CHEMISTRY LETTERS, pp. 1159-1162, 1973. Published by the Chemical Society of Japan

THE SECONDARY STRUCTURE AND MOLECULAR CHAIN ORIENTATION OF POLY-γ-METHYL-D-GLUTAMATE CAST FROM SOLUTION IN DICHLOROACETIC ACID

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The β-form, which is completely free from other secondary structures, has been newly observed in the case of the solid poly-γ-methyl-D-glutamate film cast from solution in dichloroacetic acid. The a- and c-axes lie on the plane parallel to the film surface and the molecules are packed parallel with a helical twist relative to one another about the b-axis which is perpendicular to the film surface. When the solid film is stretched, the c-axis orients along the drawing direction by rotating about the b-axis, showing double orientation.

It is widely accepted that three different secondary structures, the α-helix, the β-pleated sheet and the random coil, occur in the solid- or solution-state of synthetic polypeptides depending on the type of the hydrogen bond. Therefore, the equilibrium state between helix and random coil varies with the different polypeptides, temperature, pH and solvents. Inasmuch as dichloroacetic acid (DCA), a so-called random solvent, would have a great affinity for the relatively polar environment of the side chain in poly-γ-methyl-D-glutamate (PMDG), the molecular chains of PMDG in dilute DCA solution occur in the random coil conformation in preference to the α-helix.

In this paper, we have focused on the secondary structure and molecular orientation of the PMDG film cast from solution in DCA.

The films of PMDG about 1 mm thick were cast from a 10 % PMDG - DCA solution. The solution was kept at 40°C for around 50 days to remove DCA. The PMDG film was stretched to about twice the original length at room temperature and then, annealed in vacuo at 200°C for 2 hrs. under constraint in order to remove DCA solvent completely and increase the degree of crystallinity. The X-ray photographs were taken with the X-ray beam normal, edge on and end on to the drawn polymer film as designated in

Figure 1.

Figure 2 shows the photographs of the through, edge and end views, respectively. These photographs indicate that double orientation is caused by simple uniaxial drawing. The very strong diffraction from the $(10\bar{1}0)$ plane characteristic of the α-form corresponding to the spacing of 10.36 Å was not observed and, moreover, the equatorial reflections as a whole do not fit the reciprocal lattice points reproduced from the data reported for the α-form of PMLG1) (a=11.95 Å, c=27.0 Å, hexagonal cell). The reciprocal lattice of the α-form is drawn by thin lines in Figure 3.

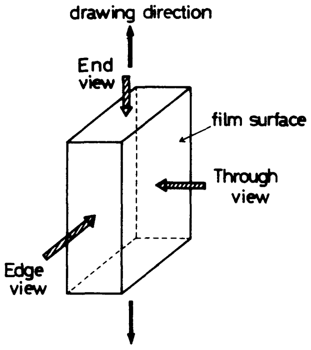
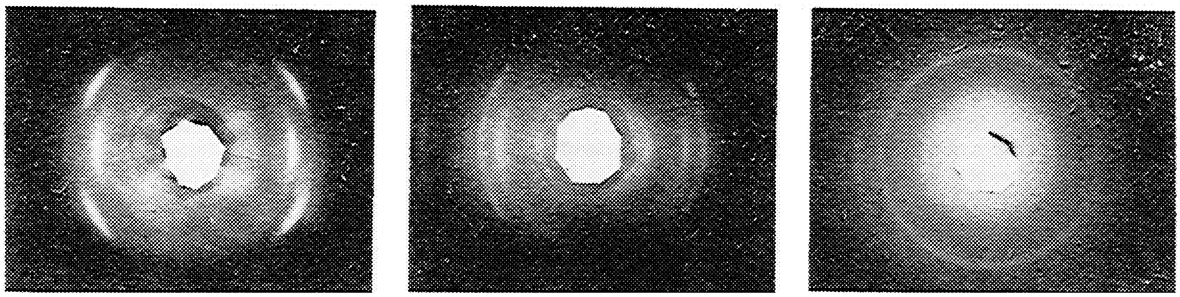


Figure 1. Designation of X-ray photographs in terms of X-ray beam incident from three different directions.



(a) (b) (c)

Figure 2. X-ray photographs of oriented PMDG, (a)Through view, cylindrical-film, (b)Edge view, cylindrical-film, (c)End view, flat-film.

In consideration of the magnitude of spacings and variations in intensity of the equatorial reflections listed in Table 1, the lattice constants for the secondary structure of PMDG cast from solution in DCA have been determined so that all equatorial reflections are in accord with the reciprocal lattice points as shown in Figure 3. The values of a=9.44 ± 0.02 Å, b=23.37 ± 0.03 Å and γ=90° are consistent with the spacings of equatorial reflections. The c-axis repeat (fiber period) has been determined as 6.81 ± 0.02 Å from the reflections on the first and second layers. These lattice constants are comparable with the orthorhombic unit cell of the β-form with a=4.70 Å, b=21 Å reported by Brown et al.2). The a-axis dimension corresponding to the backbone separation along the direction of the hydrogen bonds, was decided to be twice as much as Brown's report because the antiparallel-chain pleated sheet is more favorable for hydrogen bonding, compared with the parallel-one. The b-axis dimension depends on spacing and conformation of the side chain, and increases with increasing length of the side chain. The side chain spacing of 23.37 Å lies within the range of the spacing expected from the length of the side chain[3]. The β-form studied here may be consistent with the cross-β form prepared as the precipitate from PMLG-DCA solution, which has been reported by Ishikawa and Kurita[4] using electron diffraction method, though they observed only two diffraction spots.

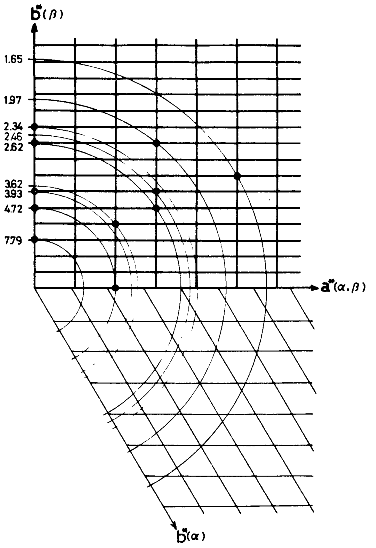


Figure 3. Reciprocal lattice for the α- and β-form of PMDG of equatorial reflections.

From the variation in intensity of the (hk0) reflections and the diffraction direction in the end view photograph, it is possible to deduce the preferred molecular orientation of crystallites with respect to the film surface. Figure 2 and Table 1 show that double orientation is induced by simple uniaxial drawing without any special treatment such as pressing or rolling, indicating that the a-axis lies in the film surface, the b-axis is perpendicular to that and the c-axis aligns along the drawing direction. The process of the double orientation behavior is easily expected from molecular arrangement, packing and orientation which occur in the original specimen. It was confirmed from the X-ray photographs shown in Figure 4 that the molecules were packed approx-

Table 1. Observed and Calculated Spacings, Intensities and Indices for Equatorial Reflections.

$d_{obs.}$(Å)	$d_{calc.}$(Å)	$I_{through}$	I_{edge}	I_{end}	Index
7.79	7.79	w	s	m	(030)
4.72	4.72	s	s	s	(200),(050)
3.93	3.90	w	m	m	(060)
3.62	3.67	m	w	w	(240)
2.62	2.60	m	s	m	(350),(090)
2.46	2.45	w	-	vw	(360)
2.34	2.34	-	w	vw	(0100)
1.97	1.95	vw	w	-	(0120)
1.65	1.64	vw	-	-	(570)

imately parallel to each other, but with a small helical twist relative to one another about the b-axis and also, the b-axis was normal to the film surface in the case of the PMDG solid-state as schematically shown in Figure 5(a).

The mesomorphic region of poly-γ-benzyl-L-glutamate and PMLG probably maintains the same relative disposition as in cholesteric mesomorphic phase in concentrated solution as discussed by Robinson$^{5)}$. It is likely that somewhat similar structure is retained in the solid state of PMDG due to the extremely small freedom of movement of molecules in PMDG concentrated solution, during the process of solvent removal. Then, the ac-plane lying in the plane parallel to the film surface rotates about the b-axis during drawing and finally, the c-axis orients parallel to the drawing direction as shown in Figure 5(b).

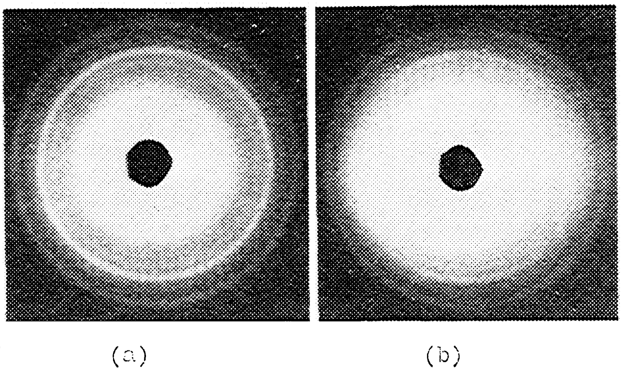


Figure 4. X-ray photographs of original PMDG cast from DCA solution, (a) normal to beam, (b) edge on to beam.

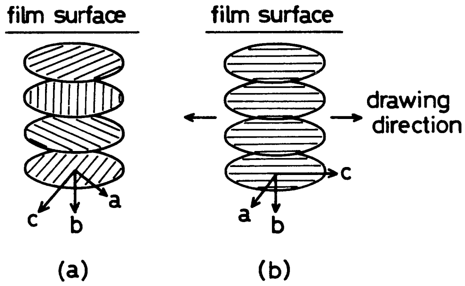


Figure 5. Schematic representation of molecular chain orientation. (a) original PMDG, (b) oriented PMDG.

From the X-ray study, we may conclude that the characteristic molecular packing of PMDG cast from DCA solution, resembling the cholesteric state, induces double orientation by simple uniaxial drawing.

We are grateful to Ajinomoto Co., Ltd. for supplying a sample of PMDG.

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(Received July 28, 1973)