

Electromagnetic Orientation of Liquid Crystals of Poly(γ -ethyl-glutamate)s

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ABSTRACT: The orientation of liquid-crystalline solutions of poly(γ -ethyl-L-glutamate) and its blend with an equal proportion of its D-isomer in static electric and static magnetic fields has been studied by infrared dichroic ratio, NMR, scattering of laser light, X-ray diffraction, and other methods. The polymers undergo an electric-field orientation which is less striking than in the case of poly(γ -benzyl-L-glutamate) when dibromomethane or dichloromethane is used as the solvent. This suggests some important role for the side-chain groups of the polypeptide molecule in stabilizing the liquid-crystalline structure. The polymers orient in magnetic fields, proving that those polypeptides with no benzene groups in their side chains are also magnetically susceptible.

KEY WORDS Poly(γ -ethyl-glutamate)s / Liquid Crystals / Electromagnetic Orientation / IR Dichroic Ratio / Scattering / Laser Light / Magnetic Susceptibility /

The electromagnetic orientation of liquid crystals of polypeptides is a topic of increasing interest. For the electric-field orientation of poly(γ -benzyl-L-glutamate) (PBLG), the author has proposed the formation of independent molecular clusters with huge dipole moments in solution under very low electric fields by measurements of the infrared dichroic ratio^{1,2} and has obtained data sufficient to indicate their presence by measurements of the scattering of laser light.³ Quite recently, the author made NMR measurements⁴ and detected free solvent molecules in liquid-crystalline solutions of PBLG in electric fields, which supports the above model.

Sobajima⁵ and Go and his coworkers⁶ were the first to observe the magnetic-field orientation of liquid crystals of PBLG. In explaining this, Yomosa⁷ has considered the impurity oxygen atoms to show very large paramagnetic effects. Suzuki and his coworkers⁸ have calculated the interaction energies between a constant magnetic field and the valence-shell electrons of the peptide groups in the main chain, evaluating the diamagnetic and paramagnetic terms to be of the order of 10^{-8} eV at 10 kG for each peptide group. So far, only PBLG among the polypeptide specimen has had its orientation re-

ported except for a few preliminary works (see ref 9—11). In a previous paper,⁹ the author observed the magnetic-field effect on diffraction of light by the cholesteric structures of poly(γ -ethyl-L-glutamate) (PELG) as well as of (PBLG); the results were analyzed on the basis of Frank's curvature-elasticity theory¹² as developed by Meyer.¹³ It was found that PELG is also magnetically susceptible, though to a lesser extent, probably owing to the lack of benzene groups in its side chains. The critical field strength at which the pitch of the helicoidal structure becomes infinite was calculated to be 7 kG or more depending on the system being observed, suggesting that PELG may possibly undergo the cholesteric—nematic transition in sufficiently high magnetic fields as well.

The purpose of this paper is to present results for the electromagnetic orientation of PELG and of equal proportions of PELG and PEDG [poly(γ -ethyl-D-glutamate)].

EXPERIMENTAL

PELG and PEDG used were supplied by Dr. S. Mori of Ajinomoto Co., Ltd., as ethyl acetate solutions with intrinsic viscosities 1.40 and 1.42, respectively, at 30°C in dichloroacetic acid, and

were used after being dried in air. PELG or equal proportions of PELG and PEDG were dissolved in a solvent (such as CH_2Br_2 , CH_2Cl_2 , or dioxane) that allows the formation of liquid crystals (and of α -helices) and kept at least 2 weeks in a sample tube at room temperature. In order to obtain the infrared dichroic ratio, the scattering patterns, and the polarizing micrographs, each stock sample-solution was put in a quartz cell of path length 1 mm with a quartz spacer of thickness 0.90 mm to adjust the path length to 0.10 mm. For the measurement in electric fields, a couple of platinum needle electrodes were introduced in the cell beside both edges of the spacer and static electric fields were applied to the solution with dry cells. The dichroic ratio was measured at 3300 cm^{-1} , which is the center of the NH stretching vibration mode of polypeptides, and the light scattering was measured using 6328-\AA light from a 1-mW He-Ne gas laser. The polarizing micrographs were taken under crossed polaroids to increase contour. Details of these measurements have been described elsewhere.^{2,3} Film specimens for the X-ray diffraction patterns were prepared in a 10-mm quartz cell by drying up the solvent very slowly after the equilibrium orientation was reached in external fields. A magnetic field of 10 kG was supplied by a permanent magnet made by Mitsubishi Steelworks Co., Ltd.

For measurements of NMR, the polymer was dissolved in the solvent in a standard NMR sample tube of inside diameter 4 mm. Splitting of the proton signal of the solvent molecules were observed in the magnetic field of a high-resolution NMR spectrometer, model JNM-C-60HL (60 MHz), distributed by Japan Electron Optics Laboratory Co., Ltd. In order to measure the NMR in electric fields, parallel-plate electrodes made of Nesa-coated glass were introduced in the NMR sample tube, which was inserted in the sample room only when the NMR measurements were being carried out to minimize effects of the magnetic field on the sample solution (see ref 4). Electric currents through the liquid-crystalline solutions were also measured with this device.

The temperature of the specimen was about

27°C for the measurements of the infrared dichroic ratio and NMR, and about 22°C for the other measurements. The solvents were of reagent grade and were used without further purification. All the solutions used were of the birefringent phase only unless stated otherwise, and values of the polymer concentration were very approximate.

RESULTS AND DISCUSSION

As shown in Figure 1, PELG and the blend of equal proportions of PELG and PEDG orient both in an electric field of 140 V/cm and a magnetic field of 10 kG when measured with films prepared from the CH_2Cl_2 solutions of these polymers. When dioxane was used, the orientation could not be detected. In any case, it is clearly shown that poly(γ -ethyl-glutamate)s (PEGs) can undergo a nematic orientation in magnetic fields as well as in electric fields, showing that the author's prediction comes out to be true. The structure of the oriented films is certainly different from that of the oriented solutions, and is considered to be more complicated. Detailed measurements were carried out on the solutions only.

Electric-Field Orientation

The dichroic ratio, D_{\parallel}/D_{\perp} , of the liquid-crystalline solutions was time dependent and the equilibrium dichroic ratio increased with increasing field strength, as may be seen in Figure 2. To reach the equilibrium orientation, much more time is required for the polymers in liquid-crystalline solutions than in ordinary solutions, owing to cluster-cluster interactions. There seems to be a most suitable polymer concentration for electric-field orientation. In dioxane, PELG begins to orient in an electric field of about 140 V/cm for a 17-vol% solution, even though the orientation could not be detected in the film dried in an electric field of 450 V/cm. This may or may not be due to a decreasing electric current accompanying the drying of the solution (see the later part of the text).

Figure 3 represents the V_h scattering patterns and the polarizing micrographs in electric fields whose directions are horizontal. In the absence of the electric field, the patterns are circular,

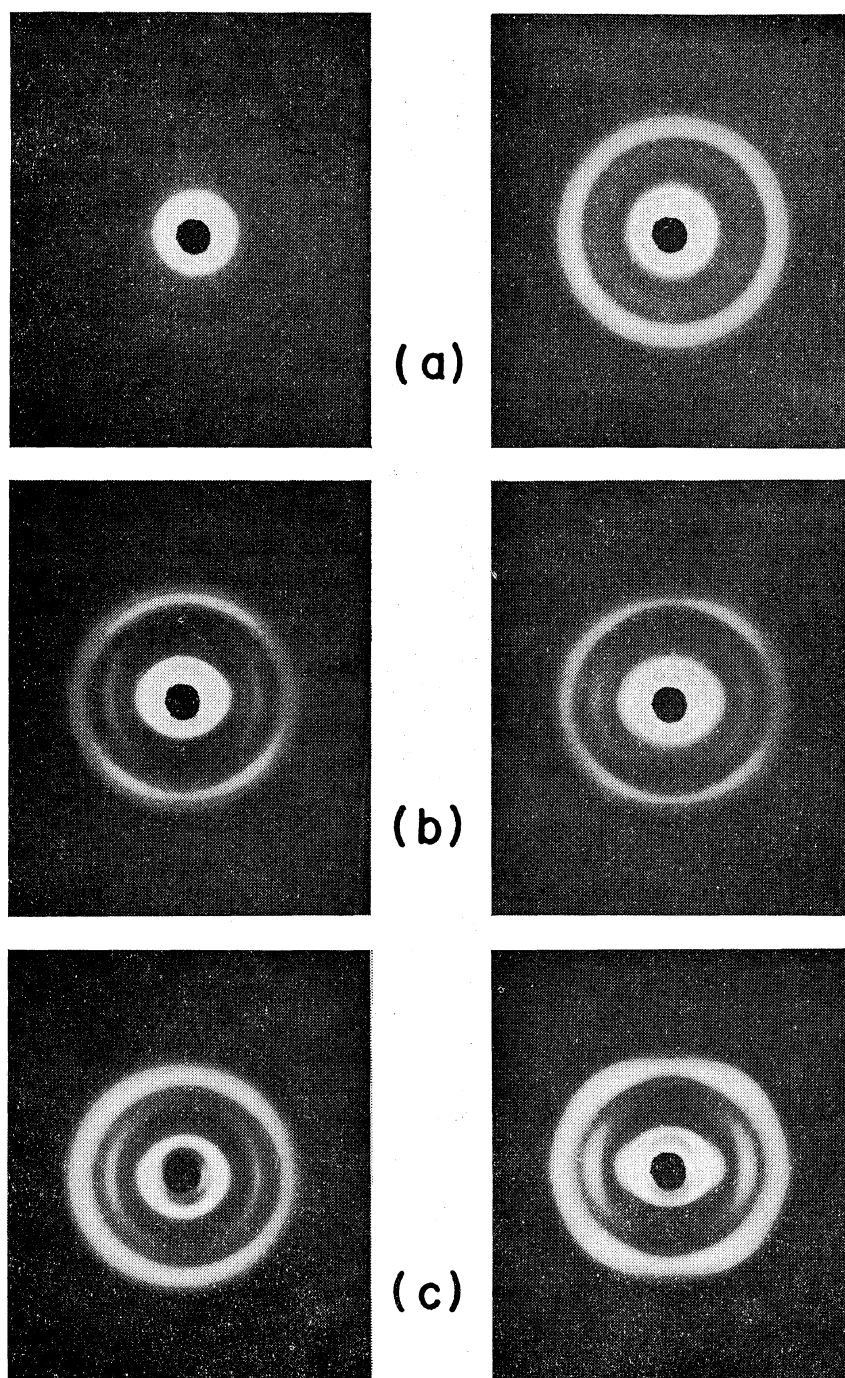


Figure 1. X-ray diffraction photographs of the films of PELGs dried in external fields. External field vertical in the plane of the films. Left, PELG in CH_2Cl_2 ; right, equal proportions of PELG and PEDG in CH_2Cl_2 : (a), no field; (b), 140 V/cm; (c), 10 kG.

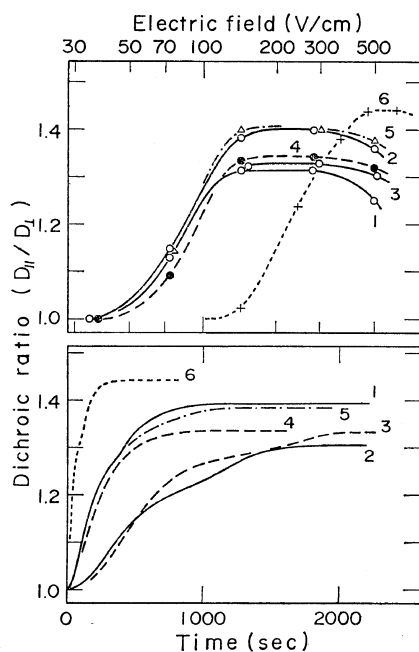


Figure 2. The dichroic ratio vs. time and the equilibrium dichroic ratio vs. strength of the electric field relationships. Upper: 1, 14 vol%; 2, 17 vol%; 3, 20 vol% (PELG in CH_2Cl_2); 4, 14 vol% (PELG in CH_2Br_2); 5, 17 vol% (equal proportions of PELG and PEDG in CH_2Cl_2); 6, 17 vol% (PELG in dioxane). Lower: 1, 17 vol%—140 V/cm; 2, 20 vol%—140 V/cm (PELG in CH_2Cl_2); 3, 14 vol%—140 V/cm; 4, 14 vol%—280 V/cm (PELG in CH_2Br_2); 5, 17 vol%—140 V/cm (equal proportions of PELG and PEDG in CH_2Cl_2); 6, 17 vol%—450 V/cm (PELG in dioxane).

except for PELG in dioxane, suggesting the presence of disordered and optically anisotropic particles with sizes comparable to the wavelength of the incident light. No cholesteric structure was observed in the starting solutions (see ref 3). The polarizing micrographs suggest the presence of domain structures whose features are dependent on the system being observed. When an electric field is applied, the scattering patterns turn into $\pm 45^\circ$ patterns, suggesting the formation of rod-like particles (molecular clusters) whose maximum polarizability direction is parallel or perpendicular to the rod axis (that is, the angle ω is 0° or 90° respectively; see ref 14). The $\pm 45^\circ$ pattern is also observable even without field in PELG dissolved in

dioxane, indicating that the molecular clusters are very easily formed even by the shearing stresses which accompanied the introduction of the quartz spacer into the cell. When the spacer was taken in and out part of the way to exert shearing stresses upon the solution, the polymer molecules (and the molecular clusters) lined up in the direction of the shearing stresses, as determined by the dichroic ratio measurement. The dichroic ratio ranged from 1.4 to 2.2, depending on the system being observed. This would lead to the conclusion that the polymer molecules are parallel to the rod axis (and $\omega = 0^\circ$) as in the case of PBLG and that the molecular clusters line up with their long axes parallel to the field direction when placed in an electric field (see ref 3). The dichroic ratio began to decrease and finally became unity after the taking in and out was repeated 100 times or so. Therefore, too much shearing is seen to destroy the molecular clusters.

Many lines parallel to the electric field appear and the interval of the lines decreases from about 50μ to 5μ or less with increasing field strength. This would be in accordance with the conclusion that the molecular clusters line up in the direction of the electric field. The scattering angles are larger in PEGs than in PBLG, suggesting that the length of the molecular clusters is smaller in PEGs. It has been suggested to be about 25μ in PBLG (see ref 3). The orientation angle which is made by the crossing leaves of the V_h pattern decreases with increasing field strength, showing that the degree of the molecular cluster orientation increases as in the case of PBLG (also see ref 3). However, the scattering starts to fluctuate and becomes finally a wide two-leaf pattern in still higher electric fields. This is considered to be due to the disturbance of the molecular clusters caused by electric currents through the solution, leading to a decrease in the molecular cluster orientation, as may be seen in Figure 2. The fluctuation is the strongest in CH_2Cl_2 and the weakest in dioxane and its order is in proportion to the order of the current strength, as may be seen in Table I. The current decreased noticeably in the beginning and became constant after about 2000 sec in any case tested. The

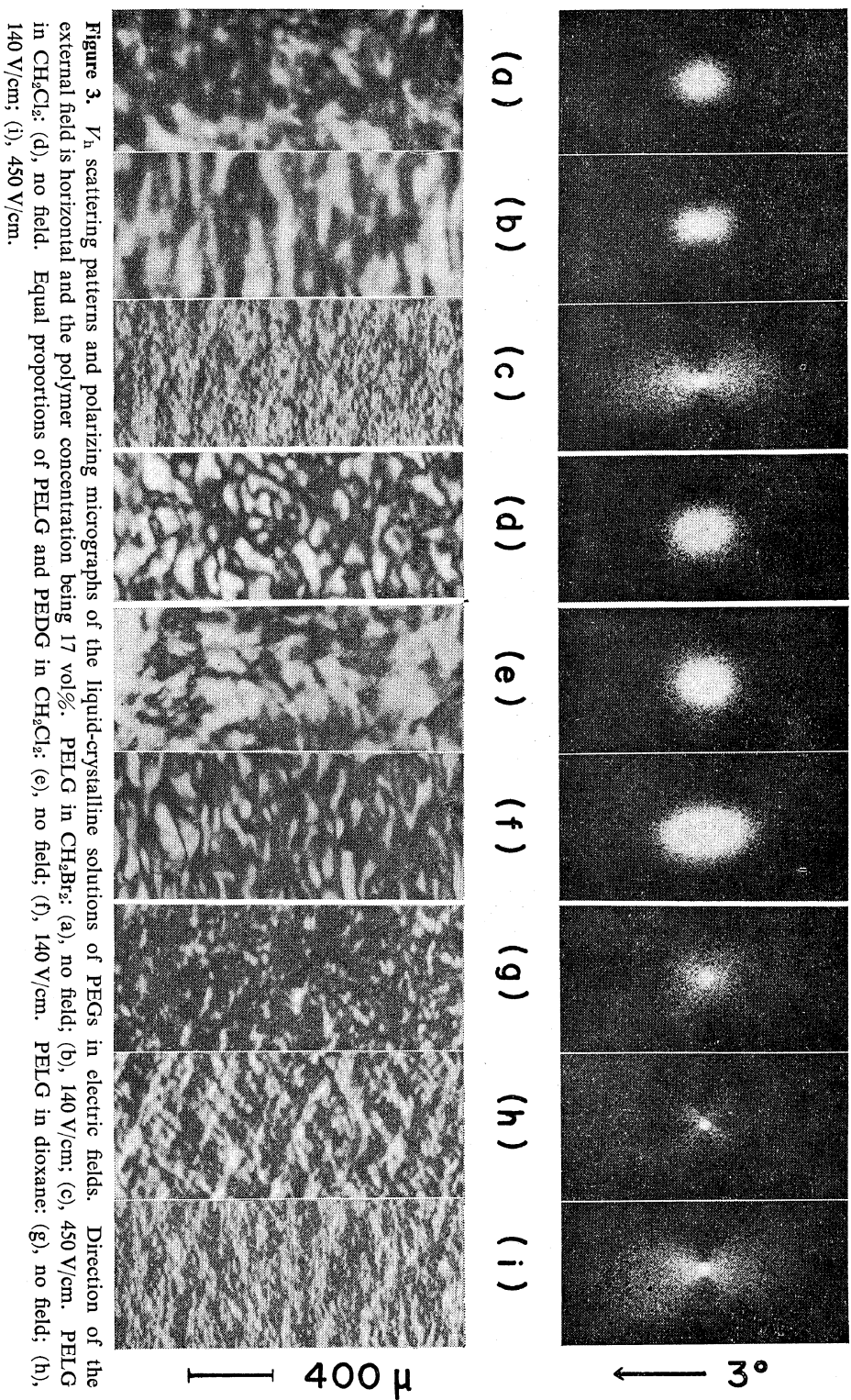


Table I. Electric conductivity of the liquid-crystalline solutions of PELG at equilibrium^a

Solvent	CH ₂ Cl ₂		CH ₂ Br ₂		CH ₂ Cl ₂ ^b	dioxane	CH ₂ Br ₂ ^c	
C, vol%	14	20	7	14	20	17	20	14
I, μ A/cm ²	130	103	69	27	35	145	2.7	5.4
ρ , M Ω cm	2.1	2.7	4.0	10.3	8.0	1.9	105	103

^a Measured in an electric field of 280 V/cm. Only the 7-vol-% solution is isotropic.

^b Equal proportions of PELG and PEDG.

^c PBLG of degree of polymerization 650.

origin of this equilibrium current seems to be, according to Heilmeyer's idea¹⁵ of low-molecular-weight liquid crystals, that the molecular clusters or/and the polymer molecules not involved in the clusters, if any, acquire an affinity for electrons owing to the presence of impurity H₂O molecules, become anions at the cathode, and carry the electric current to the anode where they become neutral again. The current is in proportion to the field strength. When CH₂Br₂ is used as the solvent, the current is more in PEGs than in PBLG. This would suggest that the liquid-crystalline structure is more stable in PBLG, assuming the above-mentioned origin of the electric current. The fact that the degree of polymer orientation is somewhat higher in PBLG (which shows a dichroic ratio as high as 4.1 in an electric field of 220 V/cm; see ref 2) indicates that the molecular clusters are larger in PBLG. This suggests that in PBLG the benzene groups stabilize the cluster structure by stacking in between the neighboring polymer chains, which would not occur in PEGs. The H_h patterns were circular or slightly lengthwise as in the case of PBLG and are not given here (see ref 3).

When direction of the electric field is reversed after an equilibrium orientation is reached, the dichroic ratio first decreases rapidly and then gradually recovers its starting ratio, as may be seen in Figure 4. This indicates that the molecular clusters, having huge permanent dipole moments, make a rightabout turn in the electric field. At first, the dichroic ratio does not decrease down to unity in an electric field of 140 V/cm. It, however, does when measured in an electric field of 280 V/cm, and from that time on it decreases to, or close to unity even in the electric field of 140 V/cm. This would indicate a growth of the molecular clusters. In the

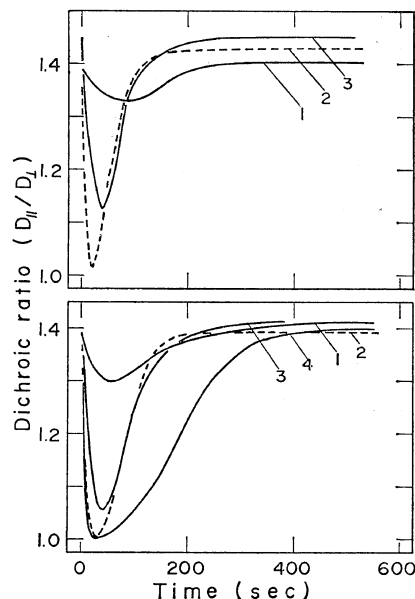


Figure 4. The change of the dichroic ratio after the direction of the electric field is reversed. Concentration, 17 vol%. Upper: PELG in CH₂Cl₂; lower: equal proportions of PELG and PEDG in CH₂Cl₂. 1, 140 V/cm; 2, switching to 280 V/cm and reversing 4 times; 3, returning to the initial field and reversed; 4, after reversing 2 times at this field.

case of PBLG, the polymers aggregate head-to-tail in CH₂Cl₂ and the aggregates line up parallel with each other to form molecular clusters; the origin of the huge dipole moments of the molecular clusters has been suggested to be the fluctuation of the distribution of the PBLG aggregates in both directions (see ref 3). This would be the case also in PEGs. When the formation of the molecular clusters is still not perfect, the rightabout turn of the molecular clusters might occur at various rates depending

on their sizes. In dioxane no change of the dichroic ratio was observed upon reversing the field direction, indicating that the electric-field orientation is generated by the induced dipoles of the molecular clusters or/and the movement of the anions through the solution. In this case, the side-by-side aggregates of the polymer molecules compose the molecular clusters, where their dipole moments are counterbalanced with each other. This difference in the manner of molecular aggregation of polypeptides depending on the solvent was already suggested by Wada¹⁶ and Watanabe¹⁷ using dilute solutions of PBLG. As the electric current is much less in dioxane than in the other solvents used, the degree of polymer orientation does not decrease even at 600 V/cm.

Figure 5 shows how the proton signal of the solvent molecules changes in an electric field and how the equilibrium spectra depend on the field strength. The signals of CH_2Cl_2 molecules (and of CH_2Br_2 molecules) split into doublets owing to the magnetic dipole-dipole interactions, indicating that the solvent molecules orient with respect to the direction of the electric field. The direction of the orientation is parallel to the electric field, as will be mentioned

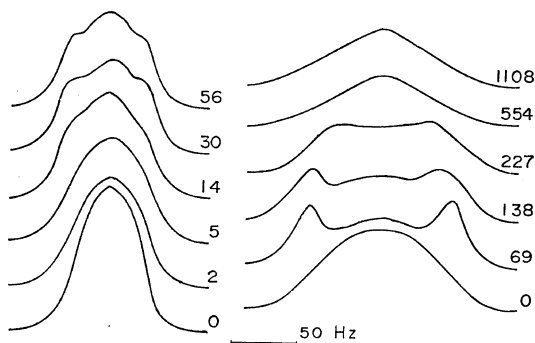


Figure 5. The NMR spectra observed after a static electric field is applied and dependence of the equilibrium spectra upon field strength for PELG in CH_2Cl_2 . The angle the direction of the orientation makes with that of the magnetic field, θ , equals 0° . Left: 14 vol%—69 V/cm; the numbers on the curves give the number of minutes after application of the field. Right: 20 vol%; the numbers on the curves give the field strength in V/cm.

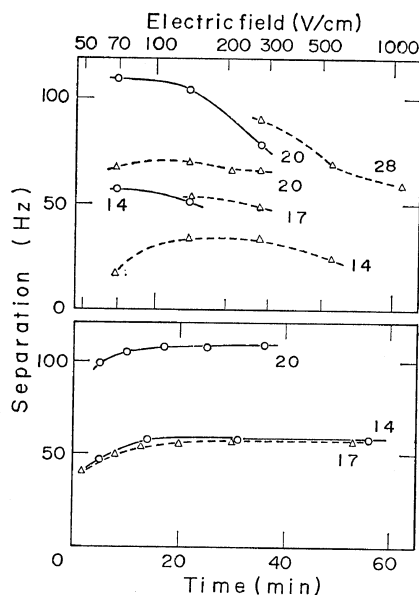


Figure 6. The separation vs. time and the equilibrium separation vs. strength of the electric field relationships. The numbers near the curves represent the polymer concentration in vol%. The equilibrium separations were obtained at 69 or 140 V/cm. Full lines, PELG in CH_2Cl_2 ; broken lines, PELG in CH_2Br_2 .

shortly, and the orientation of the solvent molecule is considered to be generated by molecular fields caused by the molecular clusters that orient in the direction of the electric field (see ref 4). When the field strength is increased beyond a certain critical strength, the separation begins to decrease and the width of the lines to increase. This indicates that the arrangement of the solvent molecules, and of the molecular clusters as may be seen in Figure 2, are disturbed by the movement of the anions. In the case of PBLG, the electric current is not marked and the decrease of the separation is less noticeable (see ref 4). The separation vs. time and vs. strength of the electric field relationships are more explicitly shown in Figure 6. The amount of the separation can not give the degree of polymer orientation, while the width of the lines may give some information about it. In dioxane, no separation of the proton signal was observed.

Magnetic-Field Orientation

In the case of PBLG, the magnetic-field orientation is poor in solution, and becomes noticeably when the solution is being dried in the magnetic field, probably owing to some cooperative behavior of the molecular clusters having huge electric dipole moments.¹⁸ This has been the case also in PEGs, and no change in the low-angle light-scattering patterns and no measurable double-refractive-index have been detected in the solutions, because the degree of orientation is low; however, the proton signals of the solvent molecules such as CH_2Cl_2 or CH_2Br_2 split into doublets when the liquid-crystalline solution of PELG or of equal proportions of PELG and PEDG is placed in the magnetic field of the NMR spectrometer (see Figure 7). The lines of the doublet narrow and the separation increases with time. After an equilibrium state is reached, the starting center signal is still maintained though weak, suggesting the presence of free solvent molecules which are not incorporated into the liquid-crystalline structure. The width of the lines is far less

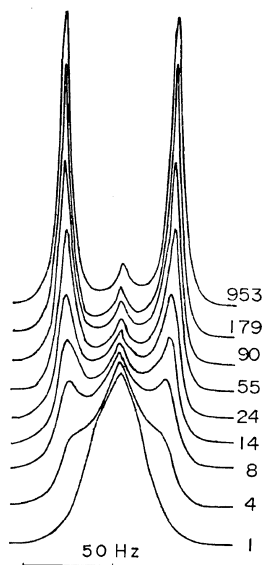


Figure 7. The NMR spectra observed after a liquid-crystalline solution is placed in the magnetic field of a NMR spectrometer (14 kG) for PELG in CH_2Cl_2 . Polymer concentration, 14 vol%. The numbers near the curves give the number of minutes.

than in the electric fields because the electrodes which make the magnetic field inhomogeneous and disturb the orientation of the solvent molecules with the electric current are missing. The separation vs. time relationship is explicitly shown in Figure 8. Although the time dependence of the orientation depends on the field strength, it still seems to take a much longer time for the polymers to reach an equilibrium orientation in the magnetic field than in the electric field. This difference would be caused by the following reason: The electric current through the liquid-crystalline solution help the formation of the molecular clusters and accelerate the change in electric fields, whereas in magnetic fields there is no such external force to act directly upon the solution. PELG was found not to orient in CH_2Br_2 , at least in the magnetic field of 14 kG, when the polymer concentration was beyond 17 vol%. This is due to the increase in the stability of the liquid-crystalline solution with increasing polymer concentration and suggests that the nature of the solvent concerning the liquid-crystalline structure is different for CH_2Br_2 and CH_2Cl_2 .

When an equilibrium solution is rotated through the angle θ which is the angle between

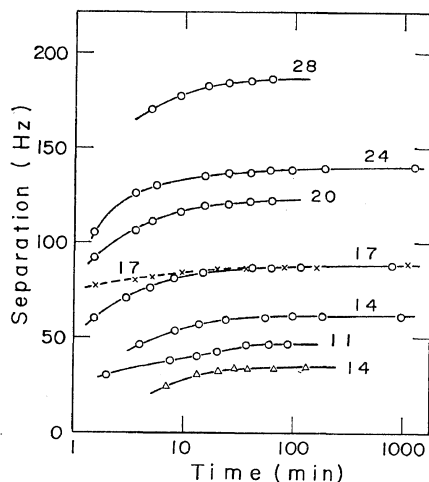


Figure 8. Separations vs. time relationship for the liquid-crystalline solutions of PEGs in a magnetic field of 14 kG. The numbers near the curves represent the polymer concentration in vol%. (O), PELG in CH_2Cl_2 ; (Δ), PELG in CH_2Br_2 ; (\times), equal proportions of PELG and PEDG in CH_2Cl_2 .

the direction of the orientation and that of the magnetic field, the separation changes following a relation given by Gutowsky and Pake,¹⁹ $h = (h_0/2)(3 \cos^2 \theta - 1)$ where h_0 is the separation at $\theta = 0^\circ$ as shown in Figure 9 (an example for the electric-field orientation is also given there). This indicates that the solvent molecules (and the molecular clusters) orient in the direction of the magnetic field as well as in the direction of the electric field.

As is shown in Figure 10, the separation depends on the polymer concentration (at a fixed temperature) and not on whether the orientation is generated by the magnetic field or by the electric field and not even on the degree of polymer orientation as in the case of PBLG (see ref 4). The separation is slightly smaller in the electric field than in the magnetic field owing to the fact that the orientation of the solvent molecules is slightly disturbed by the electric current in the electric field. In any case, this indicates that the mechanism of the solvent orientation is the same in both cases, as was mentioned already in this text. The separation is wider in CH_2Cl_2 than in CH_2Br_2 in contrast to the results for PBLG (see ref 4 and 5). The linear relationship between the separation and the concentration seen in parts of the curves can be explained, according to Orwoll and Vold,²⁰ if a time average over two states is considered, one highly ordered and the other isotropic. Explanation of this for PBLG has been given elsewhere (see ref 4). For a detailed study of the magnetic-field orientation, higher magnetic fields should be used, which would allow direct observations on the polymer orientation to be made.

When the NMR sample tube with the liquid-crystalline solution inside was rotated through 180° , the NMR spectrum did not change at all. This shows that the magnetic-field orientation is generated by the induced (magnetic) dipoles of the polypeptide molecules, as in the case of PBLG (see ref 4 and 18). On the other hand, upon reversing the direction of the electric field in the sample room of the NMR spectrometer, the NMR spectrum displayed a drastic change, indicating a right about turn of the solvent molecules (and of the molecular clusters). This is

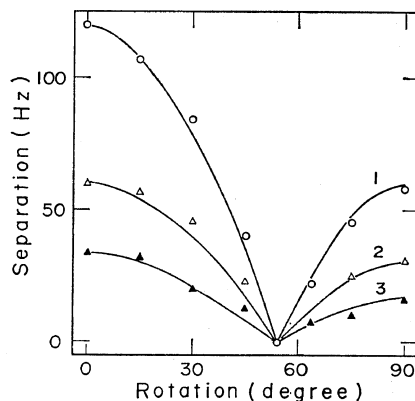


Figure 9. The separation of the doublet vs. rotation of the sample tube (the angle θ) relationship: 1, PELG in CH_2Cl_2 —20 vol%; 2, PELG in CH_2Br_2 —17 vol%; 3, PELG in CH_2Br_2 —14 vol% (the sample solution was placed in the magnetic field after an equilibrium orientation was obtained in an electric field of 138 V/cm).

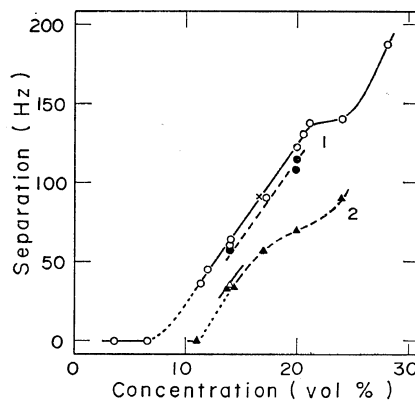


Figure 10. Effects of the polymer concentration on the dipolar splitting at equilibrium: 1, PELG in CH_2Cl_2 (\times , equal proportions of PELG and PEDG in CH_2Cl_2); 2, PELG in CH_2Br_2 . The full lines are for the magnetic-field orientation and the broken lines, for the electric-field orientation. Refer to the footnote for Figure 6.

natural because the electric-field orientation is generated by the permanent (electric) dipoles of the polypeptide molecules. When an electric field of 140 V/cm is applied to a 14-vol% CH_2Br_2 solution of PELG perpendicular to the magnetic field (of 14 kG), the electric-field orientation was given priority to occur, whereas the magnetic-field orientation was stronger in the case the

external fields were applied separately. This coincides with the observation on PBLG and indicates some important influence of the electric dipole moments of the molecular clusters upon the magnetic-field orientation (see ref 18).

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REFERENCES

1. E. Iizuka, *Biochim. Biophys. Acta*, **175**, 457 (1969).
2. E. Iizuka, *ibid.*, **243**, 1 (1971).
3. E. Iizuka, T. Keira, and A. Wada, submitted for publication in *Molecular Cryst. Liq. Cryst.*
4. E. Iizuka, *J. Phys. Soc. Jap.*, **34**, 1054 (1973).
5. S. Sobajima, *ibid.*, **23**, 1070 (1967).
6. Y. Go, S. Ejiri, and E. Fukada, *Biochim. Biophys. Acta*, **175**, 454 (1969).
7. S. Yomosa, Abstracts, 9th Annual Meeting of the Biophysical Society of Japan, Nagoya, Oct. 14, 1970, No. 1-C-8p.
8. M. Honda, H. Suzuki, and T. Kato, *Repts. Progr. Polym. Phys. Jap.*, **14**, 607 (1971).
9. E. Iizuka, *Polymer J.*, **4**, 401 (1973).
10. E. Iizuka, *Kobunshi (High Polymers, Japan)*, **21**, 463 (1972).
11. M. Miyata, K. Tohyama, and Y. Go, *J. Phys. Soc. Jap.*, **33**, 1180 (1972).
12. F. C. Frank, *Disc. Faraday Soc.*, **25**, 19 (1958).
13. R. B. Meyer, *Appl. Phys. Letters*, **12**, 281 (1968).
14. M. B. Rhodes, and R. B. Stein, *J. Polym. Sci., Part A-2*, **7**, 1539 (1969).
15. G. H. Heilmeyer, L. A. Zanoni, and L. A. Barton, *Proc. IEEE*, **ED-17**, 22 (1970).
16. A. Wada, *J. Polym. Sci.*, **45**, 145 (1960).
17. H. Watanabe, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan)*, **86**, 179 (1965).
18. E. Iizuka, and Y. Go, *J. Phys. Soc. Jap.*, **31**, 1205 (1971).
19. H. S. Gutowsky, and G. E. Pake, *J. Chem. Phys.*, **18**, 162 (1950).
20. R. D. Orwoll, and R. L. Vold, *J. Amer. Chem. Soc.*, **93**, 5335 (1971).