Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 21 Mar 2007.

To cite this article: Eisaku Iizuka (1974): Birefringence of Liquid Crystals of Polypeptides in a Magnetic Field, Molecular Crystals and Liquid Crystals, 27:1-2, 161-174

To link to this article: http://dx.doi.org/10.1080/15421407408083127

Mol. Cryst. Liq. Cryst., Vol. 27, pp. 161–174

Printed in Dordrecht, Holland

Birefringence of Liquid Crystals of Polypeptides in a Magnetic Field

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(Received October 15, 1973)

The behavior of liquid crystals of poly-γ-benzyl-L-glutamate, its equimolar mixture with the D-isomer and poly-γ-ethyl-L-glutamate was studied in magnetic fields up to 25 KG mainly by measurements of the birefringence. In all the systems tested, rod-like molecular clusters were formed and oriented in the direction of the magnetic field. Presence of diamagnetic benzene rings in the side chains of the polypeptide molecule was known not to be absolutely necessary for the magnetic-field orientation. Degree of the orientation was somewhat dependent on the systems being observed. Magnitude of the induced dipole moment was estimated for the molecular cluster and was compared among the systems.

INTRODUCTION

Magnetic field acting on the anisotropy of the magnetic susceptibility exerts torques within a liquid crystal which competes with the elastic torques determining its internal structure. The structure changes in order to minimize the total free energy of the system. Meyer[1] and de Gennes[2] have derived equations predicting the change for a cholesteric liquid crystal on the basis of Frank's curvature-elasticity theory.[3] Change of the pitch of the helicoidal structure of cholesteric liquid crystals placed in magnetic field has been measured for poly-γ-benzyl-L-glutamate (PBLG) and poly-γ-ethyl-L-glutamate ((PELG).[4] The value of $k_{22}/(\chi_p - \chi_t)$ ranges from 1 to 10 where k_{22} and $\chi_p - \chi_t$ are the tortional elastic modulus and the magnetic anisotropy, respectively. Tohyama and others[5,6] have measured the magnetic anisotropy of PBLG and PELG by means of the magnetic balance, and have obtained values of $(5 - 8)\times10^{-8}$ emu/g and

1.64×10^{-8} emu/g, respectively. Sobajima[7] was the first to report the magnetic-field orientation of PBLG. He observed it indirectly by measurements of the NMR on the solvent molecules such as CH_2Br_2 and CH_2Cl_2, and several reports[8] have followed his report. An attempt to observe the solute molecules was carried out first by measurements of the infrared dichroic ratio in magnetic fields 7.4 KG or less.[9] When CH_2Br_2 was used as the solvent, degree of the polymer orientation was rather low and had an apparent maximum at around 18 vol% for PBLG of degree of polymerization (DP) 1460. This was interpreted to be due to wall effects that prescribe the ordering of the solute molecules with respect to the surfaces of the measuring cell in the absence of the external field. Molecular clusters were considered to be formed in the magnetic field and orient in the field direction as in the case of the electric-field orientation (see Refs. 10 and 11). Film specimens cast and dried in a magnetic field of 7.4 KG showed very good orientation in contrast with the solution specimens. Some interactions among the molecular clusters having huge electric dipole moments were considered to become intense in the process of drying up to promote the magnetic-field orientation.[9] These have been the case also in PELG and an equimolar mixture of PELG and its D-isomer (PEDG).[12] The purpose of this paper is to present results observed in magnetic fields high enough to overcome the wall effect and to evaluate side-chain effects on the magnetic-field orientation of polypeptides.

EXPERIMENTAL PROCEDURES

PBLG used was of mean DP 470 and prepared from the N-carboxy-α-amino acid anhydride of γ-benzyl-L-glutamate by Prof. T. Hayakawa of this Faculty. PBDG used was of mean DP 530, prepared in the similar method as above and was donated by Prof. Wada of Department of Physics, the University of Tokyo. PELG used was supplied by Dr. S. Mori of Ajinomoto Co., Ltd. as an ethylacetate solution with an intrinsic viscosity 1.42 in dichloroacetic acid (DCA) at 30 °C, and was used after being dried up. PBLG, an equimolar mixture of PBLG and PBDG, or PELG was dissolved in a solvent such as CH_2Br_2, CH_2Cl_2 and dioxane that allows the formation of liquid crystals (and of α-helices) and was kept 1 – 8 weeks in a sample tube at room temperature before using.

The solution was put in a rectangular quartz cell of path length 1.00 mm, and then a quartz spacer of 0.90 mm thickness was introduced in the cell to adjust the path length to 0.10 mm. The solution was placed between the poles of an electromagnet, a modified model of JM-151 manufactured by Japan Electron Optics Laboratory Co., Ltd., with the cell surfaces parallel to the magnetic field. *Birefringence measurements* Measurements of the birefringence on the liquid crystalline solutions were then carried out with the incident beam perpendicular

to the direction of magnetic fields up to 25 KG using a double refractometer manufactured by Shibayama Scientific Instrument Co., Ltd.

Light scattering measurements Patterns of low-angle light scattering of the solutions were photographed with the method using a laser beam described elsewhere (see Refs. 12 and 13).

Wide-angle X-ray diffraction measurements The measurements were carried out on film specimens of polypeptides instead of the solution specimens. The liquid crystalline solution was put in a 1-cm rectangular quartz cell and was placed in the magnetic field for 24 hours without the solvent loss. Film specimens of thickness about several microns were then prepared by allowing the solvent to evaporate in another 24 hours. They were used for the birefringence measurements as well.

All the solvents were of reagent grade and were used without further purification. The temperature of the solutions was regulated at 20 °C in a thermostatted room unless stated otherwise. The values of the polymer concentration were only very approximate. All the 0.10-mm solutions introduced in the measuring cell with the spacer were no longer cholesteric even when the solutions were so in the sample tubes. As Robinson[14] reported, no cholesteric structure was observed when they were less than 0.25 mm thick.

RESULTS AND DISCUSSION

Film specimens

All the specimens tested displayed an excellent magnetic-field orientation, and some representative X-ray diffraction patterns are shown, in Figure 1. The magnetic-field orientation of the PBLG film east from a dioxane solution was observed clearly, which had not been detected so far. The PELG that has no benzene rings in its side chains underwent the magnetic-field orientation as well. These new findings, however, would be natural because these polypeptides are magnetically anisotropic as mentioned in the introduction.

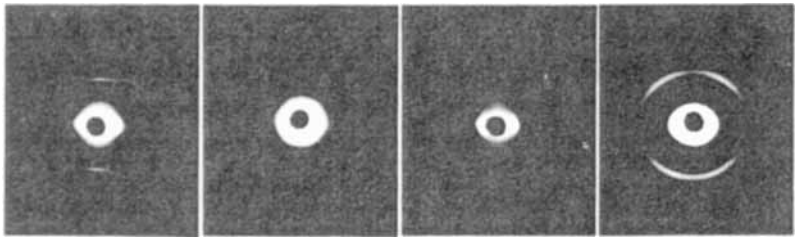

FIGURE 1 X-ray diffraction photographs of the magnetically oriented polypeptide films. The magnetic field direction is vertical and the X-ray beam is normal to the plane of the film. From the left to the right: PBLG in CH_2Br_2, 10 KG; PBLG in doxane, 25 KG; 1:1 PBLG+PBDG in CH_2Br_2, 10 KG; PELG in CH_2Cl_2, 10 KG.

The birefringence, Δ n, of a rigid molecule is expressed by [15]

$$\Delta n = (2\pi(g_2 - g_3)/n)\Phi,\ g_2 - g_3 \equiv (n + 2)N_\rho(a_2 - a_3)/9M$$

where n, Φ, N, ρ, M and $a_2 - a_3$ are the refractive index in the absence of a magnetic field, the orientation factor, the Avogadro number, the density, the molecular weight and the optical anisotropy factor, respectively. a_2 is the polarizability parallel to the molecular chain and a_3 being the polarizability perpendicular to the molecular chain. The observed birefringence was positive and indicated that the maximum polarizability was in the direction of the axis of the polymer molecule (and of the molecular cluster). This proves that the assumption adopted in the analysis of the low-angle light scattering by the molecular clusters was adequate (see Ref. 13).

In the molecular cluster, the polymer molecules are considered to align nearly parallel to the cluster axis forming itself a crystallite. The degree of the crystallite orientation, Π, was determined for the film specimens using the following relation given by Go and Kubo,[16]

$$\Pi = (90^\circ - H^\circ/2)/90^\circ$$

where H° is the half width read from the intensity of the circular record of the equatorial diffraction corresponding the polypeptide chain interval (see Ref. 17). As may be seen in Figure 2, the intensity, I, was well expressed by the following relation,

$$I = I_0 e^{x \cos 2\theta}. \tag{1}$$

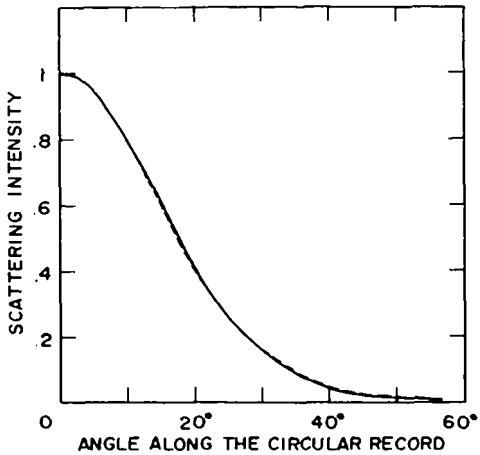

FIGURE 2 Scattering intensity of the circular record of the equatorial X-ray diffraction for the magnetically oriented film of PBLG. Full line: calculated with the relation, $I = I_0 e^{x \cos 2\theta}$ where x is chosen as 3.7. Broken line: observed in a magnetic field of 25 KG at a scattering angle of 6.70°. Degree of the crystallite orientation is 0.80.

The induced dipole moment of the molecular cluster is considered to be $\mu_0 \cos\theta$ where θ is the angle the molecular cluster axis makes with respect to the magnetic field direction and μ_0 being the dipole moment at $\theta = 0°$. As the polymer axis is parallel to the film surfaces (see Refs. 10 and 18), the intensity at any angle θ is in proportion to the number of polymer molecules ordering in the θ-direction. The potential energy of the molecular cluster in the magnetic induction, B, has the magnitude $-(\mu_0 B/4)\cos 2\theta$ + const. Therefore, the above relation indicates that the molecular clusters correspond to a two-dimensional Boltzmann distribution in the plane of the film. The constant, x, is interpreted to be substituted for $\mu_0 B/4kT$ (k and T are the Boltzmann constant and the absolute temperature, respectively). The degree of the cluster (and of the polymer) orientation is then expressed as a function of x:

$$\Pi = 1 - (\cos^{-1}(1 - 0.6932/x))/180° \qquad (2)$$

By substituting the obtained data in this relation, the values of the maximum induced dipole moment, μ_0, were calculated, and are shown in TABLE 1. The mean value was about 2.4×10^{-17} erg/gauss for all the systems tested and any noticeable side chain effect on the magnitude of the dipole moment was not observed. The maximum magnetic energy in a magnetic field of 10 KG is then calculated to be 0.15 eV. The number of PBLG molecules in each molecular cluster has been estimated to be about 5×10^5 (see Ref. 13). So that, the magnetic energy per each peptide residue turns to be about 6×10^{-10} eV, which is about 1/100 of that calculated by Suzuki and his coworkers[19] on a theoretical basis. The number of PELG molecules composing the molecular cluster has not

TABLE I

Maximum induced dipole moment of the molecular cluster in magnetically oriented polypeptide films

Origin	Degree of orientation	$\mu_0 \times 10^{17}$ erg/gauss
PBLG/CH_2Br_2	0.77	2.1
	0.81	2.7
	0.80	2.5
PBLG/dioxane	0.81	2.7
	0.78	2.0
(1:1 PBLG+PBDG)/CH_2Br_2	0.80	2.5
	0.79	2.3
PELG/CH_2Cl_2	0.85	3.1
	0.78	2.0
	0.81	2.7

yet been estimated and the comparison between BLG and PELG concerning the magnetic susceptibility is unable to be made.

The orientation factor, Φ, was calculated for various x's with the following relation,

$$\Phi = \frac{1}{2}\int_{0^\circ}^{90^\circ} (3\cos^2\theta - 1)e^{x\cos 2\theta}d\theta \quad \int_{0^\circ}^{90^\circ} e^{x\cos 2\theta}d\theta \qquad (3)$$

by the aid of an electric computor, CEC 555 manufactured by Chuo Denshi Co., Ltd. The relation between Π and Φ was obtained through x and is given in Figure 3, and with this relation the values of Π were exchanged for those of Φ. The birefringence of the films at complete orientation was then estimated by dividing the observed birefringence by Φ, and are summarized in TABLE 2 together with the spacings used for determining the degree of the crystallite orientation. The mean birefringence was 0.023 for PBLG and 0.021 for PELG.

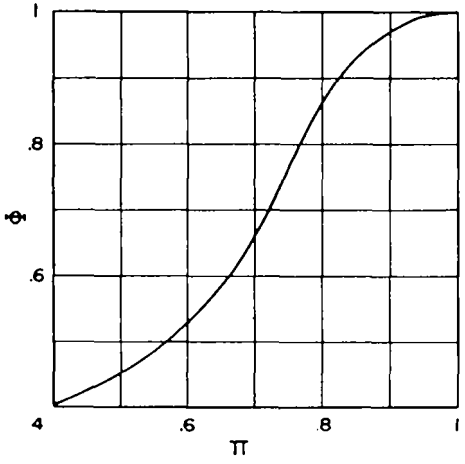

FIGURE 3 Relation between the degree of orientation (Π) and the orientation factor (Φ) for the two-dimensional Boltzmann distribution.

TABLE II

Estimated birefringence at complete orientation for magnetically oriented polypeptide films

Specimen	Birefringence	Spacing used
PBLG	0.023	13.2 Å
1:1 PBLG+PBDG	0.032	13.0 Å
PELG	0.021	11.4 Å

These values are very close to 0.020 obtained for PBLG by measurements of the electric-field orientation (see Ref. 11) and to 0.019 or 0.024 that was given by Ishikawa and his coworkers[20] for poly-γ-methyl-L-glutamate (PMLG) crystals. The birefringence of the racemic system was somewhat larger than the others, suggesting that the crystal structure was different from the others.

The intermolecular spacing for PELG was somewhat smaller than that for PBLG, reflecting the difference in the size of the side chain groups. The intermolecular spacing for the racemic system was slightly smaller than that of the isomer (PBLG). This coincides with the observation[21] that the distortion of the α-helix occurs to facilitate sidechain-sidechain interactions between neighboring D and L helices in the crystal lattice for drawn fibers. Sumulski and Tobolsky[22] have detected a distorted α-helix with 3.5 residues per turn in magnetically oriented PBLG films when cast from $CHCl_3$ and the normal α-helix in the similarly prepared films cast from CH_2Cl_2.

Solution specimens

1. Time Dependence

TABLE 3 shows the dependence of the steady-state birefringence of the liquid crystalline solutions upon incubation time. In most cases, the liquid crystalline structure was fully grown about a few weeks after preparation judging from the magnitude of the steady-state birefringence. The birefringence decreased considerably for PBLG in CH_2Br_2 and PBLG in CH_2Cl_2 when measured after 7-8 weeks, indicating the collapse of the ordered liquid crystal. This coincides with the low-angle light scattering observation by Frenkel and his coworkers [23] on the PBLG-DCA system. The PELG-CH_2Cl_2 system showed slightly higher

TABLE III

Dependence of the steady-state birefringence upon incubation time for liquid crystalline solutions of polypeptides

Solution		1	2–3	5	7–8 weeks
PBLG in CH_2Br_2,	14 vol%	0.018	0.017	0.018	0.010
	24	–	0.014	–	0.005
PBLG in CH_2Cl_2,	14 vol%	–	0.019	–	0.008
PBLG in dioxane,	14 vol%	0.012	0.027	–	0.027
1:1 PBLG+PBDG in CH_2Br_2,	14 vol%	–	0.016	–	0.018
PELG in CH_2Cl_2,	14 vol%	–	0.019	–	0.025
PELG in dioxane,	14 vol%	–	0.006	–	0.004

Measured in a magnetic field of 25 KG. The birefringence is given as $\Delta n/c_v$.

value after about 7-8 weeks. All the measurements were carried out on the mature solutions showing the maximum birefringence.

The birefringence of the liquid crystalline solutions was time dependent, and some representative curves are shown in Figure 4. When in the liquid crystalline state, the dioxane solutions were more viscous than the CH_2Br_2 solutions and more concentrated solutions were more viscous than less concentrated solutions.[24] It may be seen that more viscous solutions took reasonably more time to attain the equilibrium orientation. A time lag may be observed in some cases when the birefringence increased in the presence of the magnetic field. This would indicate the distruction of the initial structure (and of the formation of separate molecular clusters). The birefringence increased apparently in two steps. The first step may or may not be indicative of the yielding of the wall effect. In any case, all the solutions tested attained the steady-state orientation after about 2 hours in a magnetic field of 25 KG.

2. Field-Strength Dependence

Figure 5 shows the steady-state birefringence as a function of the magnetic field strength. When the field strength increased, the steady-state birefringence increased in a different way depending on the system being observed. This is considered to originate from the differences present among the systems concerning the critical field strength to form (or separate) molecular clusters and the wall effect to prevent the magnetic-field orientation. Unlike in the case of the electric-field orientation, no asymptotic value was obtained (see Ref. 11). The

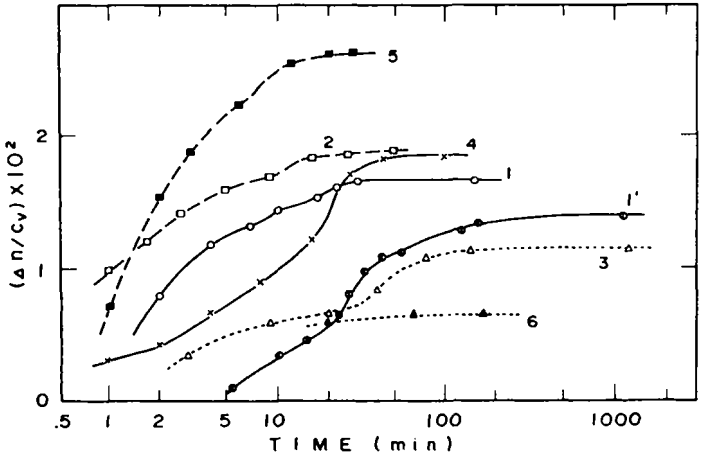

FIGURE 4 Change of the birefringence after the application of a magnetic field of 25 KG. Lines: 1 and 1', PBLG in CH_2Br_2; 2, PBLG in CH_2Cl_2; 3, PBLG in dioxane; 4, an equimolar mixture of PBLG and PBDG in CH_2Br_2; 5, PELG in CH_2Cl_2; 6, PELG in dioxane. The polymer concentration is 14 vol% except for 1' (24 vol%).

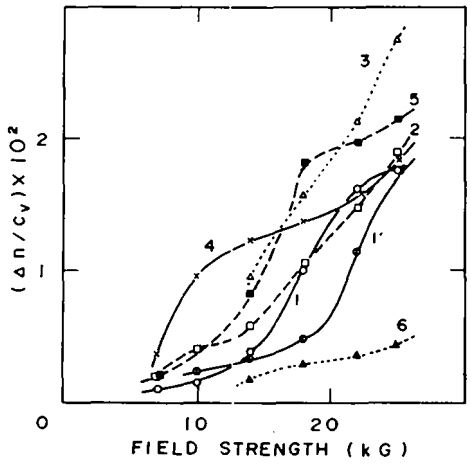

FIGURE 5 Steady-state birefringence *vs.* magnetic field strength relationship. The lines, same as in Figure 4.

reproducibility of the data concerning magnitude of the steady-state birefringence was not always good, indicating a complicated nature of the liquid crystals.

By comparing the results on the solutions with those on the films, it may be seen that the orientation of the solutions was very good when placed in a magnetic field of 22 KG or 25 KG. In this comparison, the difference of the refractive index among the systems being compared should be taken into consideration. Unlike in the case of the films, the solutions are considered to make a three-dimensional Boltzmann distribution and Φ can be expressed as follows (see Ref. 11):

$$\Phi = 1 - \frac{3\coth x}{x} + \frac{3}{x^2} \tag{4}$$

where x is substituted for $\mu B/kT$ this time and μ is considered to be constant. As the orientation was very good, that is, the values of θ for the molecular clusters were small, the assumption that μ was constant would be acceptable. When x is large, say 10 or more as in this case, the third term is negligible and the following relation is obtained,

$$\Delta n/c_v = (2\pi(g_2 - g_3)/n)(1 - 3kT/\mu B) \tag{5}$$

where c_v is the volume fraction of the solute and n is the refractive index of the solution in the absence of a magnetic field. Using this relation, the magnitude of μ was calculated at 25 KG and it was known that the values were very close to those calculated for the films. The contribution of supposed cluster – cluster

interactions (as mentioned in the introduction) may be small at high magnetic fields concerning the magnetic-field orientation.

Figure 6 shows small-angle light scattering patterns of the liquid crystalline solutions. Both the V_h and the H_h patterns were circular in the absence of a magnetic field. In a magnetic field of 7 KG or more, the V_h pattern turned to a $\pm 45^\circ$ cross pattern and the H_h pattern became long lengthwhise. This indicates the formation of rod-like molecular clusters and justifies the idea upon which the birefringence data were analyzed. The maximum polarizability direction is

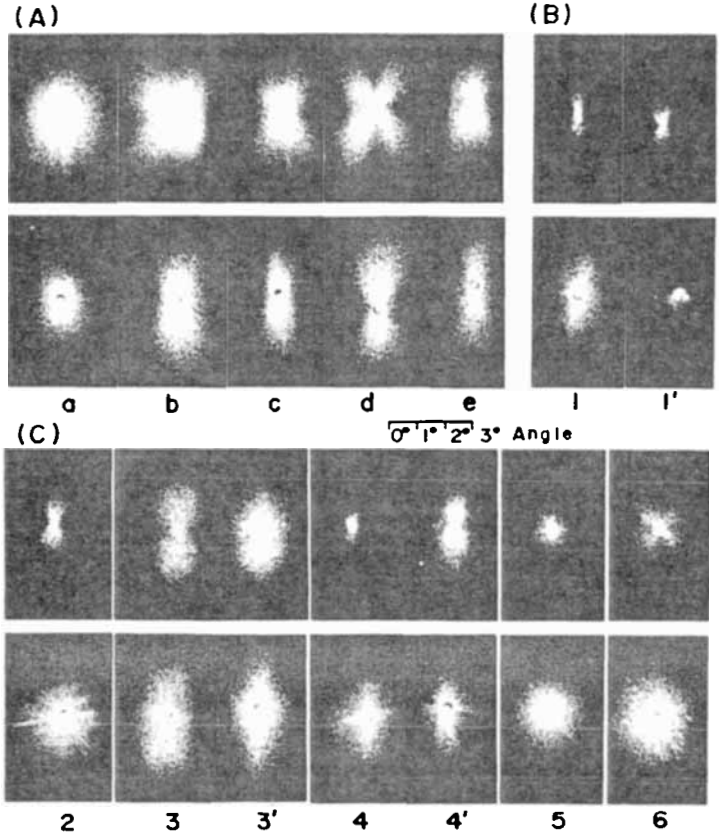

FIGURE 6 Low-angle light scattering patterns of the liquid crystalline solutions of polypeptides in the magnetic field. (A): PBLG in CH_2Br_2, 24 vol%, path length 0.10 mm. a, 0 KG; b, 7 KG; c, 10 KG; d, 18 KG; e, 25 KG. (B): PBLG in CH_2Br_2 placed in a magnetic field of 25 KG. 1, 14 vol% – 0.10 mm; 1', 11 vol% – 1.00 mm. (C): 14 vol%, 25 KG, path length 0.10 mm or 1.00 mm (those with the prime (')). 2, PBLG in CH_2Cl_2; 3 and 3', PBLG in dioxane; 4 and 4', an equimolar mixture of PBLG and PBDG in CH_2Br_2; 5, PELG in CH_2Cl_2; 6, PELG in dioxane. In (A) – (C), the upper photographs are the V_h patterns and the lower photographs are the H_h patterns.

parallel to the cluster axis in this case (see Ref. 25). According to Wilkes,[26] a 0°-90° H_v (equivalent to V_h here) pattern is very common for many polypeptide systems in the absence of a magnetic field, suggesting that the principal optic axis is at 45° to the rod axis. This was certainly true for PBLG in $CHCl_3$, however it was also true that the 0°-90° V_h pattern changed very easily to the ±45° pattern in the presence of an external field whatever it may have been, electric, magnetic or mechanical.

The orientation angle, the upper (and the lower) included angle of the cross of the V_h pattern, decreased with increasing field strength. This indicates the orientation of the molecular clusters in the field direction as in the case of the electric-field orientation (see Ref. 13). The intensity of the H_h scattering was higher only by several times at most than the V_h scattering in the starting solutions, and decreased markedly with increasing field strength. This indicates that the transition from the molecular-cluster structure to a (continous) nematic structure occured (see also Ref. 13). When the solution thickness was 1.00 mm, the starting solutions were cholesteric except for the PBLG-CH_2Br_2 and racemic systems. However, the feature of the scattering patterns in the presence of the magnetic field was same as that observed for the 0.10-mm solutions, except that the contour of the patterns was not clear-cut because of possible multiple scattering of the incident beam in the solution. Miyata and his coworkers[27] have shown that the helicoidal axis of the cholesteric structure of PELG aligns perpendicular to a magnetic field of 23 KG when ethyl acetate is used as the solvent and that[28] the nematic orientation needs a magnetic field higher than 30 KG. The aligment of the helicoidal axis was not observed when CH_2Cl_2 or dioxane was used as the solvent (see Ref. 4), showing the difference of the solvent effect on the cholesteric structure.

On the microscope stage, Wilkes[29] has observed super rods of width about 40 μ running perpendicular to the magnetic field direction (and to the orientation direction of the polymer molecules) in magnetically oriented PBLG films. These super rods are made up of fibrils (or thin sheets) which have diameter (width) of about 1.2 μ, and are at an angle of about 23° (in some regions, almost 0°) to the super rod axis. The author[13] observed a striped pattern of width about 10 μ running parallel to the electric field direction (and to the orientation direction of the polymer molecules) in PBLG solutions. This observation is in contrast to Wilkes' result. However, immediately after the reversion of the field direction a new striped pattern which was perpendicular to the field direction changed places with the initial pattern. The fine structure of the liquid crystalline solutions will be a topic for the further investigation.

3. Concentration Dependence

The steady-state birefringence of the PBLG-CH_2Br_2 system was almost independent on the polymer concentration when measured in a magnetic field of

25 KG as may be seen in Figure 7. As has been mentioned in the introduction section, the infrared dichroic ratio of the DP 1460 PBLG had a maximum with respect to polymer concentration in a magnetic field of 7.4 KG. This maximum would have been caused by the presence of wall effects and have been only apparent. The wall effects are considered to have been overcome in the present case.

4. Temperature Dependence

Figure 8 shows the birefringence as a function of temperature. The steady-state birefringence decreased linearly when the temperature increased. This linearity may be explained by the relation (5). However, the slope of the lines is steeper by several times than that expected for the obtained values of μ. This would suggest that micro-Brownian motion of the polymer chains were present in the molecular clusters and became intense with increasing temperature to lower the apparent dipole moment of the molecular cluster. The dependence of the magnitude of the dipole moment on the cluster orientation may be involved in this.

SUMMARY

In conclusion it is safe to say that in liquid crystalline solutions of polypeptides placed in a magnetic field rod-like molecular clusters are formed and orient in the field direction. For this the presence of diamagnetic groups in the side chains of the polymers such as benzene rings are not necessary. The maximum induced dipole moment of the molecular cluster was estimated to be about 2.4×10^{-17} erg/gauss, and there was no difference among the systems being ob-

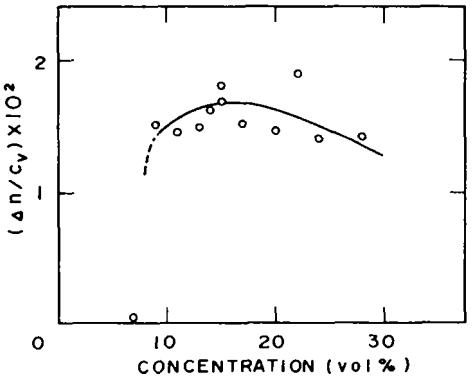

FIGURE 7 The steady-state birefringence as a function of the polymer concentration for PBLG in CH_2Br_2. Measured in a magnetic field of 25 KG.

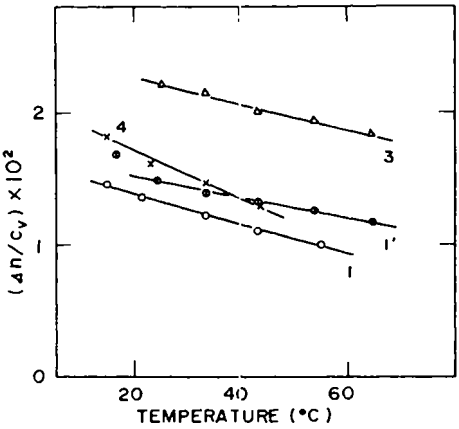

FIGURE 8 The steady-state birefringence as a function of temperature. Measured in a magnetic field of 20 KG. The lines, same as in Figure 4.

served. When measured on the films, the molecular clusters corresponded to a two-dimensional Boltzmann distribution in the plane of the film. The birefringence of the film at complete orientation was estimated to be 0.023 for PBLG films, and some difference were seen among the systems being observed. The structure of the molecular clusters and the fine structure of the magnetically oriented films and solutions in connection with the side-chain structure will be topics for the further investigation.

Acknowledgements

The author wishes to thank Professor T. Hayakawa of this Faculty for the preparation of the PBLG specimen, Professor A. Wada of the University of Tokyo for the donation of the PBDG specimen and Dr. S. Mori of Ajinomoto Co., Ltd. for the donation of the PELG specimen. His thanks are also due to Mrs. Y. Ohnishi for the analysis with the electric computor and Miss T. Kawai for assisting him in a part of the measurements. This work was supported by the Grant-in-Aid for Individual Research of the 1972-1973 fiscal year from the Ministry of Education (746108).

References

1. Meyer, R. B., *Appl. Phys. Letters* 12, 281 (1968).
2. de Gennes, P. G., *Solid State Commun.* 6, 163 (1968).
3. Frank, F. C., *Disc. Faraday Soc.* 25, 19 (1958).
4. Iizuka, E., *Polymer J.* 4, 401 (1973).
5. Tohyama, K. and Miyata, N. *J. Phys. Soc. Japan* 34, 1699 (1973).
6. Tohyama, K. and Miyata, N., Bussei (in Japanese) 14, 437 (1973).
7. Sobajima, S. *J. Phys. Soc. Japan* 23 1070 (1967).
8. For examples: Samulski, E. T. and Tobolsky, A. V., *Macromolecules* 1, 555 (1968);

Panar, M. and Phillips, W. D., *J. Am. Chem. Soc.* 90, 3880 (1968); Orwoll, R. D. and Vold., R. L., *ibid.* 93, 5335 (1971).
9. Iizuka, E. and Go, Y., *J. Phys. Soc. Japan* 31, 1205 (1971).
10. Iizuka, E., *Biochim. Biophys. Acta* 175, 457 (1969).
11. Iizuka, E., *ibid.* 243, 1 (1971).
12. Iizuka, E., *Polymer J.* 5, 62 (1973).
13. Iizuka, E., Keira, T. and Wada, A., *Mol. Cryst. and Liq. Cryst.* 23, 13 (1973).
14. Robinson, C., *Trans. Faraday Soc.* 52, 571 (1956).
15. Peterlin, A. and Stuart, A., *Z. Physik* 112, 129 (1939).
16. Go, Y. and Kubo, T., *J. Soc. chem. Ind. Japan* (in Japanese) 39, 929 (1936).
17. Bamford, C. H., Elliott, A. and Hanby, W. E., *Synthetic Polypeptides*, Academic Press, N.Y. (1956), Chapt. 8.
18. Go, Y., Ejiri, S. and Fukada, E., *Biochim. Biophys. Acta* 175, 454 (1969).
19. Honda, M., Suzuki, H. and Kato, T., *Repts. Progr. Polym. Phys. Japan* 14, 607 (1971).
20. Ishikawa, S., Kurita, T. and Suzuki, E., *J. Polymer Sci.* A. 2, 2349 (1964).
21. For example: Mitsui, Y., Iitaka, Y. and Tsuboi, M., *J. Mol. Biol.* 24, 15 (1967).
22. Samulski, E. T. and Tobolsky, A. V., *Biopolymers* 10, 1013 (1971).
23. Frenkel', S. Ya., Shaltyko, L. G. and Elyashevich, G. K., *J. Polymer Sci.* C. 30, 47 (1970).
24. Iizuka, E., *Mol. Cryst. and Liq. Cryst.* (in press).
25. Rhodes, M. B. and Stein, R. S., *J. Polymer Sci.* A-2. 7, 1539 (1969).
26. Wilkes, G. L., *Mol. Cryst. and Liq. Cryst.* 18, 165 (1972).
27. Miyata, N., Tohyama, K. and Go, Y., *J. Phys. Soc. Japan* 33, 1180 (1972).
28. Tohyama, K. and others, to be published in *Mol. Cryst. and Liq. Cryst.*
29. Wilkes, G. L., private communication.