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Magnetic Alignment and Diamagnetic Anisotropy of Cholesteric Liquid Crystalline Poly-γ-Ethyl-L-Glutamate

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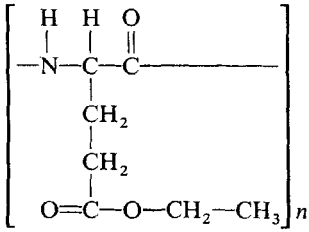
The axes of the cholesteric structure of liquid crystalline PELG solution in ethyl acetate tend to be perpendicular to a direction of magnetic field, so that the solution becomes anisotropic in the presence of an applied field. The torque exerted on such anisotropic solutions was measured by appling a magnetic field in a different direction from the original field used for alignment of the cholesteric axes. The anisotropy of diamagnetic susceptibility of the cholesteric structure and that of PELG molecule are estimated from the strength of the torque. The latter is larger than 1.64×10^{-8} emu/g. The average magnetic susceptibilities of PBLG, PEDG and PMLG in the solid state were also measured. These values are in good agreement with those calculated using Pascal's additivity rule.

1 INTRODUCTION

The magnetic properties of synthetic polypeptides have been mainly studied on poly-γ-benzyl-L-glutamate(PBLG). For instance, it is well known[1–5] that the helical axis of the PBLG molecule is oriented parallel to the magnetic field in certain solvents such as methylene chloride, methylene bromide, dioxane and chloroform. This phenomenon demonstrates the existence of the magnetic anisotropy of the PBLG molecule. The anisotropy may be due partly to anisotropic diamagnetic susceptibility of benzyl-radicals.

Poly-γ-ethyl-L-glutamate(PELG) is also one of the available synthetic polypeptides, having the formula



From the diffraction pattern of a He—Ne laser beam by a solution of PELG in ethyl acetate, it was shown by the present authors[6] that the solution forms a cholesteric liquid crystal and the axis of the cholesteric structure tends to be perpendicular to the direction of magnetic field. This phenomenon exhibits by magnetic methods the anisotropic character of the PELG cholesteric liquid crystal. It is interesting because both solute and solvent molecules have no magnetically anisotropic radical such as the phenyl-group in PBLG or phenylene-radical found in many liquid crystalline aromatic compounds.

In the present work, the anisotropy of diamagnetic susceptibility of the PELG liquid crystal and that of the PELG molecule are reported. They are obtained from the torque measurement on the magnetic anisotropy induced in the liquid crystal. Average magnetic susceptibilities of poly-γ-methel-L-glutamate(PMLG), poly-γ-ethyl-D-glutamate(PEDG) and PBLG in a solid state are also reported.

2 EXPERIMENTAL

Specimens

The degree of polymerization of PELG used for the torque measurement is about 1800. Two solutions (20 and 31 wt.%) of PELG in ethyl acetate were prepared to form cholesteric mesophases. Both solutions have the same amount of PELG, 0.416 g. Solutions were put into glass tubes, 1 cm in diameter and 7 cm in length, and set in a torque magnetometer.

PBLG, PEDG and PMLG in the fibrous solid state were used for the measurement of average magnetic susceptibilities. The degrees of the polymerization of these samples were 2400, 1800 and 2800, respectively. Each specimen was inserted into a glass tube, 0.7 cm in diameter and 2 cm in length, and set in the magnetometer.

All polypeptide samples used in this experiment were supplied from Ajinomoto Co.

Apparatus and method

A high sensitivity torque magnetometer (2.42×10^{-2} dyne-cm/degree) was made utilizing a galvanometer. The strength of the torque was obtained from the measurement of the current passing through the coil of the galvanometer necessary to compensate the existing torque, so that the specimen does not rotate against magnetic field during the measurement.

To obtain the equilibrium distribution of axes of the cholesteric structure, samples were kept in the magnetic field (H_a) for two or three days. The field H_a was cut off and the electromagnet rotated 45 degrees. The magnetic field for measurement (H_m) was then applied along the new direction. A

torque, which originated from the anisotropic magnetostatic energy induced by H_a, was observed.

H_a and H_m were set between 11.6 and 16.2 kOe. It has been noticed that application of magnetic field lower than 20 kOe affects only the distribution of axes of cholesteric structure but has no effect on the pitch of the structure.[6] In the torque experiment, temperature of the specimen was kept at 30°C throughout measurements.

The magnetometer for measurement of the diamagnetic susceptibility was of the torsion balance type. The sensitivity of the magnetometer was calibrated with pure NaCl and LiF, specific susceptibilities of which are -0.5167×10^{-6} and -0.3909×10^{-6} emu/g, respectively.[7] Measurements were performed at 20°C.

3 RESULTS

Torque measurements

The time dependence of the torque L for 20 wt.% solution is shown in Figure 1.[8] Each curve in the figure corresponds to the time dependence of the torque under the field (H_m) of various strength. In each case, H_a is 15.8

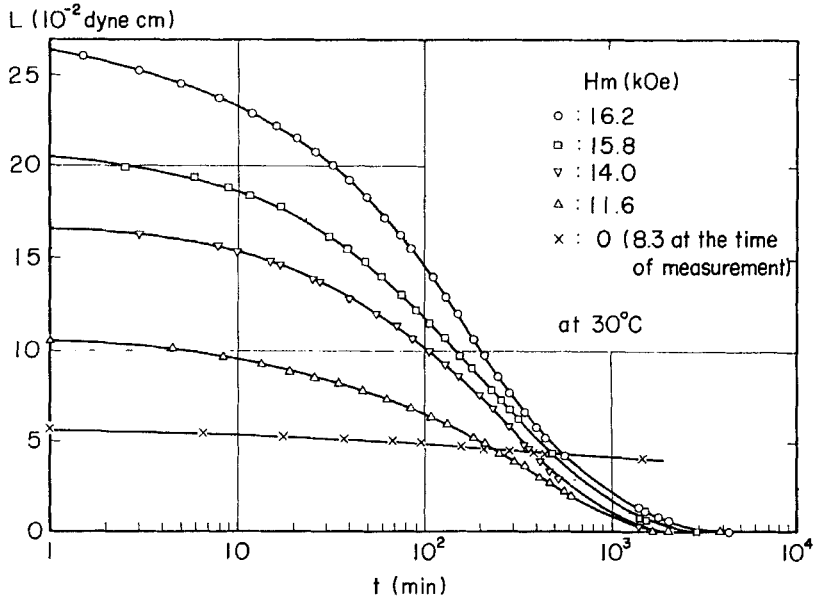


FIGURE 1 Time dependence of the torque exerted on the 20 wt.% solution of PELG in ethyl acetate under various magnetic field strengths, H_m. The sample was kept beforehand in the field (H_a) of 15.8 kOe to attain the equilibrium state. The angle between H_a and H_m is 45 degrees.

kOe. The torque decreases with time due to the formation of a new uniaxial anisotropy along H_m. L_0 is plotted against a square of H_m in Figure 2, where L_0 is the initial value of the torque. L_0 depends linearly on H_m^2.

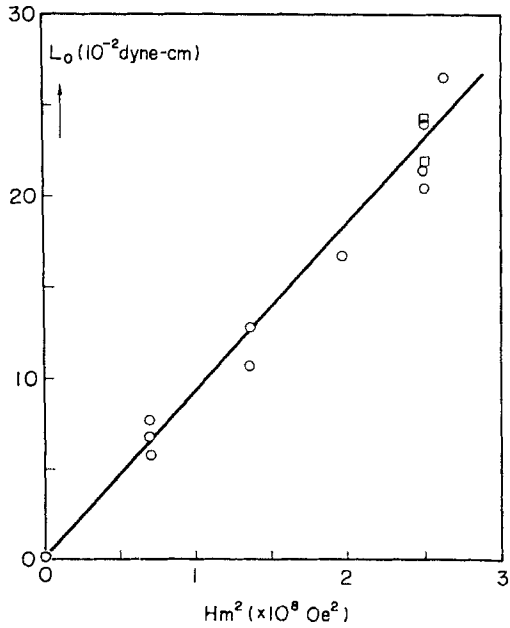


FIGURE 2 Values (L_0) of torque at $t = 0$ plotted against the square of magnetic field (H) for measurement. ○ and □ represent L_0 for 20 and 31 wt.% solution, respectively. Each solution contains 0.416 g of PELG.

It was also noticed that, in spite of the different strength of H_a (11.6 ~ 16.2 kOe), the values of L_0 for the same strength of H_m were nearly equal. This result means that the distribution of the axes of the cholesteric structure in the equilibrium state is effectively saturated as far as the induced magnetic anisotropy is concerned.

Both H_a and H_m were set at 15.8 kOe for the 31 wt.% solution. The values of L_0 are also plotted in Figure 2. They agree with those of 20 wt.% solution for the same strength of the field H_m. Since both the 20 and 31 wt.% solutions contain the same amount of PELG, this means that only the PELG molecules are responsible for the induced anisotropy and the solvent is not involved.

In Figure 3, reduced torque (L/L_0) vs. time (t) curves for 20 and 31 wt.% solutions under the same condition are shown. It is noted that the torque for 31 wt.% solution decreases more rapidly than that of 20 wt.% solution.

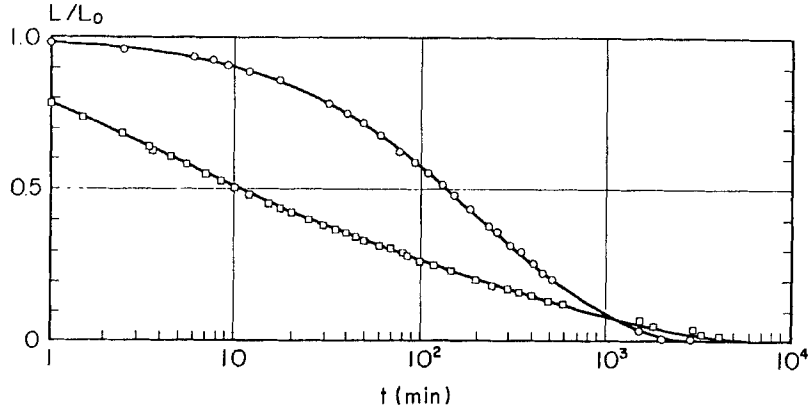


FIGURE 3 L/L_0 vs. t for 20(○) and 31(□) wt.% solutions at 30°C. Both H_a and H_m are 15.8 kOe.

Average magnetic susceptibilities

The average magnetic susceptibility $\bar{\chi}$ of the polypeptides, PMLG, PEDG(antipode of PELG) and PBLG in a solid state was measured.

As shown in Table I, experimental results are in good agreement with the calculated values using the Pascal's additivity rule.[9] Atomic susceptibility (χ_{AT}) and susceptibility due to phenyl group (χ_{phenyl}) used for the calculations are given in Table II.

TABLE I

Diamagnetic susceptibility $\bar{\chi}$ of some polypeptides in the solid state at 20°C $\{10^{-6} \times (-\bar{\chi})$ emu/g$\}$

Substance	Experimental value	Calculated value using Pascal's additivity rule[a]
PMLG	0.500 ± 0.010	0.510
PEDG	0.530 ± 0.010	0.540
PBLG	0.556 ± 0.010	0.563

[a] $\bar{\chi}_{molecule} = (\sum\chi_{AT})_{except\,phenyl} + \bar{\chi}_{phenyl}$. The last term is included only for PBLG. (refer to Table II)

Although an accurate value of $\bar{\chi}$ for the PELG solution in ethyl acetate could not be obtained owing to a limitation of the apparatus for volatile solutions, $\bar{\chi}$ for the 20 wt.% solution was roughly -0.5×10^{-6} emu/g which is near to the calculated value -0.58×10^{-6} emu/g by Pascal's rule.

TABLE II

Atomic susceptibilities, χ_{AT}, and the average susceptibility of the phenyl group, $\bar{\chi}_{phenyl}$, used for the calculated values in Table I (10^{-6} emu/mole)[9-10]

atom	χ_{AT}
H	−2.93
C	−6.0
N	−5.55
O(ketone)	+1.73
O(carboxyl group)	−3.36
phenyl group	$\bar{\chi}_{phenyl}$
$-C_6H_5$	−53

4 DISCUSSION

Usually, the local director is defined as the average direction of molecules in a local region of liquid crystal. Specific magnetic susceptibilities along the direction parallel and perpendicular to the local director of PELG liquid crystal are expressed by notation $\chi_{\parallel}$ and $\chi_{\perp}$, respectively. Susceptibilities parallel and perpendicular to the axis of cholesteric structure are $\chi_{\perp}$ and $(\chi_{\parallel} + \chi_{\perp})/2$, respectively, because the local director is perpendicular to the cholesteric axis. The contribution of PELG to susceptibilities of the anisotropic solution parallel and perpendicular to H_a are $(\chi_{\parallel} + \chi_{\perp})/2$ and $(\chi_{\parallel} + 3\chi_{\perp})/4$, respectively, if the axes of the cholesteric structure in the equilibrium state are distributed at random in the direction perpendicular to H_a. Consequently, the anisotropy of magnetic susceptibility of the anisotropic solution is $A = (\chi_{\parallel} - \chi_{\perp})/4$.

Anisotropy energy density E of the solution is expressed by

$$E = \tfrac{1}{2} \cdot A \cdot H_m^2 \cdot \sin^2 \theta,$$

where θ is an angle between H_a and H_m. The observed torque is given by

$$L = -\left(\frac{\partial E}{\partial \theta}\right) \cdot m,$$

where m is the mass of PELG in the solution. In the present experiment θ is fixed on $\pi/4$, so that the torque at $t = 0$ is given by

$$L_0 = \tfrac{1}{2} \cdot m \cdot A \cdot H_m^2.$$

From the relation of L_0 vs. H_m^2 shown in Fig. 2, it is found that $\chi_{\parallel} - \chi_{\perp} = 4 \cdot A = (1.64 \pm 0.15) \times 10^{-8}$ emu/g. The order parameter, the degree of order of macromolecular alignment, is smaller than unity at room temperature. Moreover, if we take account of the possibility of deviation of the cholesteric axes from the direction perpendicular to H_a, this value is considered to give a lower limit for the anisotropy of diamagnetic susceptibility of PELG molecule.

The existence of the anisotropy in PELG molecule is interesting because it has no magnetically anisotropic radical such as a phenyl group. The origin of the anisotropy may be at least partially in the π-electrons of CONH-groups in the main chain of this molecule. Experimental values of the average magnetic susceptibility are in line with the diamagnetism of ordinary organic compounds.

The magnetostatic anisotropy energy of each molecule in the magnetic field is much smaller than the thermal energy, so that no molecular alignment is expected in dilute solutions under a magnetic field. In the liquid crystalline state, however, molecules are combined and ordered strongly with each other to form domains or clusters. When a magnetic field is applied, each domain is affected and rotates to minimize the total free energy of the cholesteric liquid crystalline solution. The magnetic alignment of PELG liquid crystal is decided by competition of the magnetostatic anisotropy energy of a domain and the thermal energy. The experimental results show that magnetic field of about 12 kOe is large enough to overcome the thermal agitation at 30°C. The number of molecules, n, in a domain may be estimated by using the relation

$$\tfrac{1}{2} \cdot \Delta\chi \cdot H^2 \cdot \left(n \frac{M}{N_0} \right) \cdot S > kT,$$

where $\Delta\chi$ is the anisotropy of specific susceptibility of PELG molecules, H magnetic field (1.2×10^4 Oe), M molecular weight of PELG (157×1800), N_0 Avogadro's number, S the order parameter, k Boltzman constant and T absolute temperature (303°K). Since $\Delta\chi \cdot S = \chi_{\parallel} - \chi_{\perp} = 1.6 \times 10^{-8}$ emu/g, we get $n > 8 \times 10^4$.

As already mentioned in the previous paragraph, the PELG 31 wt.% solution has the faster mean relaxation time for redistribution of domains than 20 wt.% solution. This phenomenon may be related to the combination of viscosity and domain size of these solutions. Refering to the dependence on concentration of the viscosity of PBLG liquid crystal,[11] we may expect that of PELG liquid crystal is also slight in the concentration regions in the present work. So, the faster relaxation time in the more viscous solution of PELG could be due to the formation of domains of larger size in the more concentrated sample.

Since the microscopic mechanism of redistribution of the axes of the cholesteric structure is not known, further discussions about the time dependence of the torque is not given here. But, L vs. $\log t$ curves in Figures 1 and 3 seem to show that the process of reorientation of the cholesteric axes is accompanied by a wide distribution of relaxation times, and the distribution for the 31 wt.% solution is wider than that for the 20 wt.% solution.

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