperature is complicated, the DMP molecules up to 30% clearly interact with PMLG side-chains, which is consistent with the X-ray result.

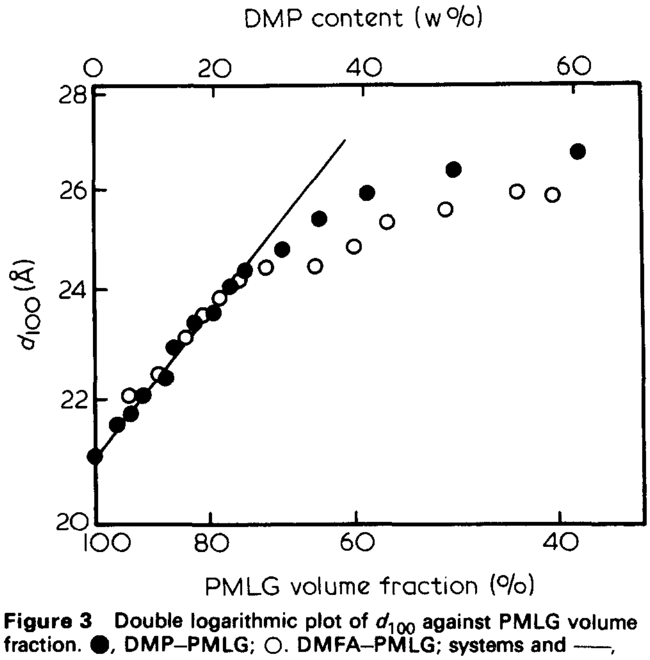


Figure 3 Double logarithmic plot of d_{100} against PMLG volume fraction. ●, DMP–PMLG; ○, DMFA–PMLG; systems and ——, the theoretical expansion of d_{100} calculated by equation cited in text

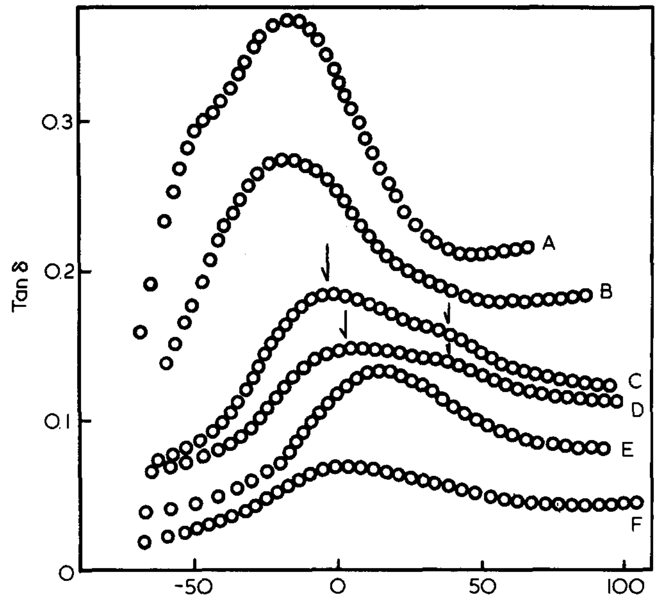


Figure 4 Temperature dependence of tan δ for the films with various DMP contents. The measurements were made at a frequency of 110 Hz. The curves, with the exception of form II at the bottom, have been displaced upward on the ordinate axis by 0.02 tan δ with the increment from curve immediately below. A, 70.0; B, 49.5; C, 29.8; D, 24.5; E, 16.2; F, 0 wt%

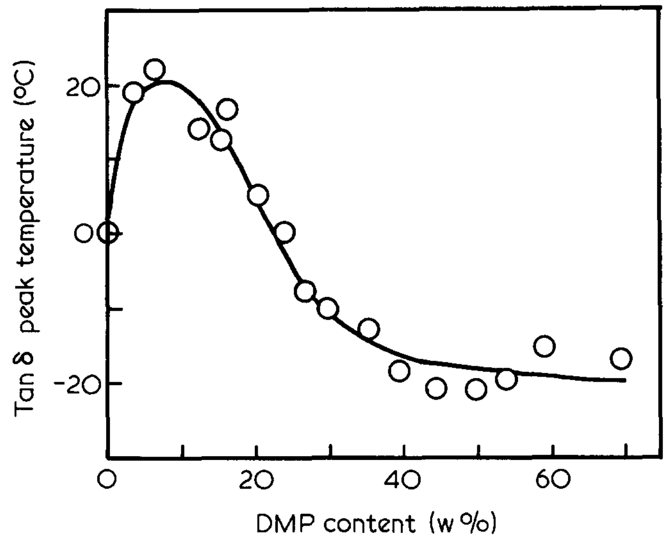


Figure 5 Variation of tan δ peak temperature with DMP content

Both X-ray data and mechanical data show that the DMP molecules up to a critical content between 25 and 30%, have good compatibility with PMLG side-chains to form a crystalline complex. This critical content of DMP offers the stoichiometry of 1 mol of DMP to three or four molar residues of PMLG.

Transformation from crystalline complex to form I

The crystalline complex showed an irreversible endothermic first-order transition as seen in the d.s.c. thermograms of *Figure 6*. Transition temperature decreased gradually from 120 to 100°C with the increase in DMP content of 20 to 70%.

In the films with DMP contents of 20–40%, the endothermic peak was successively followed by an exothermic peak. By these transitions, the large hexagonal unit cell was lost and the characteristic 5.07 Å meridional reflection also disappeared. In place, a highly crystalline form appeared, in which α-helical molecules are packed together to form a small hexagonal unit cell with the dimensions of $a = b = 11.95$ Å, $c = 27$ Å and $\gamma = 120°$ (see *Figure 1d* and *Table 1*). The structure thus obtained is the same in size and shape of unit cell as form I and, therefore, DMP molecules have been excluded from the crystalline domain. This result is consistent with the fact that the DMP molecules are not miscible with PMLG when the films were prepared from the solvents making form I. Two peaks in the d.s.c. thermograms can be attributed to melting of the crystalline complex and subsequent crystallization of PMLG accompanied with phase separation of DMP.

In the films with higher DMP contents, >45%, only an endothermic peak was observed. By this irreversible transition, the collapse of the crystalline complex is also evident because the equatorial reflection of ≈26 Å and the 5.07 Å meridional reflection disappeared. The resultant films, different from those previously, displayed only a few broad reflections with spacings such as 11, 5.3 and 4.7 Å. Accordingly, the poor order in the packing of α-helices and/or the small crystalline size dictate their structure, which may cause no clear appearance of the succeeding exothermic peak. For the specimens with DMP contents <20%, however, d.s.c. peaks became obscure with decrease in DMP content and finally disappeared. In this case, the transformation to form I gradually occurred at temperatures >200°C, similar to form II[2,4]. The relation between form I, form II and the crystalline complex, is shown in *Figure 7*.

It is noteworthy that the enthalpy change (ΔH), estimated for endothermic peaks of films with DMP contents >40%, were almost constant per mol residue of PMLG. The average ΔH was 0.23 kcal/mol residue of PMLG.

Proposed structure of crystalline complex

The structure of the crystalline complex was examined with respect to two characteristics in the X-ray pattern;

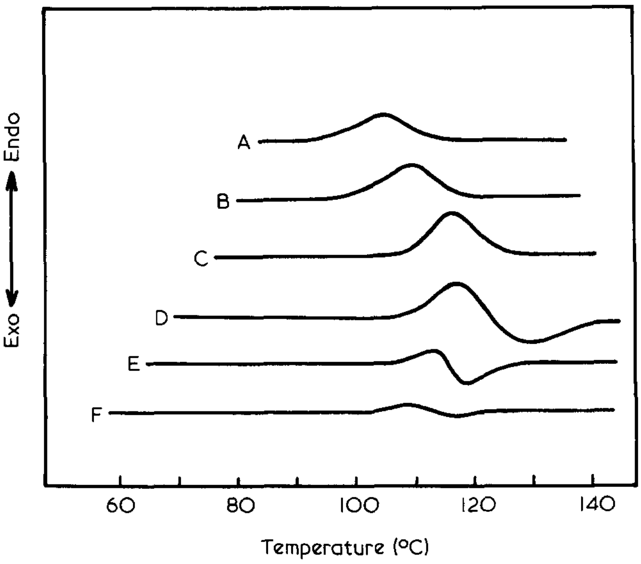
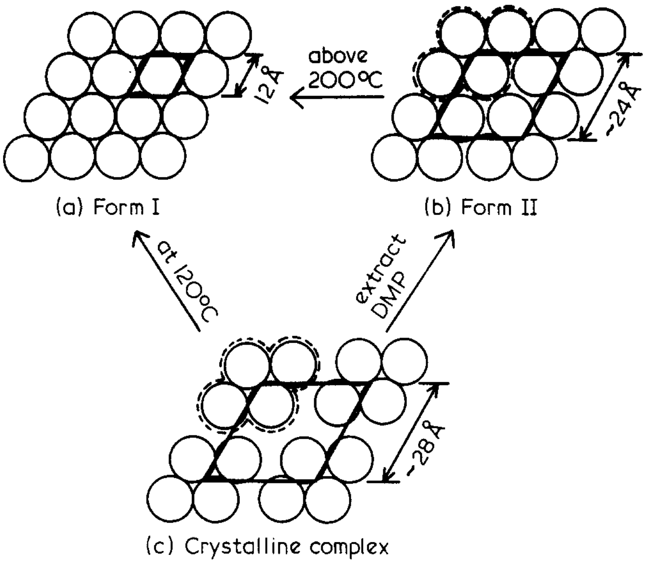


Figure 6 D.s.c. thermograms of the films with various DMP contents. The measurements were made at a heating rate of 10°C min^{-1}. A, 70.0; B, 60.0; C, 49.5; D, 40.1; E, 29.8; F, 20.0 wt%



(a) Form I

(b) Form II

(c) Crystalline complex

Figure 7 Diagram of the relation between crystalline complex, form I and form II and their hypothetical lateral packing structures. The circle with the diameter of 12 Å indicates the PMLG chain projected on the plane perpendicular to its long axis. In *Figures 7b* and *7c*, a group composed of four close-packed chains is represented by dashed curve

one is the 'extra' 5.07 Å meridional reflection, the other the indication of a large hexagonal lattice.

Origin of 5.07 meridional reflection. The substituents of DMP sticking out of the benzene ring have the same chemical structure as that of the terminal group of the PMLG side-chain. Therefore, the compatibility of DMP and PMLG can be achieved by mixing of them in a manner such that two substituents of DMP are locked between the side-chains. It is noteworthy that dimethyl isophthalate and dimethyl terephthalate are not miscible with PMLG probably because of steric disadvantage.

Stereochemically, it is possible for the number of DMP molecules to be equimolar to those of the PMLG residue around the α-helix. Then, the adjacent benzene rings of DMP directing outside the side-chain region may favour lateral attractions, partly by enhanced van der Waals attractions, due to the presence of polarizable π-electrons, and partly through enhanced polarity due to the conjugation with adjacent carbonyl groups[10], i.e., they may assume the face-to-face arrangement with a contact distance ≈3.4 Å corresponding to the van der Waals thickness perpendicular to the plane of ring[11]. The stabilization may be further achieved by consecutive stacking, which forms a DMP super helix superimposed on the PMLG α-helix. Then, the 5.07 Å reflection can be attributed to an axial translation of rings along the chain axis and the d.s.c. endothermic peak is associated with the melt of the consecutive stack. This inference may be correct for a stacking arrangement is a typical mode of crystallization or organization of the aromatic rings in low molecular weight compounds[12,13] and polymers[14-16].

Figures 8a and *8b* show the c.d. and u.v. spectra of DMP measured in a crystalline complex with DMP content of 25%, respectively. The u.v. spectrum of DMP, as measured in hexane solution, is dominated by two bands at ≈240 nm and 280 nm which are attributed to the carbonyl and benzene groups, respectively. DMP in the crystalline complex showed the latter band clearly without spectral abnormality, indicating no significant π-electron interaction between benzene rings[17]. At the same absorption band, positive c.d. was induced. Such induction of c.d. requires the helical array for DMP molecules as proposed in the acridine orange–polyglutamic acid system[18,19]. Thus, the spectral results are also consistent with the postulated model of a superhelical arrangement of DMP due to the van der Waals attraction of benzene rings.

The type of stacking was examined using the radical projection of the α-helix shown in *Figure 9*. The open circle indicates the position of side-chain in an α-helical symmetry. The DMP molecule, represented by a rectangular shape, may be displaced between side-chains and the stack can form between DMP molecules in the nearest neighbours, i.e., the third (1, 4) or fourth (1, 5) neighbours along α-helix axis. To satisfy approximately the 5.07 Å repeating length, there are two possible ways of stacking along the directions shown by A and B lines, which are attained by linking two residues in the 10th (1, 11) and 17th (1, 18) neighbours, respectively. Then, the displacement of DMP from α-helical symmetry, indicated by the arrow in *Figure 9*, is necessary for the formation of a co-operative stack. The flexible side-chains may allow DMP molecules to move independently to a certain extent on the α-helical back bone. The A and B lines show the 5.00 Å and 5.10 Å reflections, respectively, as an axial translation of benzene rings. Other ways of stacking were rejected because of

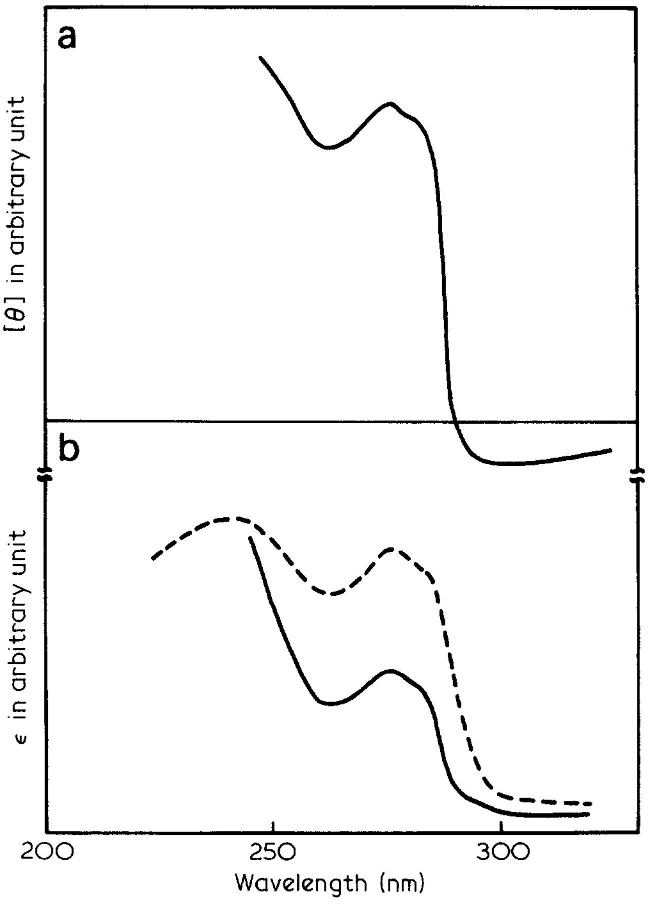


Figure 8 Circular dichroic (a) and ultraviolet absorption (b) spectra of DMP. The solid and dashed curves indicate the spectra measured in crystalline complex with DMP content of 25% and solution in straight-chain hexane with DMP concentration of 2×10^{-5} M, respectively

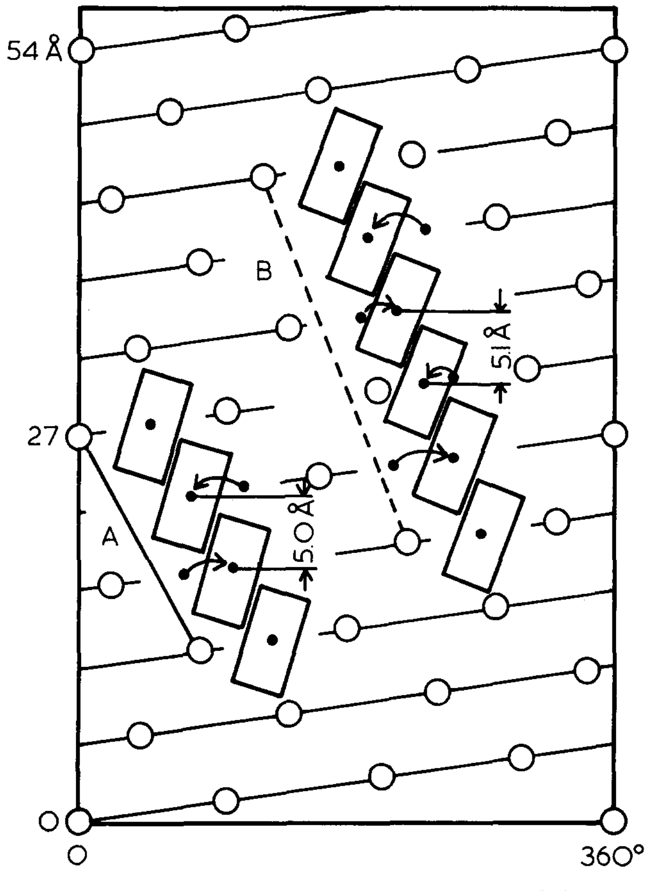


Figure 9 Radial projection of an α-helix. The open circle indicates the position of PMLG side chain in an α-helical symmetry and the rectangle represents the benzene ring of DMP molecule. Two types of stacking for DMP benzene rings are illustrated along A and B lines

the relatively large or small values of translation. The actual stack yielding the 5.07 Å reflection may be displaced along the line with a slope between those of the A and B lines. In this model, the benzene rings can attain the van der Waals contact of 3.4 Å by tilting so that their normals are inclined at ≈65° to the helix axis as shown in *Figure 9*.

Origin of large hexagonal lattice. If the diluents penetrate homogeneously in the side-chain domain of each chain, the lateral packing structure should appear to have a one-chain unit cell with the edge similar in diameter to PMLG. The large edge observed here, therefore, indicates that DMP molecules mix heterogeneously with the side-chains so that a group consisting of four chains is distinguished as a unit of the crystal lattice.

Such a large unit cell has been observed for biological molecules which are almost circular in shape, as in collagen, TMV, DNA and α-kelatin fibrils, and is attributed to the fibrillar assemblies of cylindrical rods[20,21]. In these systems, the large unit cells are favoured when such assemblies contain significant amounts of water in the gaps between molecules. Statistical rotation and continuous shifts are characteristic of such an assembly, because the diluents cause the fibrils to be in incomplete contact. The system studied here is in the same situation. By analogy, a set of four close-packed α-helical rods construct a group similar to a fibril, the centres of the groups form a two-dimensional hexagonal net, and DMP molecules are located in the gaps between groups. This disposition of DMP is reasonable, because the observed stoichiometry allows DMP molecules to anchor on one third or one fourth of the whole available sites around a PMLG chain. The hypothetical packing structure is shown in *Figure 7c*.

The removal of DMP causes the fibrils to come into closer contact so that the individual chain becomes equivalent to that shown in *Figure 7b*. This seems to explain why the (100) reflection of the large hexagonal lattice became weak with a decrease in DMP content (refer to *Figure 2*). However, the slight difference between interaction of the molecules in the same group and that of the molecules in different groups still may be retained to interrupt the formation of a small hexagonal lattice composed of one chain such as in form I of *Figure 7a*.

Such fibrillar assemblies should give two different mechanical loss peaks due to the motions of the two types of side-chains directed inside and outside of group. In fact, the specimens with DMP contents from 25 to 30% showed the main peak at ≈ −10°C and a shoulder at ≈40°C as shown by the arrows in *Figure 4*, although it failed to produce the well separated peaks by changing the applied frequency from 110 to 3.5 Hz.

The large hexagonal lattice was also observed when *N*,*N*-dimethylformamide (DMFA) was used as a diluent. For this X-ray measurement, the samples were sealed into capillary tubes after exposure to the vapour of DMFA at ≈60°C. As shown in *Figure 3*, the variation in spacings of the (100) reflection with PMLG concentration is almost the same as in DMP system. In this case, a reversible structural change was observed on absorption and desorption of DMFA. In the specimen with a DMFA content of 25%, approximately the critical content, three equatorial reflections of 24.3, 14.0 and 12.1 Å were observed, which were interpreted as representative of a large hexagonal lattice with a cell edge of 28.0 Å. This lattice is coincident with that in the DMP system, but no 'extra' meridional reflection appeared, which can be understood because the chemical structure of DMFA molecule seems to offer no ability for the formation of the ordered structure along the PMLG chain. In the same DMFA system, poly(γ-benzyl L-glutamate) and poly(γ-ethyl L-glutamate) also showed the similar large hexagonal packing, while polyglutamates with the side-chains such as phenethyl, phenylpropyl, propyl and butyl groups showed the normal hexagonal lattice composed of one chain[23]. This leads to the conclusion that the short side-chains facilitate the four-chain assembly of α-helices. In addition, solvents with a large dielectric constant, such as DMFA, benzyl alcohol, pyridine and DCE, are also responsible for this assembly of PMLG. This result is compared with those from small-angle X-ray scattering experiments which was carried out to determine the radius of gyration of the cross-section of the PMLG α-helix in the dilute solutions[24]. The observed variation of the radius of gyration with the solvents has shown that the more extended conformation is assumed in the solvent with the higher dielectric constant. These effects of side-chain length and solvent indicate that the four-chain assembly of α-helices may be closely associated with the side-chain orientation or side-chain conformation.

The overall structure of the crystalline complex may be attained by combining the two characteristics: the DMP stacking arrangement and the four-chain assembly of PMLG. Although no detailed structure can yet be presented, some comment on the relation between them is possible. If the formation of the stack is confined to one chain, only a limited number of DMP molecules participate to form a short stack in a linear arrangement. The longer linear stack can be obtained by joining such a short stack in a chain to that in its neighbouring chain. This method of stabilizing the stack has been proposed as a possible self-organization of benzene rings at the end of side-chains of poly(γ-benzyl L-glutamate)[14,22]. Thus, the close-packed chains forming a group might offer a suitable site for this organization such that the longer linear stack surrounding each group may be formed.

Recently, many examples of the complex formation between polymer and low molecular weight compounds have been reported[19,25-28]. They have been produced by van der Waals, Coulombic, and hydrogen bonding forces. The present system, involving van der Waals forces, suggests the possibility of complex formation of polyglutamates with various types of low molecular weight compounds by changing the type of side-chain. The crystalline complex based on polypeptides is especially interesting because their helical conformation offers the sterically restricted field or chiral field for complexed molecules. This suggests that the polymerization of complexed molcules, if properly processed, will result in a polymer with high stereoregularity or optical activity. The first attempt is in progress by using the methyl methacrylate as a complexed monomer.

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