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

Light Scattering by Liquid Crystals of Poly-γ-benzylglutamates in Electric Field

Eisaku Iizuka [a], Tatsuhiko Keira [b] & Akiyoshi Wada [b]
[a] Faculty of Textile Science and Technology, Shinshu University Ueda, Japan
[b] Department of Physics Faculty of Science, The University of Tokyo, Tokyo, Japan

Version of record first published: 21 Mar 2007.

To cite this article: Eisaku Iizuka , Tatsuhiko Keira & Akiyoshi Wada (1973): Light Scattering by Liquid Crystals of Poly-γ-benzylglutamates in Electric Field, Molecular Crystals and Liquid Crystals, 23:1-2, 13-49

To link to this article: http://dx.doi.org/10.1080/15421407308083359

Molecular Crystals and Liquid Crystals. 1973. Vol. 23, pp. 13–49

Light Scattering by Liquid Crystals of Poly-γ-benzylglutamates in Electric Field

EISAKU IIZUKA

Faculty of Textile Science and Technology
Shinshu University
Ueda, Japan

and

TATSUHIKO KEIRA and AKIYOSHI WADA

Department of Physics, Faculty of Science
The University of Tokyo
Tokyo, Japan

Received June 6, 1972; *in final form November* 14, 1972

Abstract—Liquid crystalline solutions of poly-γ-benzylglutamates have been measured in static electric fields using light scattering methods. It has been made clear that molecular clusters are present in solution when high dielectric solvents are used. Sufficient conditions, though not the necessary ones, have been obtained to indicate that the molecular clusters are rod-like in a very low electric field supporting an idea previously proposed. From the change of the V_h scattering mode, polymer (and molecular cluster) orientation can be determined. Change in the scattering mode when the direction of the external electric field is reversed is drastic, and a tentative explanation for this is given. In dioxane, formation of the rod-like molecular clusters and their orientation are brought about by the induced dipole of the polymer and/or the electric current through the liquid crystalline solution unlike that in the high dielectric solvents.

1. Introduction

Robinson(1) was the first to report on the liquid crystalline nature of polypeptides. Frenkel and his coworkers(2) have made clear that the specific ordered states in binary PBLG(poly-γ-benzyl-L-glutamate)-DCA(dichloroacetic acid) system are characterized by successive transition from one form (mesophase) to another by means of a polarized low-angle light scattering technique. This transition takes place when the polymer concentration is beyond a certain critical concentration C where an isothermic coil to α-helix transition occurs.

The concentration C is 20 g/100 ml for PBLG of molecular weight 10^5. Powers and his coworkers$^{(3)}$ have observed that when the concentration of solutions of helical polymers is increased beyond a certain critical concentration the solution becomes ordered spontaneously and that if the polymer possesses a sufficiently large dipole moment or polarizability the specific Kerr constants increase suddenly at that concentration. Tobolsky and his coworkers$^{(4)}$ have been studying the electric orientation of liquid crystalline solutions of PBLG by the polarizing micrograph method, and Stamatoff$^{(5)}$ by the X-ray diffraction method, reporting that PBLG begins to orient in *m*-cresol in an electric field of 100–125 V/cm and in *p*-dioxane in an electric field of 2000–3000 V/cm. Stein and his coworkers have presented many leading papers on the light scattering of unoriented and oriented polymer films (for example, see Refs. 6 and 7) and even of liquid crystals of PBLG (though not in electric field),$^{(8)}$ showing this technique is very useful in studying the morphology of polymer films. They$^{(9)}$ have shortened the exposure time when photographing the scattering pattern by the use of a laser as a light source. Wallach$^{(10)}$ has found correlations among film properties and light scattering orientation angles on drawn films of polyethylene terephthalate.

Findings by one of the authors$^{(11)}$ show that liquid crystals of PBLG orient quite well in the direction of a very low electric field such as 84 V/cm. The electric orientation of liquid crystalline solutions of this polypeptide has been extensively investigated by infrared spectroscopy. Consequently, it has been known$^{(12)}$ that this liquid crystalline solution behaves as if composed of independent molecular clusters, having a dipole moment some 730 times as large as that of the single polymer (of degree of polymerization 650). An electrostatic measurement$^{(13)}$ has clarified that the surface charge induced on electrically (and highly) oriented PBLG films is about 60×10^{-12} C/cm^2 which is only 0.6% of the expected charge. This suggests that groups of the associated polymers are distributed with roughly equal likelihood in both directions to make most of the dipole moments of the groups counterbalance each other. The association is of the head-to-tail type and rod-like in CH_2Br_2.$^{(12)}$ This is true in dilute PBLG solutions as has been suggested by Wada.$^{(14)}$ The electric orientation would be caused by the excess of the dipole moments due to fluctuation of the distribution.

The purpose of this paper is to present findings on the presence of the molecular clusters and their dimensions in liquid crystalline solutions of PBLG, PBDG or equimolar mixture of both polymers as obtained mainly by the light scattering method.

2. Experimental Procedures

The PBLGs/PBDG used were of mean degree of polymerization (DP) 520 and 460/530 and prepared from the N-carboxy-α-amino acid anhydride of γ-benzyl-L-glutamate/γ-benzyl-D-glutamate. The polymers were dissolved in a high dielectric solvent such as CH_2Br_2, CH_2Cl_2 or chloroform, or in a low dielectric solvent, dioxane, and kept 2–3 weeks in sample tubes at room temperature to allow them to form liquid crystals of α-helices. The solution was then put in a rectangular quartz cell of path length 1 mm with or without a quartz spacer to adjust the path length to 0.10, 0.25 or 1.00 mm. The concentration of the solutions used were always beyond Robinson's critical concentration B.(15)

With a He-Ne gas laser model 132J (distributed by Japan Laser Co.) which produced a 1 mW light having a wavelength of 6328 Å, light scattering patterns of the liquid crystalline solutions in static electric field were photographed on a 35 mm film. A condenser lens, a polarizer with its axis placed horizontal (and parallel to the external field), the sample solution in an electric field supplied by dry cells as mentioned elsewhere,(11,12) an analyzer and a ground glass upon which the patterns were produced were placed in this order between the laser and a camera. Exposure time was 1/15 sec at f: 3.5 when the distance between the camera and the ground glass was 50 cm and the exposure index of the film was DIN 24. The pattern taken with the analyzer placed vertically is called a V_h pattern and that taken with the analyzer placed horizontally, a H_h pattern. They correspond to a H_v pattern and a V_v pattern of film samples whose direction of drawing is vertical. As the angle between the direction of the optical axis of the ordered solution and that of the polarizer (and analyzer) was always 0° (0° or 90°), effects of birefringence of the solution on the intensity of polarized scattered ray was neglected.(16) Mode pattern of the laser was negligible.

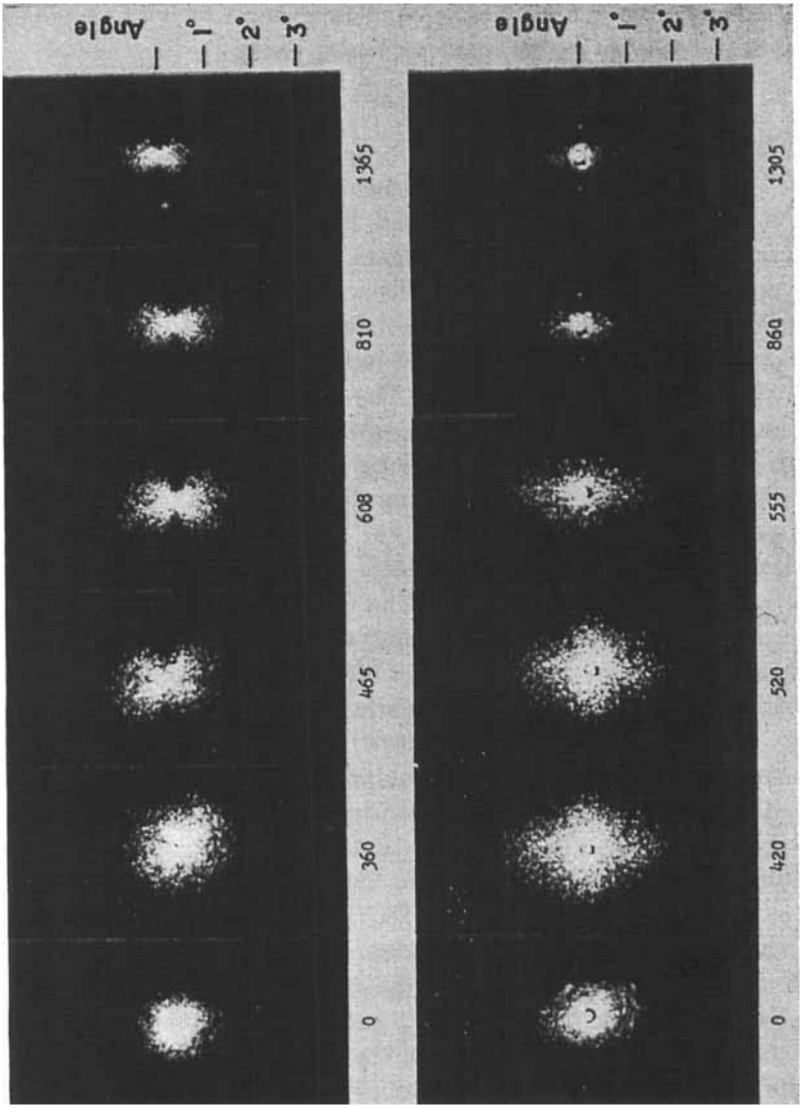

Angle
1°
2°
3°
0
360
465
608
810
1365
Angle
1°
2°
3°
0
420
520
555
860
1305

Figure 1 (above). Time dependence of the V_h (upper) and the H_h (lower) scattering patterns by liquid crystalline solution of PBLG. External electric field, 169 V/cm. The numbers near the patterns represent time in second. Solvent (CH_2Br_2), polymer concentration (14 vol %), solution thickness (0.10 mm), the scale for the scattering angle and temperature (20 °C) are the same throughout Figs. 1–13 unless stated otherwise. The direction of the electric field is horizontal throughout Figs. 1–21.

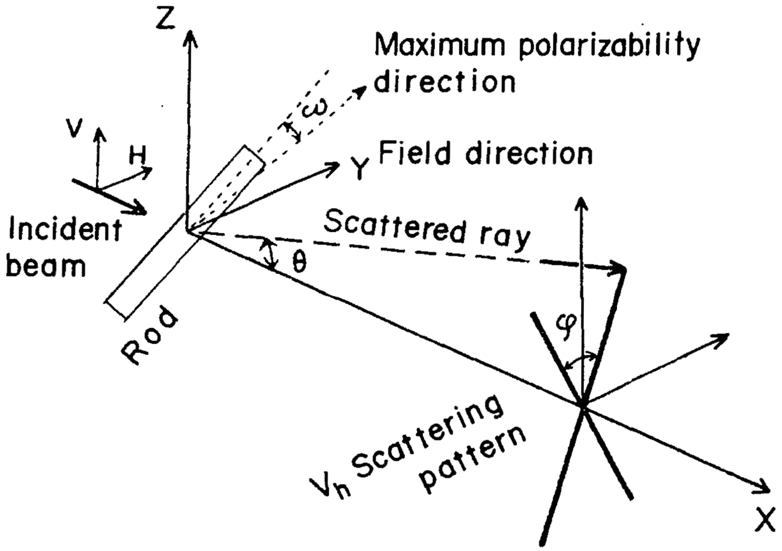


Figure 2. Coordinate system used to analyze the V_h pattern.

Polarizing micrographs of liquid crystalline solutions in static electric field were taken under crossed polaroids to increase contour.

Results and discussion will be given of a CH_2Br_2 solution of PBLG of concentration 14 vol % and of a dioxane solution of PBLG of concentration 11 vol % as measured at 20 °C with solution thickness 0.10 mm unless stated otherwise. No cholesteric structure was detected in these two liquid crystalline solutions by the optical rotation measurement. The PBLG of DP 460 was used for solutions of a single polypeptide and the PBLG of DP 520, for racemic solutions coupled with the PBDG of DP 530. The solvents used were of reagent grade and used without further purification. Values of the polymer concentration are only very approximate.

3. Results and Discussion

LIQUID CRYSTALLINE CH_2Br_2 SOLUTIONS OF PBLG

1. *Time dependence of the scattering mode in electric field*

Change of the scattering mode when an electric field is applied to the liquid crystalline solution is time dependent as shown in Fig. 1. At first both the V_h and the H_h patterns are circular and the scattering intensity decreases sharply with increasing scattering angle θ. The V_h pattern then turns into a ±45° cross pattern. With time, the orientation angle ϕ becomes smaller and the intensity of the V_h scattering decreases. The H_h pattern turns long lengthwise, its intensity decreasing with time. The coordinate system used to analyze the V_h pattern is illustrated in Fig. 2, together with the definition of the above-stated angles.

The fact that the V_h pattern is observed may show the presence of birefringent assemblies of the polymers (molecular clusters) of the order of length comparable to the wavelength of light used and justify an idea(12) based on measurements of the infrared dichroism. Decrease of the value of ϕ with time has been accompanied by increase of the infrared dichroic ratio at 3300 cm^{-1} which is the center of the NH stretching vibration mode of the PBLG molecule, suggesting that the value of ϕ may be used as a measure to estimate the degree of orientation of the liquid crystalline solution. The patterns at the steady state do not show any trace of the starting ones, indicating that all the molecular clusters in the solution participate in the electric orientation. Previously, 85% of the PBLG molecules in solution were supposed to be able to make perfect orientation and the rest, not to participate in the electric orientation at all. If all the PBLG molecules are included in the molecular clusters and participate in the orientation, the arrangement of the PBLG molecules in the clusters must fall in disorder. The conclusions derived on the previous assumption, however, are confirmed still to be valid. The mean angle between the axis of the molecular cluster and the NH transition moment, γ, turns out to be 33° when it is calculated to let the value of $2\cos^2\gamma/\sin^2\gamma$ (see Ref. 12) coincide with the experimentally obtained asymptotic value 4.6. According to Tsuboi,(17) the angle between the molecular axis and the transition moment is 29°.

2. *Effects of strength of the external electric field on the scattering mode*

Figure 3 shows how the steady-state scattering mode of the liquid crystalline solution changes when the external field is increased. Clough and his coworkers(18) have shown that when the draw ratio is increased the low-angle light scattering mode of the polytetrafluoroethylene (PTFE) films display similar change except that the profile of the V_h patterns change place with those of the H_h patterns. If the molecular cluster is assumed to be rod-like, this difference may be explained by assuming that the maximum polarizability direction of the molecular cluster makes an angle (ω), 0° or 90° with respect to the rod axis unlike that in the PTFE films where it is proposed to be 45° (see Ref. 6). Measurements of the infrared dichroic ratio on sheared liquid crystalline solutions of PBLG show that the polymers orient in the direction of shearing stresses, which would indicate that the helical polymers arrange in the direction of the rod axis and that the value of ω is 0° unless the molecular clusters are destroyed by the shearing stresses. Quite recently, Wilkes(19) observed a H_v 0°–90° scattering in a " pool " of the chloroform solution of PBLG placed on a glass slide as well as in several solid films of various polypeptides and interpreted this observation as implying the presence of a superstructure. In his case, however, the value of ω equals 45° in contrast with our case. This difference may be due to

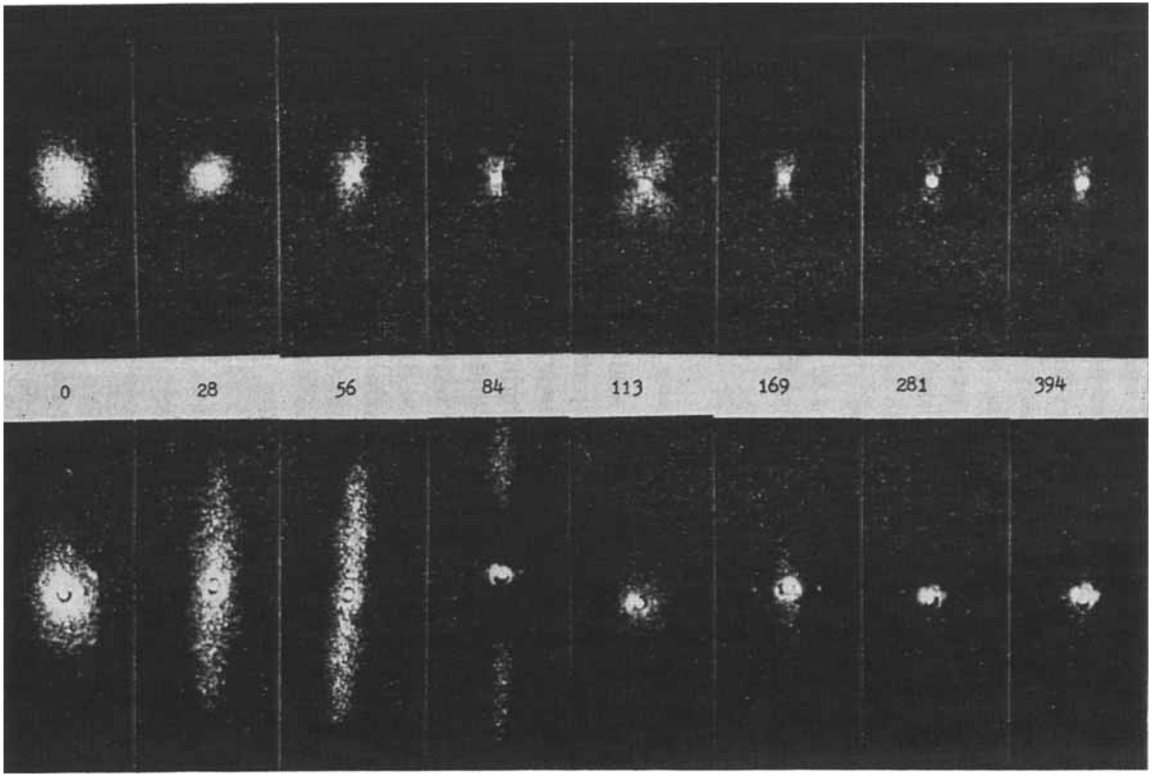


Figure 3. Dependence of the steady-state V_h (upper) and the steady-state H_h (lower) scattering patterns by liquid crystalline solution of PBLG upon strength of the external electric field. The numbers near the patterns represent the field strength in V/cm. Two equatorial spots seen in the H_h pattern taken in an electric field of 169 V/cm are due to light reflected by the spacer inserted in the quartz cell used. These are seen also in some of the other H_h patterns contained in this text.

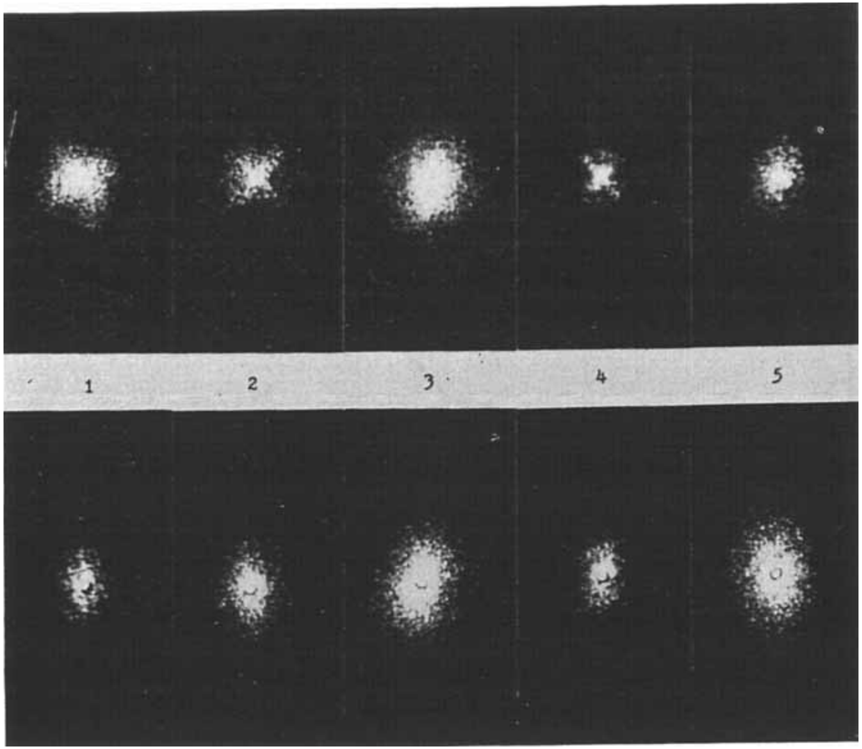


Figure 4. V_h (upper) and H_h (lower) scattering patterns by liquid crystalline solutions where no electric field is applied. 1 and 2, PBLG in CH_2Br_2; 3 and 4, PBDG in $CHCl_3$. 5, equimolar racemic solution of PBLG and PBDG in $CHCl_3$. 2, an electric field of 394 V/cm was applied for 10 min, measured 7.5 h after the field was removed.

the large difference in preparing the sample solution. In polyglutamic acid-DMF preparation, he has noted the ± 45° scattering in a region containing the solvent and the 0°–90° scattering in a dried region, suggesting that the superstructure easily depends on circumstances.

Figure 4 is presented to show that even when no external field is

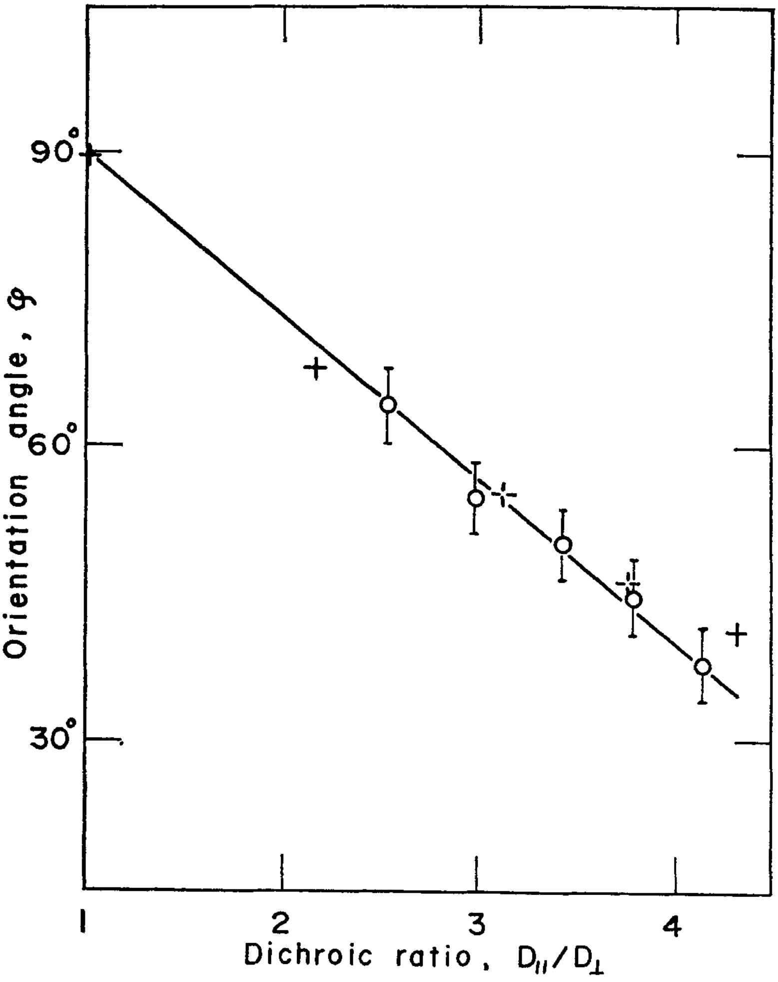


Figure 5. Orientation angle vs. dichroic ratio at 3300 cm^{-1} for liquid crystalline solution of PBLG. ○, observed; + and ÷, read on the calculated contours.

present in liquid crystalline solution the V_h pattern is often cross-shaped and that once it becomes cross-shaped in an electric field it keeps so for a long while after the field is removed and the solution structure becomes completely disorganized. Liquid crystalline solutions of equal proportions of PBLG and PBDG tested were always circular in the V_h pattern when no field was applied. An electric field of 30–80 V/cm or often shearing stresses are enough to produce the rod-like molecular clusters in liquid crystalline solutions.

A linear relationship between the orientation angle ϕ and the infrared dichroic ratio at 3300 cm^{-1} has been obtained as may be seen in Fig. 5. By extrapolation, the value of $D_{\parallel}/D_{\perp}$ at $\phi = 0°$ is shown to be 6.2, which is smaller than 6.5 for the completely oriented PBLG molecule (see Ref. 12), but is larger than the experimentally obtained asymptotic value 4.6. However, it is not sure whether the extrapolation is meaningful or not. In any case the light scattering method would be one of the useful techniques to estimate the degree of ordering of the liquid crystalline solution. Intensity of the V_h scattering becomes more weakened with increasing degree of ordering of the liquid crystalline solution, indicating the decrease of orientation fluctuation. It is known that the H_h scattering is due to a combination of orientation and density fluctuation of the sample. Intensity of the H_h scattering becomes more weakened when the ordering of the liquid crystalline solution is more advanced, and this may be an indication that boundary regions among the neighboring molecular clusters become less distinct from the cluster structure, that is, a transition from the cluster structure to the nematic structure occurs.

Polarizing micrographs of the liquid crystalline solution taken in an electric field are given in Fig. 6. Lateral (that is, parallel to the external field) lines may be seen to appear when the field strength is increased. The feature of the micrographs becomes somewhat similar to that of a micrograph of *p*-azoxyanisole given by Heilmeier(20) showing formation of a domain structure in an alternate electric field of 500 V/cm. Spacing of the lines is about 10 μ, as summarized in Table 1 together with other spacings to be mentioned later. Values of these spacings will be helpful to estimate the dimensions of the molecular cluster.

In order to support the above-mentioned discussion, expected

TABLE 1 Spacing of the lines which appear in liquid crystalline solutions of PBGs under electric field

Solution	Concentration (vol %)	Lateral lines Micrograph	 Diffraction	Vertical lines[a] Micrograph	 Diffraction
PBLG/CH_2Br_2	14, 24	10–15 μ	10–15 μ	15–40 μ	20–30 μ
(PBLG + PBDG)/CH_2Br_2	14	—	—	—	15–30 μ
PBLG/dioxane	11, 20	ca. 10 μ	—	7–20 μ	—
(PBLG + PBDG)/dioxane	11	—	—	8–40 μ	—

Spacing of the vertical lines decreases with increasing polymer concentration, with increasing field strength (169–1500 V/cm), or with increasing solution thickness (0.10–1.00 mm).

[a] Appear upon reversing the field direction.

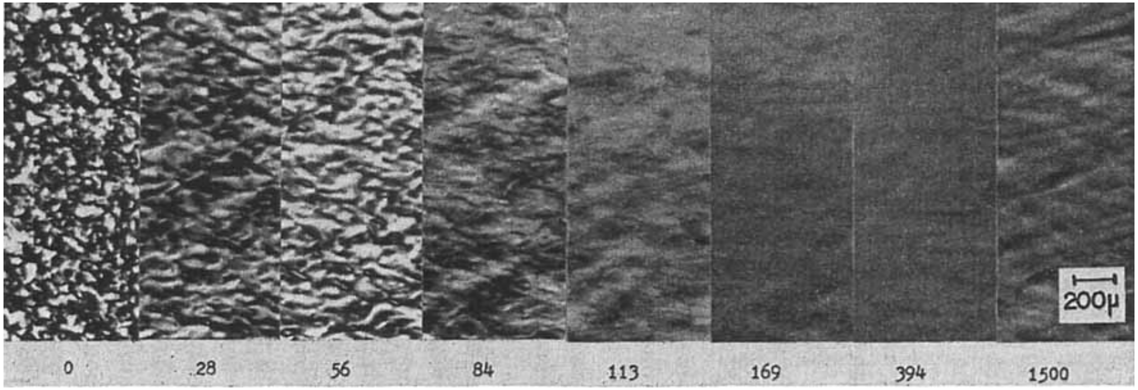


Figure 6. Dependence of the pattern of the polarizing micrograph of liquid crystalline solution of PBLG upon strength of the external electric field. The numbers, same as in Fig. 3. The scale for the micrographs is the same throughout Figs. 6–21.

scattering patterns of the rod-like particles of length L are calculated assuming $\omega = 0°$ and modifying the calculation by Rhodes and Stein⁽⁶⁾ in order to apply it to rods in three dimensions. Details of the modification will be reported elsewhere. The following distribution function has been used:

$$N(\alpha) = N_0 v^3/[1+(v^3-1)\sin^2\alpha]^{3/2}$$

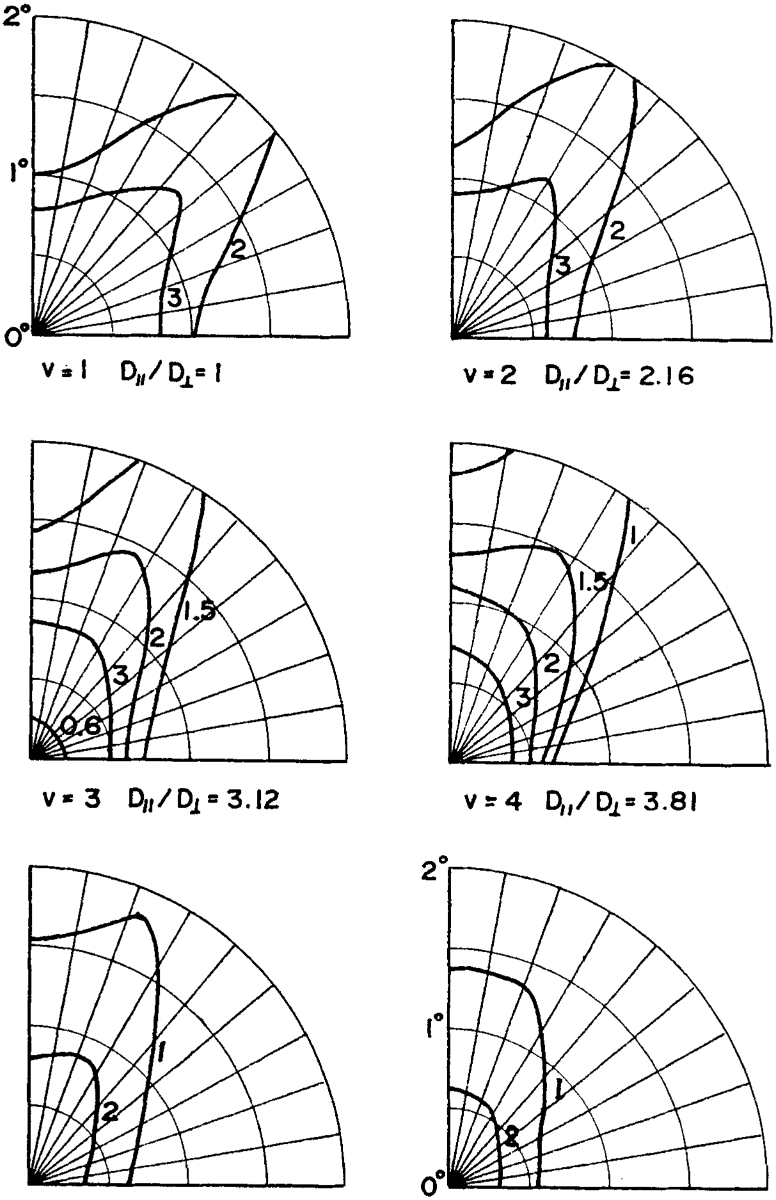
where the parameter v essentially defines the degree of the rod orientation and α is the tilt angle the rod makes with the Z-axis (Rhodes and Stein restricted this angle in the YZ-plane, refer to Fig. 2). This arbitrary distribution function has been given originally by Kratky⁽²¹⁾ for the stretched polymer films and has been proved to be pertinent for materials in the solid state. As the liquid crystal seems more like a solid than a liquid, this function is chosen for the present. Two polarizabilities parallel and perpendicular to the rod axis characterizing the rod, b_l and b_t, are expressed following Bragg and his coworkers⁽²²⁾ as

$$b_l = Kf(n_l^2-n_0^2),\ b_t = Kf(n_t^2-n_0^2)/[1+(1-f)(n_t^2-n_0^2)/2n_0^2f]$$

where n_l and n_t are refractive indices of the molecular cluster and have the values of 1.5454 and 1.5430 respectively at 5876 Å when measured by an Abbe refractometer. n_0 is the refractive index of the solvent, CH_2Br_2 (1.5419 at 15 °C, $\lambda = 5876$ Å). K is a constant and f is the volume fraction of the molecular cluster. Although the volume fraction of the solute in question is 0.14 the volume fraction of the cluster must be larger than this value because the solvent molecules are considered to be included in the cluster. b_l and b_t, however, are not sensitive to the magnitude of the value of f. b_t/δ turns out to be 0.45 where $\delta = b_l - b_t$. Assuming $kL/2 = 200$ where $k = 2\pi/\lambda$ (λ is the wavelength of the radiation in the scattering medium), expected V_h and H_h scattering contours have been calculated with an electric computer model HITAC 5020E and are presented in Fig. 7. This assumption was set up so as to let the calculated contours best fit the observed ones.† The parameter v

---

† Care should be taken to consider that the angle the scattered ray makes with the incident beam within the solution is different from that in air because of refraction (see Ref. 16).



$v = 1 \quad D_{\parallel}/D_{\perp} = 1$

$v = 2 \quad D_{\parallel}/D_{\perp} = 2.16$

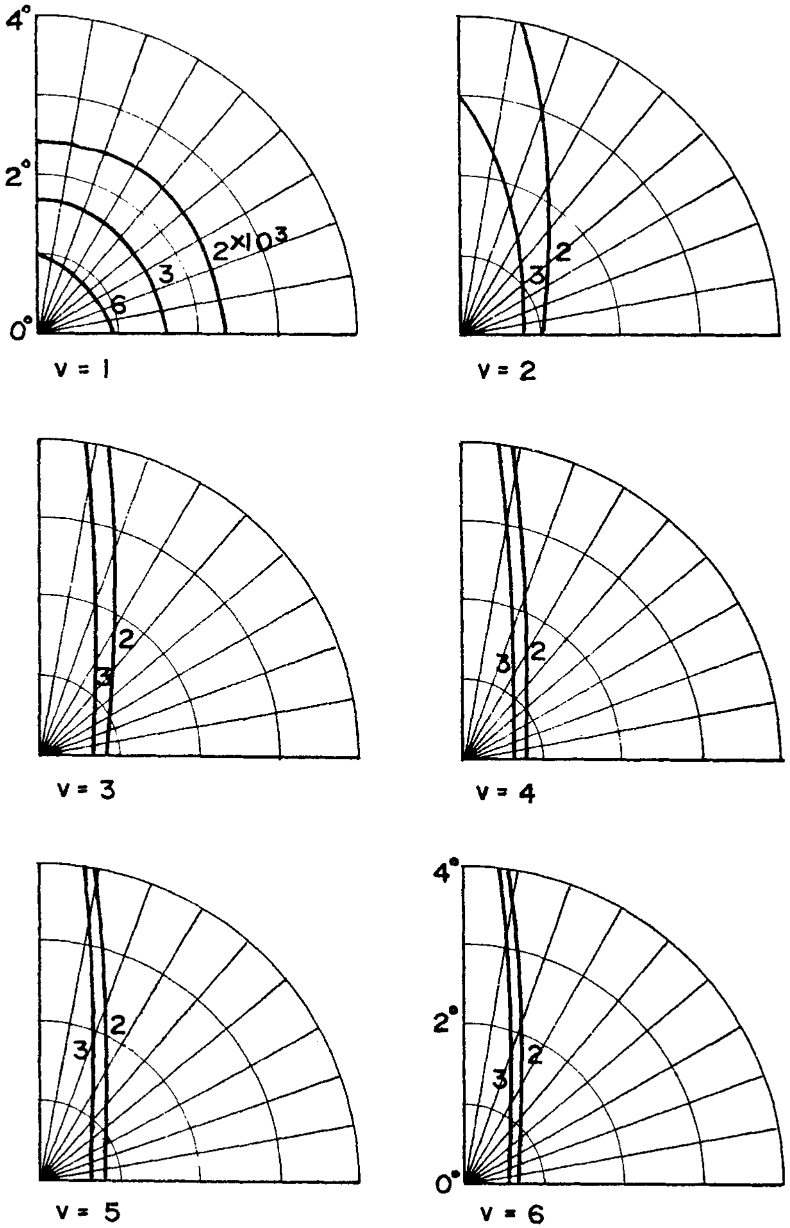
$v = 3 \quad D_{\parallel}/D_{\perp} = 3.12$

$v = 4 \quad D_{\parallel}/D_{\perp} = 3.81$

$v = 5 \quad D_{\parallel}/D_{\perp} = 4.33$

$v = 6 \quad D_{\parallel}/D_{\perp} = 4.64$

(a)



(b)

Figure 7. Calculated intensity distribution of the light scattering by liquid crystalline solution of PBLG. $kL/2 = 200$; $b_t/\delta = 0.45$; $\omega = 0°$. (a) the V_h mode; (b) the H_h mode.

in the distribution function was able to be correlated with the infrared dichroic ratio at 3300 cm^{-1} of the liquid crystalline solution and is shown in Fig. 7.

Calculated contours of the scattering, especially of the V_h scattering are very similar to the observed contours when the external field is not so low. The orientation angle read on the calculated patterns agrees quite well with the observed results except when the orientation is very high as may be seen in Fig. 5. Intensity of the H_h scattering is about 10^3 times stronger than that of the V_h scattering and does not decrease with increasing rod orientation. This is not the case in the observed H_h scattering and results from putting a high and fixed value of 0.45 into b_t/δ. The liquid crystalline solution would not be a mere dual combination of molecular clusters and free solvent molecules. Light scattering by a random assembly of anisotropic rods in three dimensions was calculated quite recently by Kawai and his coworkers,(23) their results being quite similar to those obtained by the authors although they aimed at wider angle scattering.

From the assumption, $kL/2 = 200$, the rod length L turns out to be 25 μ which coincides with the spacing estimated from the H_h patterns and from the polarizing micrographs (will be mentioned shortly) as may be seen in Table 1. When the angle α was restricted in the YZ-plane, that is, when the calculation was carried out in two dimensions, expected scattering contours were circular and did not change when the value of v was changed.

3. *Effects of reversing the electric field on the scattering mode*

When the direction of the external electric field is reversed, the scattering contours display a striking change as shown in Fig. 8, accompanying the turn around (see Ref. 11) of the molecular clusters in the liquid crystalline solution. New equatorial scattering appears in both the V_h and the H_h patterns. Both the scattering and the (V_h) transmission intensities vary with time having two maxima (and one minimum). It will be natural to believe that when the direction of the axis of the molecular cluster tilts 45° with respect to both the crossed polaroids the V_h transmission becomes maximum and that when it is parallel to any one of the polaroids the transmission becomes minimum. Figure 9 is inserted in order to show how

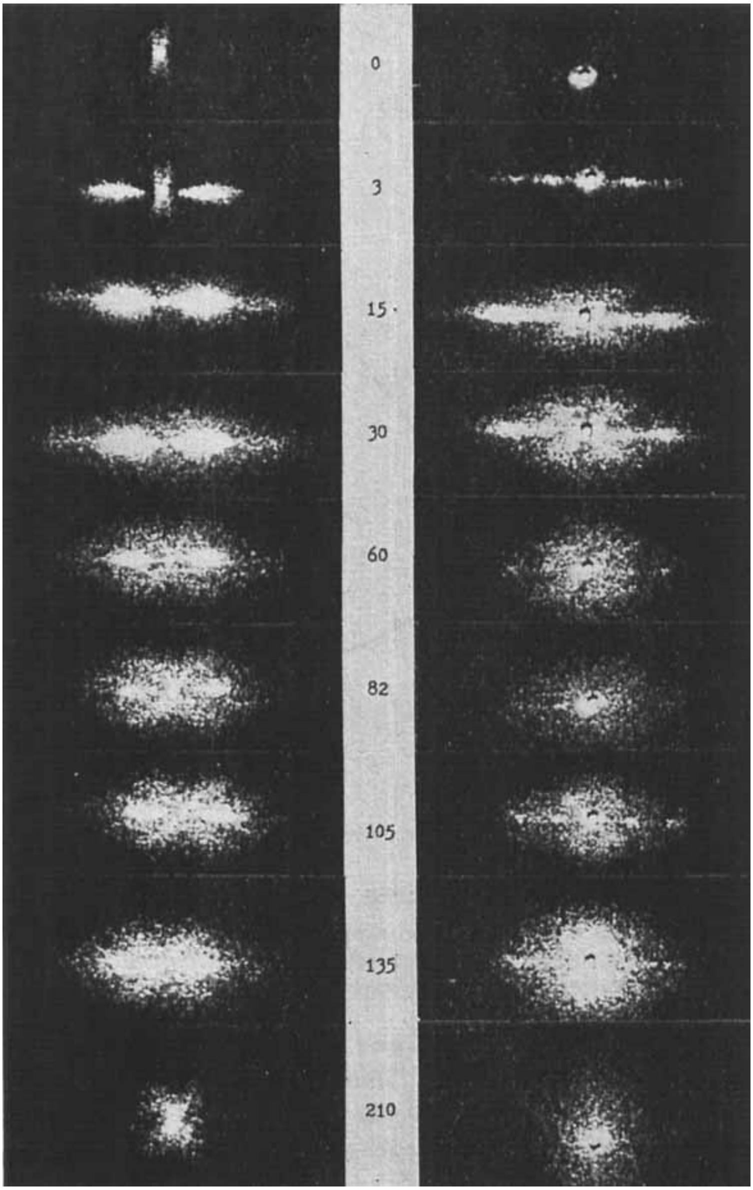


Figure 8. Change of the V_h (left) and the H_h (right) scattering patterns by liquid crystalline solution of PBLG when the direction of the external electric field (169 V/cm) is reversed. The numbers, same as in Fig. 1.

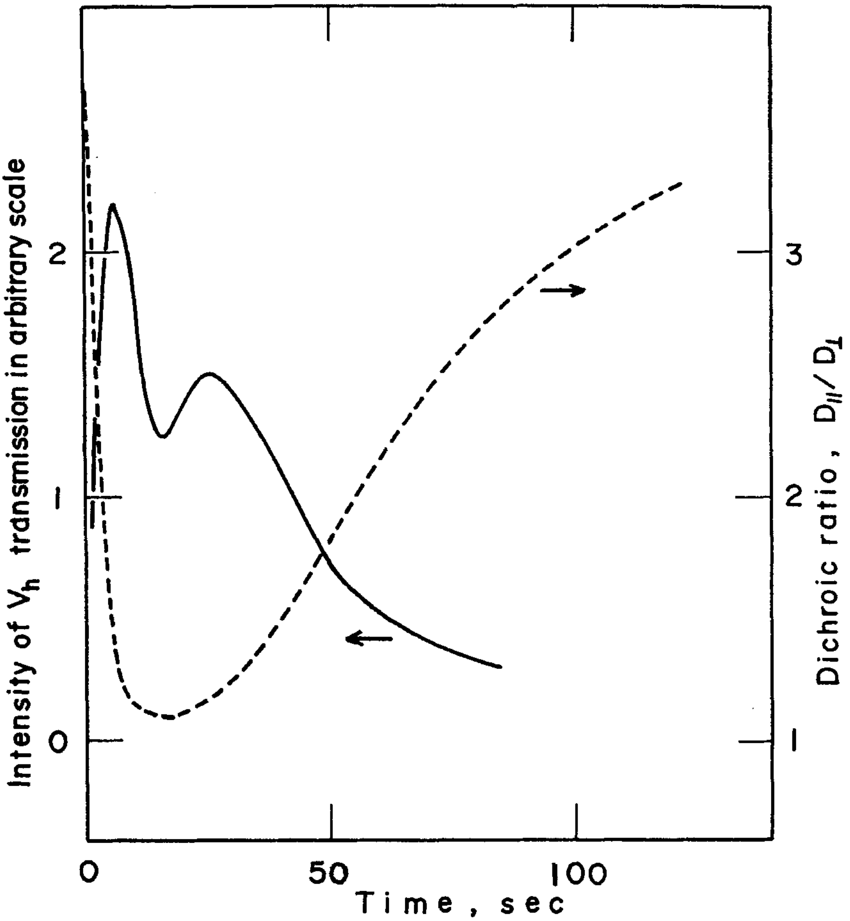


Figure 9. Change of the scattering intensity and of the infrared dichroic ratio at 3300 cm^{-1} of liquid crystalline solution of PBLG when the direction of the external electric field (394 V/cm) is reversed.

the intensity of the V_h transmission† and the infrared dichroic ratio at 3300 cm^{-1} change with time. These three limited intensities may be seen to occur while the dichroic ratio decreases and keeps its minimum value of about unity in the cluster reversal process indicating that the belief stated above is reasonable although the cause of the intensity change of the scattering is still to be determined.

† The intensity of the transmitted light was measured using an amplifier with a photoelectric tube. In the steady state, the intensity ratio of the scattered ray to the transmitted ray was no greater than 0.10 in any case tested.

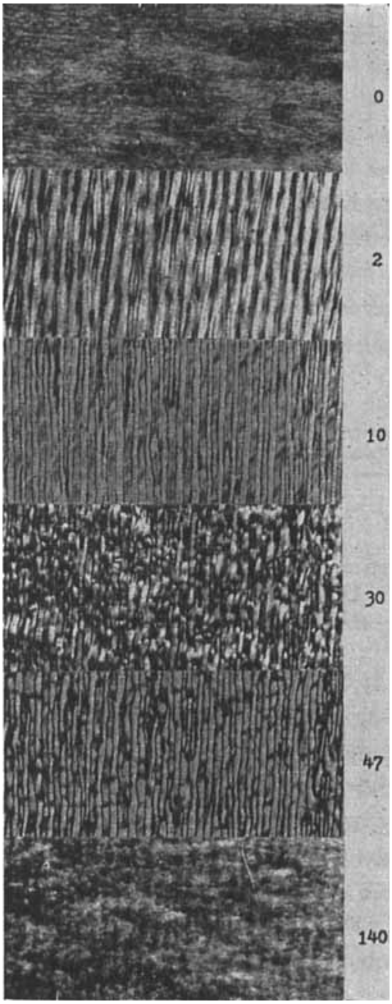


Figure 10. Change of the pattern of the polarizing micrograph of liquid crystalline solution of PBLG when the direction of the external electric field (394 V/cm) is reversed. The numbers, same as in Fig. 1.

In Fig. 10, polarizing micrographs of liquid crystalline solutions are presented showing the results of reversing the direction of the external electric field. Many equidistant lines perpendicular to the external field appear since the molecular clusters still remain oriented in the starting direction judging from the time dependence of the dichroic ratio. The spacing of the lines coincides with that calculated from the equatorial spots in the H_h patterns considering that they are due to diffraction of light through the bright and dark stripes of the solution. These lines would be a kind of disclination line (for example, see Refs. 24 and 25) and may indicate the least upper bounds of the length of the molecular cluster having a mean value of about 25 μ. This value coincides perfectly with the above-stated one derived from the scattering pattern. The molecular clusters are tentatively considered to behave in the liquid crystalline solution as illustrated in Fig. 11. The spacing of the lines are already given in Table 1 as the spacing of the vertical lines. The vertical spacing decreases when the polymer concentration is increased or when the field strength is increased.

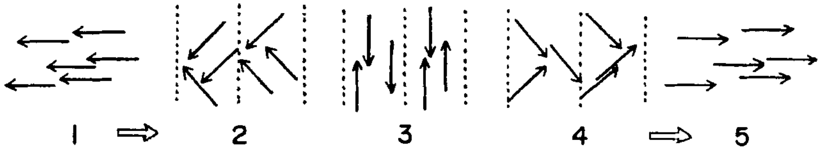


Figure 11. Proposed mode of the behavior of the molecular clusters of PBLG in liquid crystalline solution of PBLG when the direction of the external electric field is reversed.

If the antiparallel lineup of the associated polymers (of the head-to-tail type) is given priority to the parallel lineup in the molecular cluster owing to their permanent dipole, fluctuation of the polymer arrangement may be less than $1/\sqrt{N}$ where N is the number of the polymer molecules in the cluster. When $\sqrt{N}$ is assumed to be 730, however, $1/\sqrt{N}$ turns out to be 0.15×10^{-2} whose order coincides with the ratio of the detected surface charge to the expected charge (for this part of discussion, see Introduction). If it is assumed that a molecular cluster of length 25 μ is composed of 730^2 polymers, its diameter turns out to be 0.4 μ for the 14 vol % solution allocating 18 Å to the diameter of helical PBLG molecule and including the solvent molecules in the molecular cluster. The above-stated mean lateral spacing of about 10 μ is much larger than this diameter and would show the thickness of bundles of the molecular clusters (domains). Suzuki and his coworkers(26) have estimated the diamagnetic and the paramagnetic effects of the polypeptide group as about 10^{-8} eV for a magnetic field of 14 kG and have concluded that the effects are still too small (at least 10 times) to cause the actual magnetic orientation of liquid crystals of PBLG even if each molecular cluster is composed of 730 polymers of DP 650. The molecular cluster is now sure to be composed of far more than 730 polymers and this is in favor of their idea to explain the magnetic orientation. The fact that(13) the magnetic orientation is slight in solution, becoming striking when the solution is evaporated is still to be expected. Further discussion would be hazardous at the present moment.

4. *Effects of conditions of the measurement on the scattering mode*

a) *Temperature*

Any remarkable difference in the scattering mode when the temperature is raised up to 60 °C or decreased down to 7 °C has not been observed except that the change of the contours, upon applying an electric field or upon reversing the field direction, progresses faster when the temperature is higher. This is natural because the response of the molecular cluster in an electric field becomes more rapid owing to a decrease in the viscosity of the solution (see Ref. 12).

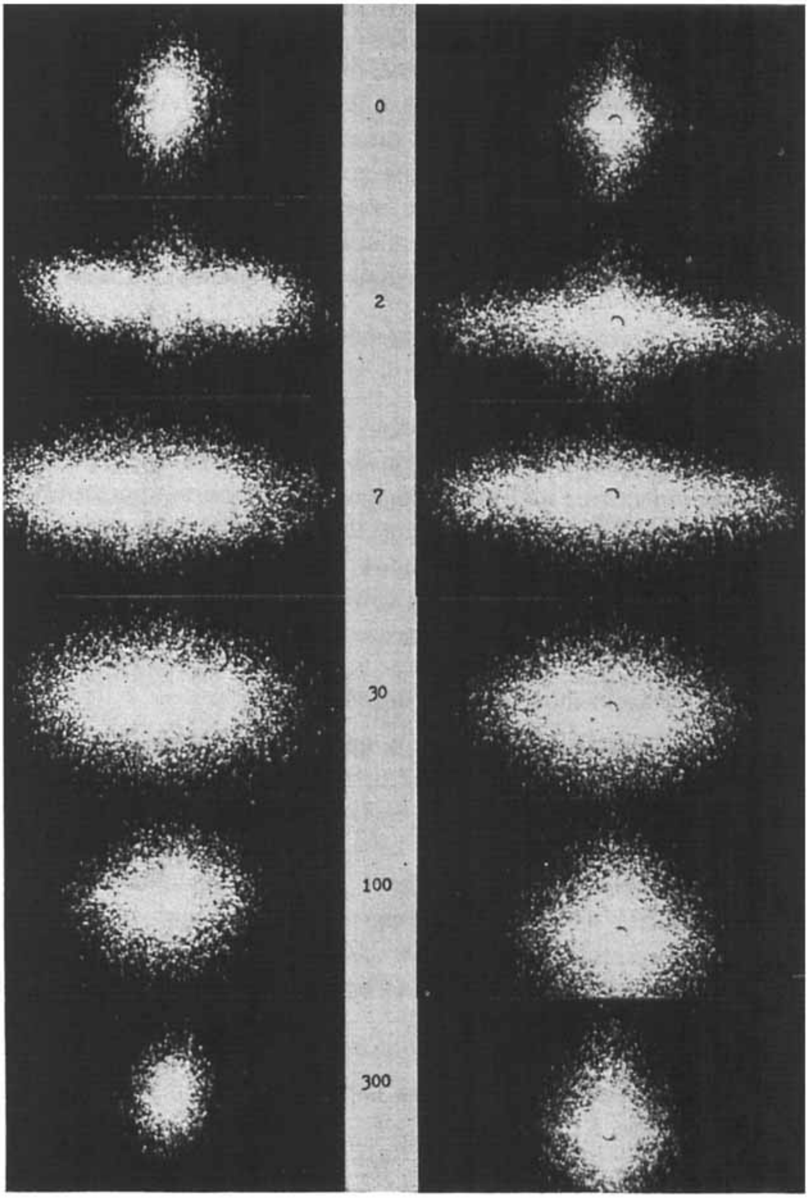
b) *Polymer concentration and solution thickness*

When the polymer concentration is increased or when the solution thickness is increased, the profile of both the V_h and the H_h scattering patterns does not seem to change basically, but the patterns become less sharp and ambiguous as may be seen in Fig. 12. This would be due to a multiple scattering of light by the molecular clusters in liquid crystalline solutions. Spacing of the lines that appear upon reversing the direction of the external field decreases at the same time, the reason for which is still to be determined.

OTHER LIQUID CRYSTALLINE SOLUTIONS

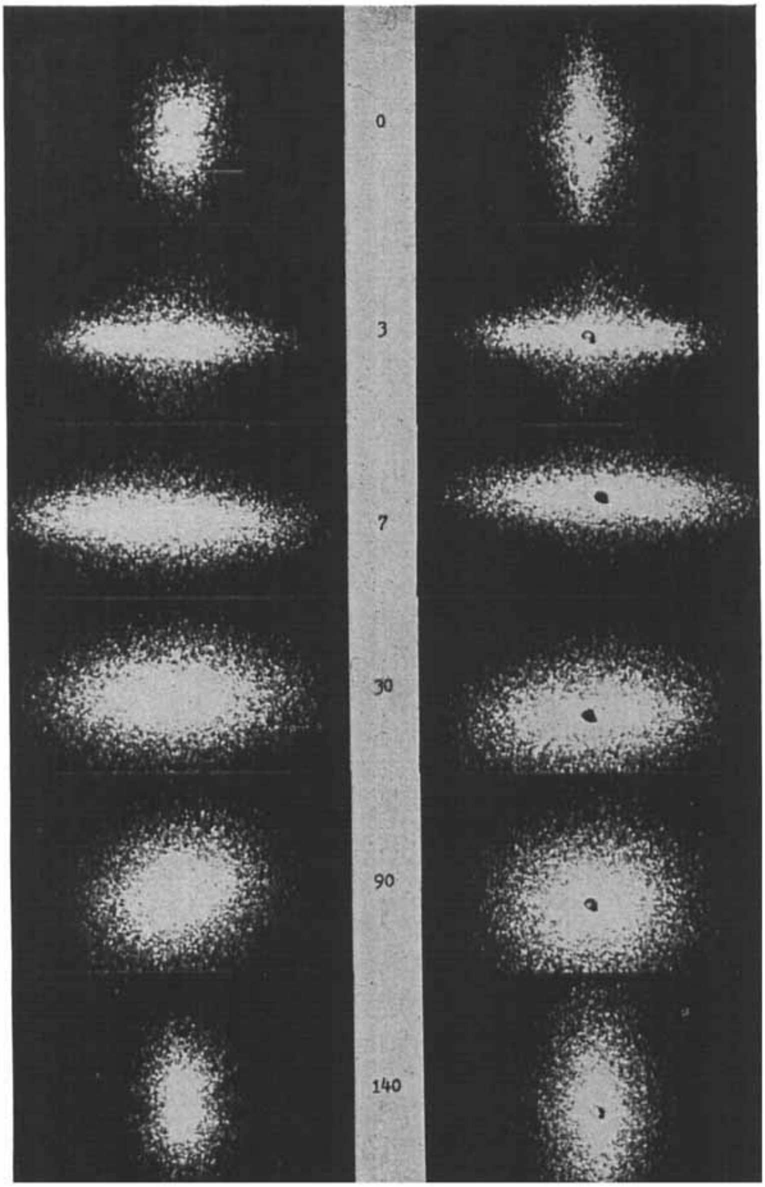
a) *Chloroform solution of PBLG and* CM_2Br_2 *solution of a* 1 : 1 *mixture of PBLG and PBDG*

No differences in the V_h and the H_h scattering patterns among a 14 vol % PBLG solution in chloroform, a 14 vol % racemic solution of equal proportions of PBLG and PBDG in CH_2Br_2 and the previous 14 vol % PBLG solution in CH_2Br_2, has been observed when measured in an electric field of 169 V/cm. This indicates that in these solutions the liquid crystalline structure and the processes of orienta-



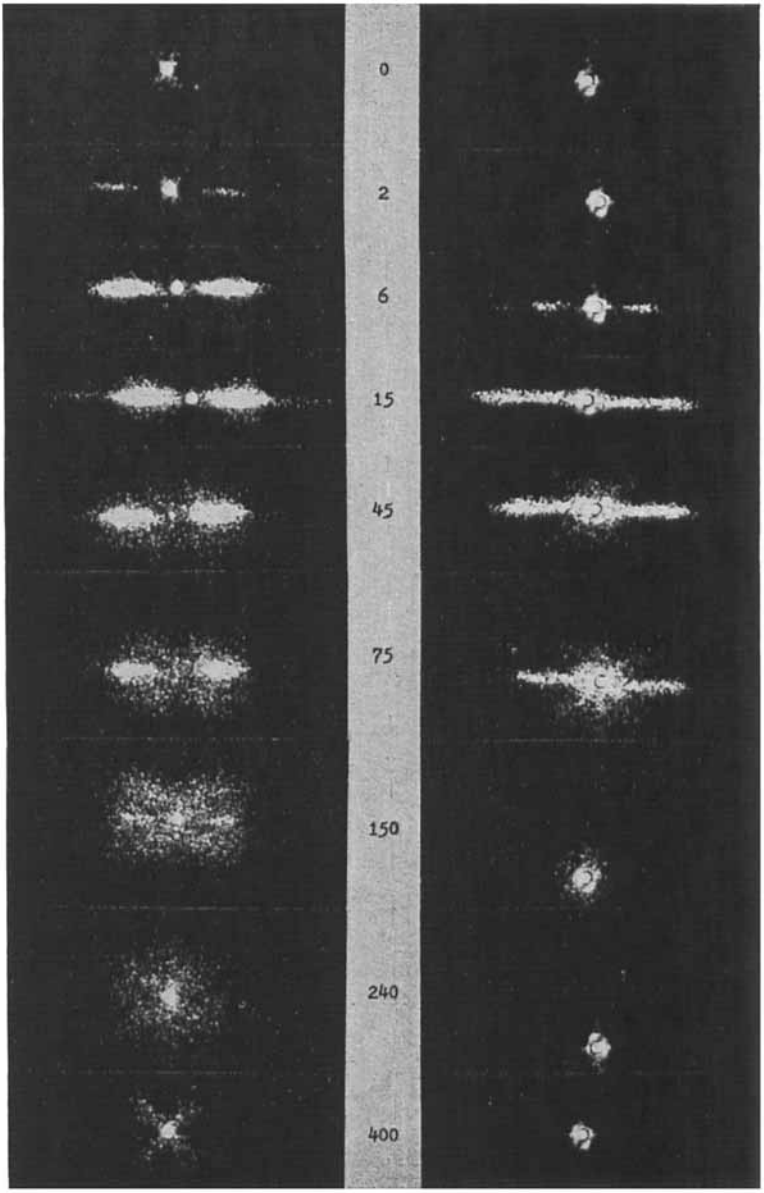
(a)

Figure 12. Change of the V_h (left) and the H_h (right) scattering patterns by liquid crystalline solution of PBLG when the direction of the external electric



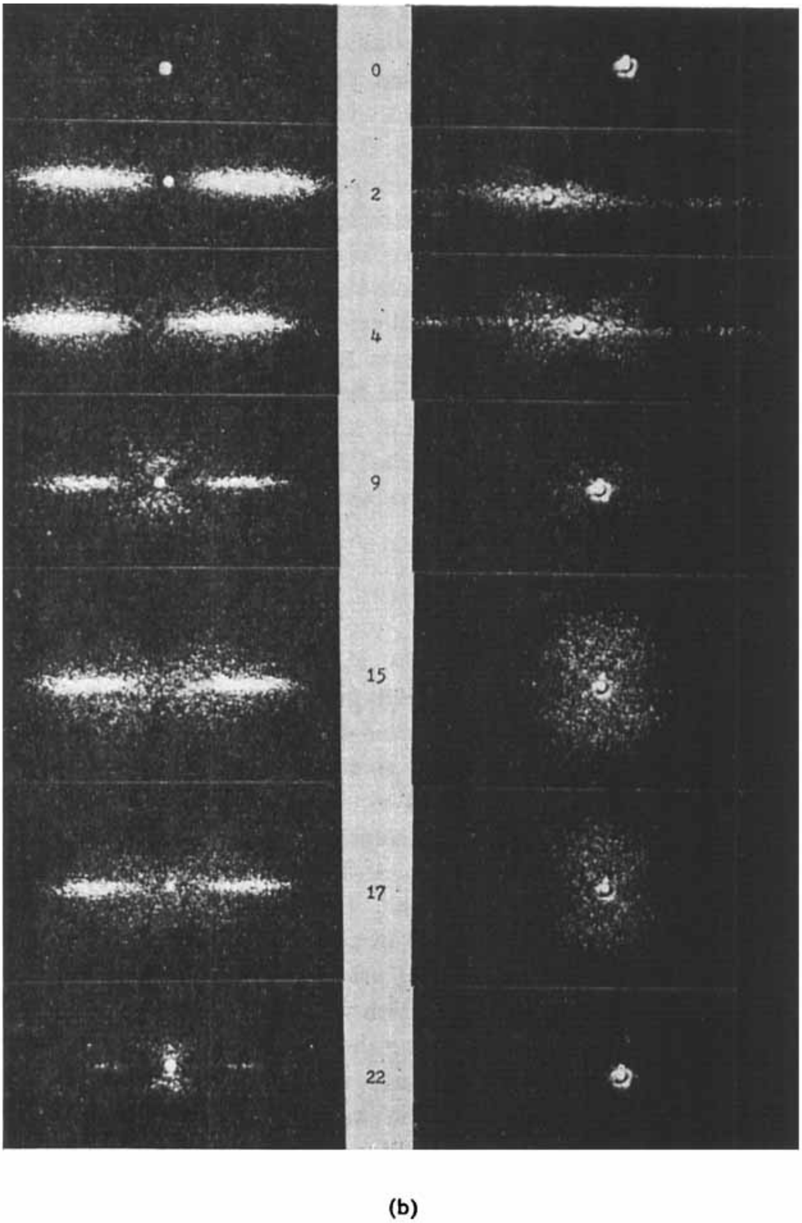
(b)

field (169 V/cm) is reversed. The numbers, same as in Fig. 1. (a) concentration, 24 vol %; (b) solution thickness, 1.00 mm.



(a)

Figure 13. Change of the V_h (left) and the H_h (right) scattering patterns by equimolar racemic liquid crystalline solution of PBLG and PBDG when the



direction of the external electric field is reversed. The numbers, same as in Fig. 1. Electric field: (a) 169 V/cm; (b) 394 V/cm.

tion and reversal of the molecular clusters in a static electric field are the same. To avoid confusion only typical scattering patterns of the racemic solution taken when the direction of the external field is reversed are shown in Fig. 13. It may clearly be noticed that the scattering patterns, especially the V_h patterns, taken in an electric field of 394 V/cm are different from those taken in the electric field of 169 V/cm. The sign of such difference has also been observed in the previous PBLG solution in CH_2Br_2 though not pointed out there. This difference corresponds to the idea proposed a little while ago that when ordering of the liquid crystalline solution proceeds the molecular cluster structure becomes gradually destroyed to form the nematic structure. The critical field strength to cause such a difference, say about 300 V/cm, is in agreement with that observed by Toth and Tobolsky(4) as a critical field above which the transmittance of light through liquid crystalline solutions of PBLG begins to decrease.

b) *Dioxane solutions of PBLG*

Figure 14 shows the steady-state V_h and the steady-state H_h scattering patterns and the polarizing micrographs of a 11 vol % liquid crystalline solution. The cross-shaped V_h pattern similar to that of the other solutions stated so far does not appear until the external electric field is raised up to, say 1125 V/cm. Still in this electric field no orientation of the solution has been observed by the measurement of the dichroic ratio, and the profile of the polarizing micrograph does not change much. The infrared dichroic ratio at 3300 cm^{-1} of this solution was 1.3 in an electric field of 2500 V/cm, indicating a weak ordering of the solution; no change in the dichroic ratio upon reversing the field direction was observed. The angle of ϕ becomes smaller, but upon reversing the field direction the scattering patterns show only a slight change as may be seen in Fig. 15. Orientation of the solution would be caused by induced dipoles of the polymers or by electric current through the solution, or by both. Figure 16 shows this current and is presented here by way of suggestion. The way of polymer association in the molecular cluster may be of antiparallel type and the permanent dipole moments of the polymers counterbalance each other.

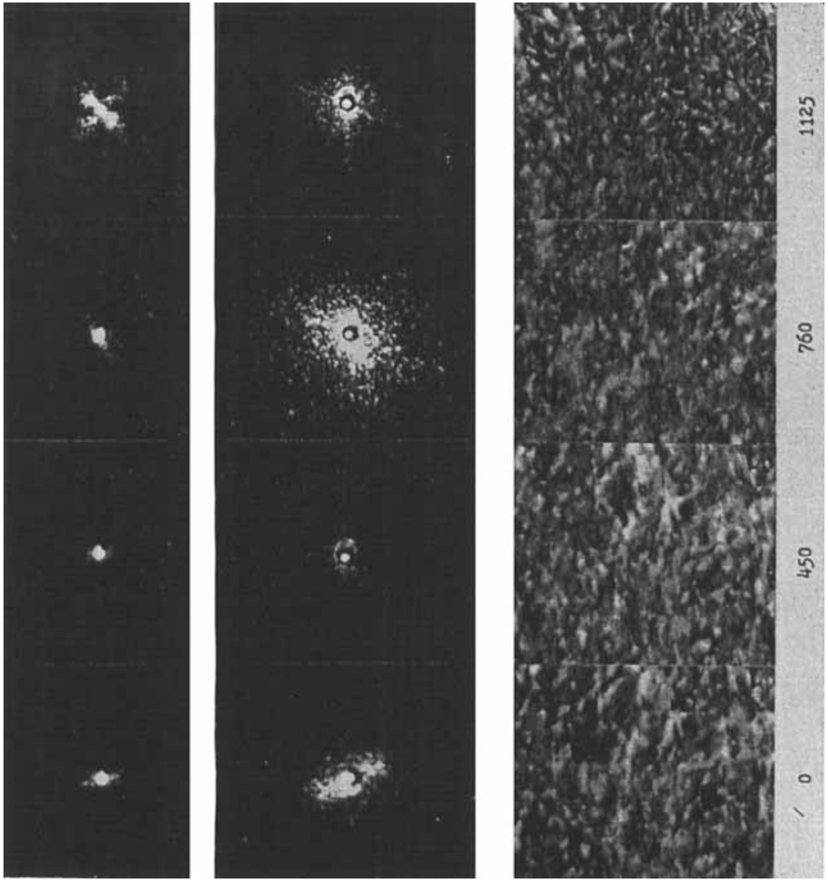


Figure 14. Dependence of the V_h pattern (upper), of the H_h pattern (middle) and of the pattern of the polarizing micrograph (lower) of a liquid crystalline solution of PBLG upon strength of the external electric field. Solution thickness, 0.10 mm. The numbers, same as in Fig. 3. Solvent (dioxane) and polymer concentration (11 vol %) are the same throughout Figs. 14–21.

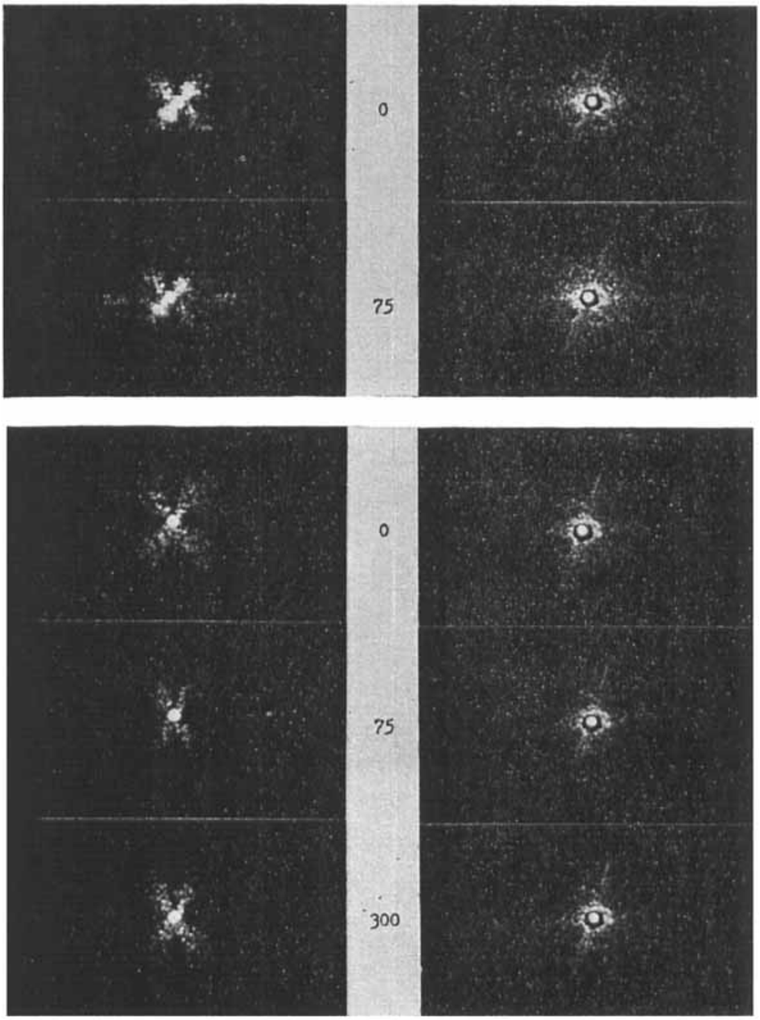


Figure 15. Change of the V_h (left) and the H_h (right) scattering patterns by liquid crystalline solution of PBLG when the direction of the external electric field is reversed. Solution thickness, 0.10 mm. The numbers, same as in Fig. 1. Electric field: upper, 1125 V/cm; lower, 2500 V/cm.

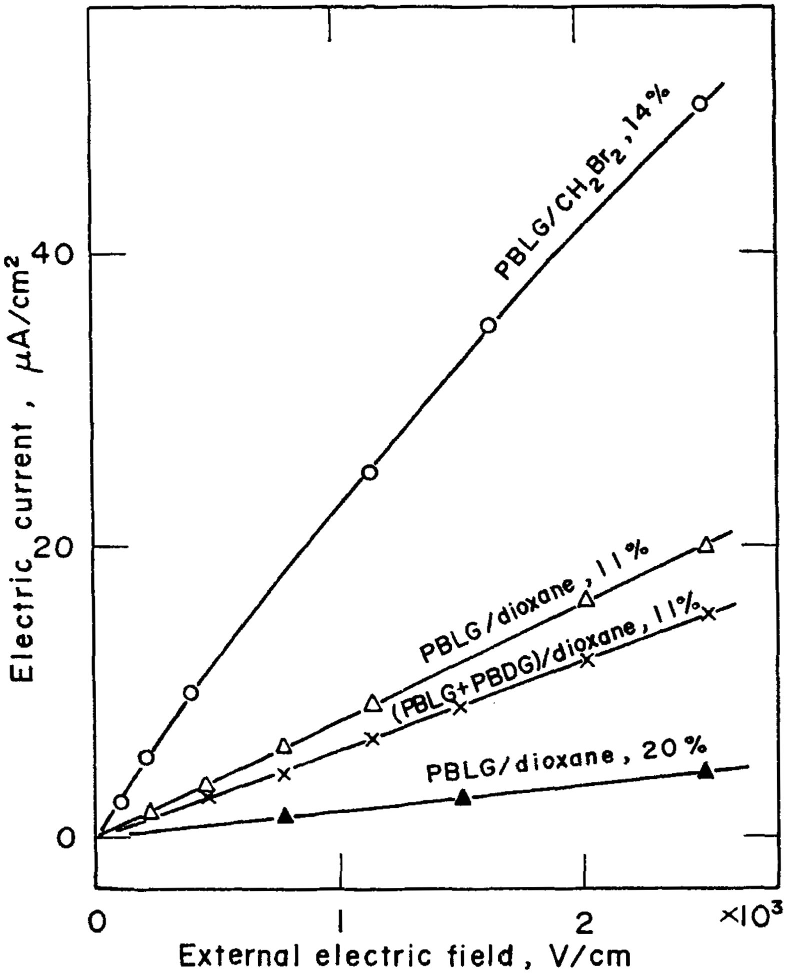


Figure 16. Electric current vs. external electric field for various liquid crystalline solutions.

It has been known that when the thickness of the liquid crystalline solution of PBLG is beyond 0.25 mm a cholesteric structure is formed as was suggested by Robinson.⁽¹⁾ Visible equidistant lines, associated with an oscillating value of retardation, are shown by the cholesteric solution when observed with incident light perpendicular to the axis of the helicoidal structure. The very large periodicities in the ability of passing light make it possible to obtain diffraction patterns with

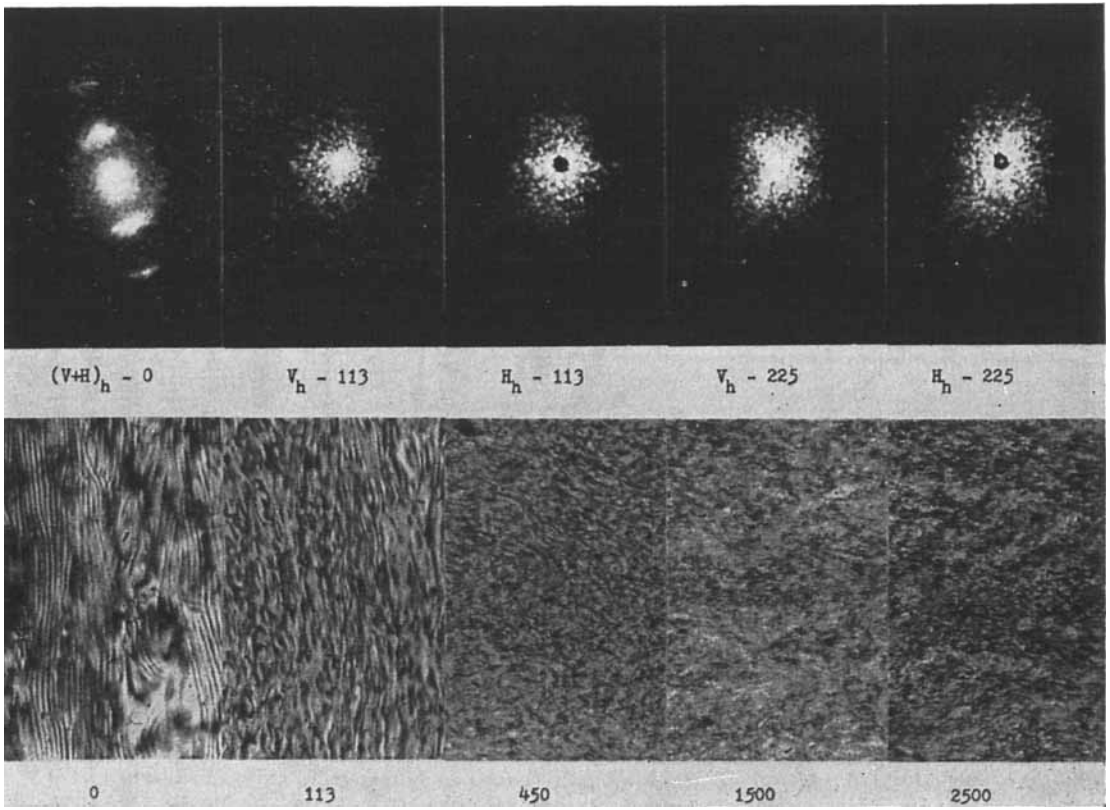


Figure 17. Light scattering patterns (upper) and polarizing micrographs (lower) of liquid crystalline solution of PBLG. Solution thickness, 0.10 mm. The numbers, same as in Fig. 3.

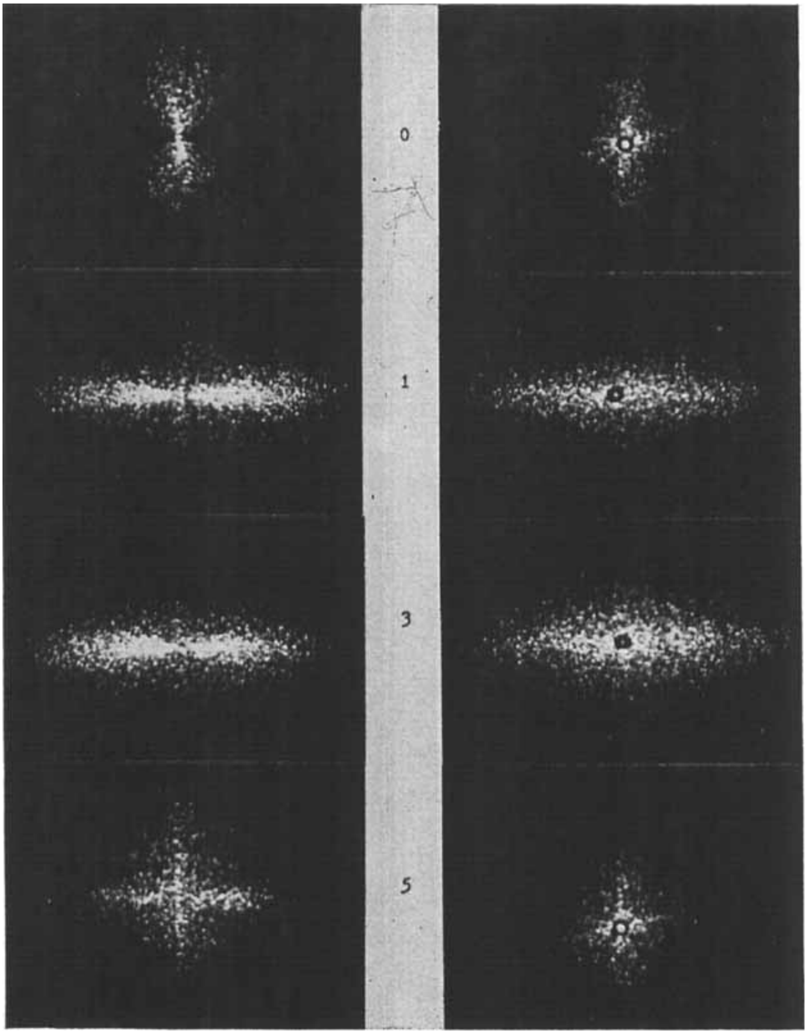


Figure 18. Change of the V_h (left) and the H_h (right) scattering patterns by liquid crystalline solution of PBLG when the direction of the external electric field (2500 V/cm) is reversed. Solution thickness, 1.00 mm. The numbers, same as in Fig. 1.

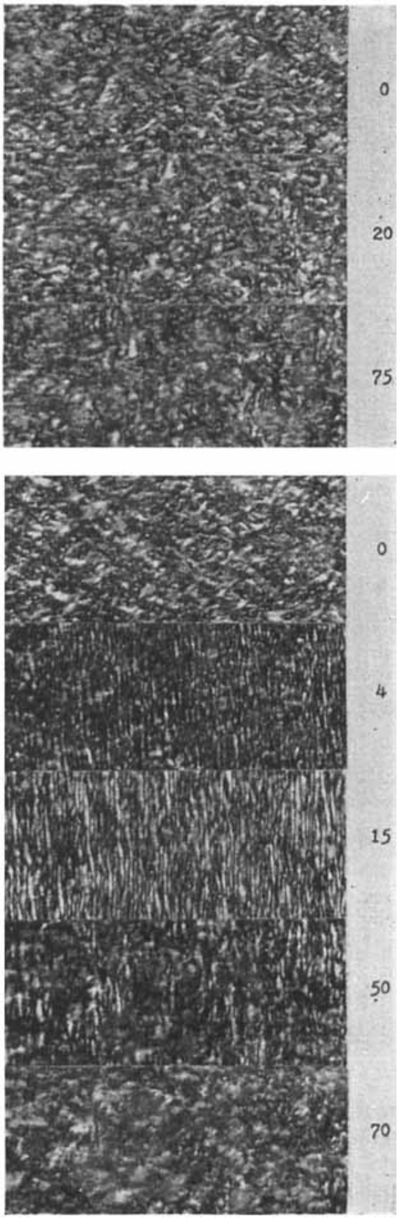


Figure 19. Change of the polarizing micrograph of liquid crystalline solution of PBLG when the direction of the external electric field is reversed. Solution thickness, 1.00 mm. The numbers, same as in Fig. 1. Electric field: upper, 1125 V/cm; lower, 2500 V/cm.

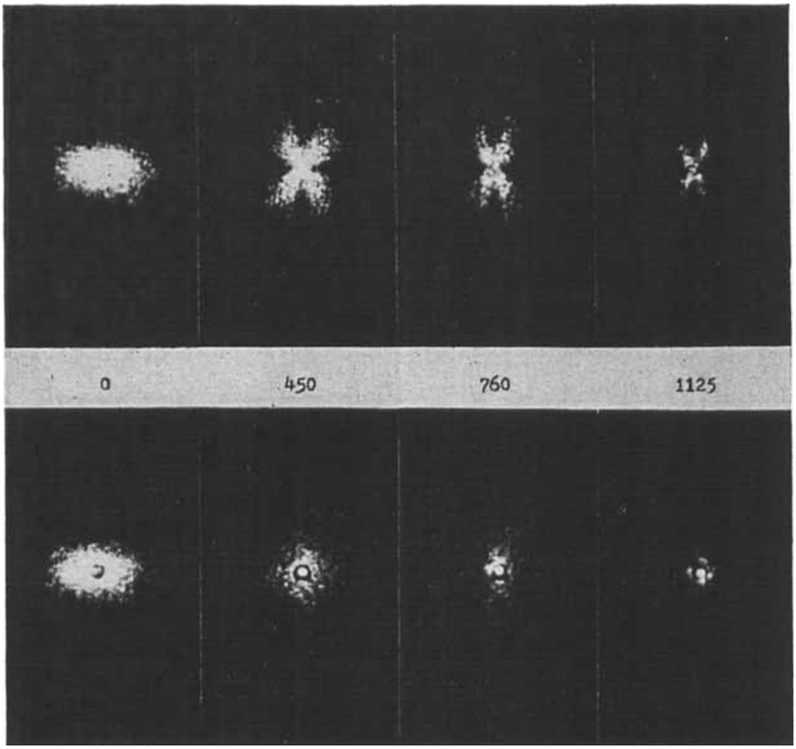


Figure 20. Dependence of the V_h (left) and the H_h (right) scattering patterns by liquid crystalline solution of equal proportions of PBLG and PDBG upon strength of the external electric field. Solution thickness, 1.00 mm. The numbers, same as in Fig. 3.

visible light. The cholesteric structure formed when the solution thickness is 1.00 mm is destroyed in an electric field of 113 V/cm when judged by the diffraction patterns. Under crossed polaroids, however, the remains of the cholesteric structure are still observed as may be seen in Fig. 17. When the electric field is high enough, say 2500 V/cm, the steady-state scattering patterns differ considerably from those observed when the solution thickness is 0.10 mm, fluctuating continuously probably due to electric current through the solution. Typical V_h and H_h patterns and the polarizing micrographs taken when the field direction is reversed are shown in

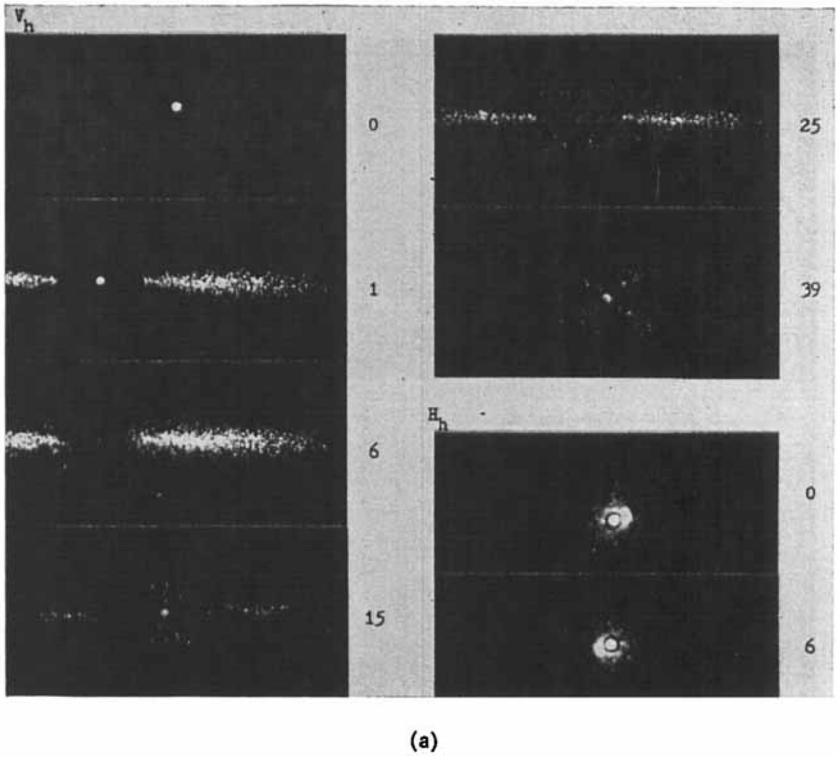
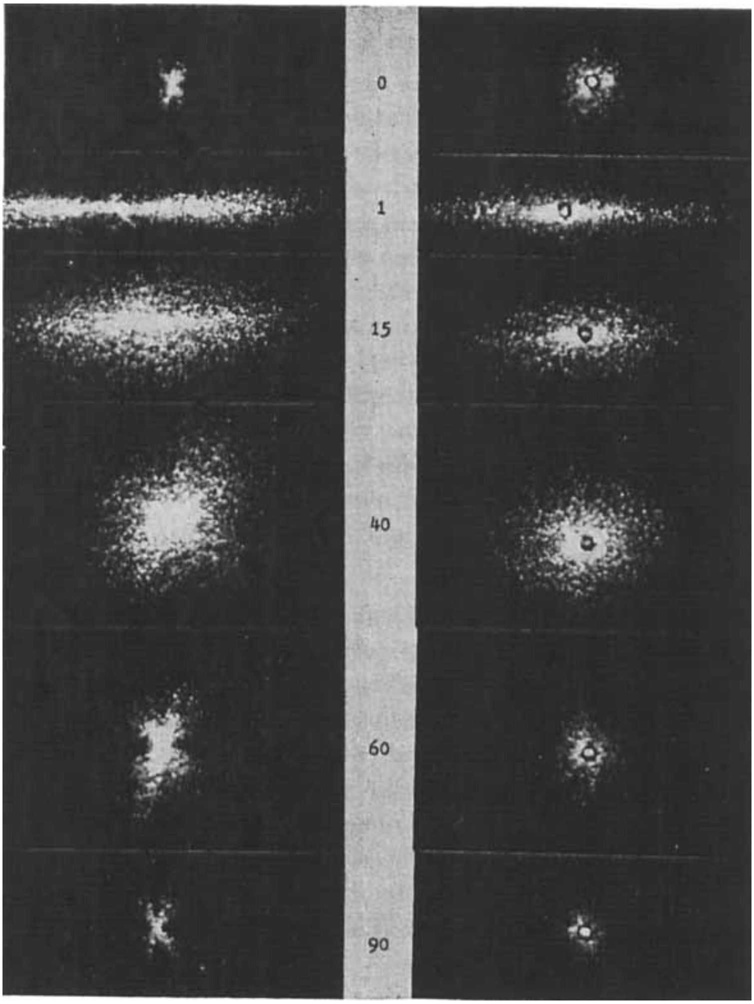


Figure 21. Change of the V_h (left) and the H_h (right) scattering patterns by liquid crystalline solution of equal proportions of PBLG and PBDG when the direction of the external electric field (2500 V/cm) is reversed. The numbers, same as in Fig. 1. Solution thickness: (a) 0.10 mm; (b opposite) 1.00 mm.

Figs. 18 and 19, respectively. Change of the scattering mode upon reversing the field direction appears this time. Vertical equidistant lines also appear though not regular unlike the other solutions already stated. It was impossible to confirm whether the reversal of the molecular clusters occurred or not because the solution thickness is large.



(b)

(c) *Dioxane solution of a* 1 : 1 *mixture of PBLG and PBDG*
It has been known that racemic solutions containing equal proportions of PBLG and PBDG do not form the cholesteric structure even when the solution thickness is 1.00 mm. The V_h ± 45° pattern appears when measured in an electric field of 450 V/cm for a 11 vol % solution as may be seen in Fig. 20. The infrared dichroic

ratio at 3300 cm^{-1} began to increase from unity at this field strength and was 1.3 in an electric field of 2500 V/cm when measured with the solution thickness 0.10 mm, the molecular cluster reversal process not being observed. The correlation of the azimuthal dependence of the V_h scattering and the dichroic ratio is observed as in the other solutions with the high dielectric solvent, but in a different way, suggesting that the molecular arrangement in the cluster is different. A drastic change of the scattering contours upon reversing the field direction does not appear until the field strength is raised up to, say 2500 V/cm. Aspect of the change seems to differ from those seen in any of the liquid crystalline solutions tested as is shown in Fig. 21. The drastic change in the scattering contours upon reversing the field direction proves not to be necessarily an indication of the reversal of the molecular clusters in this case. Further discussion will be hazardous at the present moment.

4. Concluding Remarks

Formation of the rod-like molecular clusters in liquid crystalline solutions of PBLG or of equal proportions of PBLG and PBDG under a static electric field has been sufficiently conditioned and an estimation has been given of their dimensions. The degree of the polymer orientation in the liquid crystalline solutions with high dielectric solvent is estimated by the light scattering method. Beyond a critical field, say 300 V/cm, the molecular cluster structure seems to begin to be destroyed to form the nematic structure. The structure of liquid crystalline solutions in dioxane are different from that formed in a high dielectric solvent such as CH_2Br_2 or chloroform.

Acknowledgements

This work was aided mostly by grants from Japan Society for the Promotion of Science and carried out mostly at Wada's laboratory in the University of Tokyo. Some parts of this paper are used as a part of the Ph.D. thesis by the second author (T.K.) of this paper.

REFERENCES

1. Robinson, C., *Trans. Faraday Soc.* **52**, 571 (1956).
2. Frenkel', S. Ya., Shaltyko, L. G. and Elyashevich, G. K., *J. Polymer Sci. C.* **30**, 47 (1970).

3. Powers, J. C., Jr. and Peticolas, W. L., *Ordered Fluids and Liquid Crystals* (R. S. Porter and J. F. Johnson, eds.), Washington, D. C.: Am. Chem. Soc. (1966), p. 217.
4. Toth, W. J. and Tobolsky, A. V., *Polymer Letters* **8,** 531 (1970).
5. Stamatoff, J. B., *Mol. Cryst. and Liq. Cryst.* **16,** 137 (1972).
6. Rhodes, M. B. and Stein, R. S., *J. Polymer Sci. A-2.* **7,** 1539 (1969).
7. Stein, R. S. and Keane, J. J., *J. Polymer Sci.* **17,** 21 (1955).
8. Stein, R. S., Rhodes, M. B. and Porter, R. S., *J. Colloid and Interface Sci.* **27,** 336 (1968).
9. Rhodes, M. B., Keedy, D. A. and Stein, R. S., *J. Polymer Sci.* **62,** S73 (1962).
10. Wallach, M. L., *J. Polymer Sci. C.* **13,** 69 (1966).
11. Iizuka, E., *Biochim. Biophys. Acta* **175,** 457 (1969).
12. Iizuka, E., *Biochim. Biophys. Acta* **243,** 1 (1971).
13. Iizuka, E. and Go, Y., *J. Phys. Soc. Japan* **31,** 1205 (1971).
14. Wade, A., *J. Polymer Sci.* **45,** 145 (1960).
15. Robinson, C., Ward, J. C. and Beevers, R. B., *Disc. Faraday Soc.* **25,** 29 (1958).
16. Stidham, S. N. and Stein, R. S., *J. Polymer Sci. A-2.* **4,** 89 (1966).
17. Tsuboi, M., *J. Polymer Sci.* **59,** 139 (1962).
18. Clough, S., van Aartsen, J. J. and Stein, R. S., *J. Appl. Phys.* **36,** 3072 (1965).
19. Wilkes, G. L., *Mol. Cryst. and Liq. Cryst.* **18,** 165 (1972).
20. Heilmeier, G. H., *J. chem. Phys.* **44,** 644 (1966).
21. Kratky, O., *Kolloid Z.* **44,** 213 (1933).
22. Bragg, W. L. and Pippard, A. B., *Acta Cryst.* **6,** 865 (1953).
23. Moritani, M., Hayashi, N., Utsuo, A. and Kawai, H., *Polymer J.* **2,** 74 (1971).
24. Frank, F. C., *Disc. Faraday Soc.* **25,** 19 (1958).
25. Groupe des Cristaux d'Orsay, *La Recherche* **2,** 433 (1971).
26. Honda, M., Suzuki, H. and Kato, T., *Repts. Progr. Polym. Phys. Japan* **14,** 607 (1971).