

Molecular orientation behaviour of uniaxially stretched poly(vinyl chloride) film: 2. The fourth moment of molecular orientation measured by the polarized fluorescence method

Sadao Hibi, Matsuo Maeda, Hisao Kubota and Teruo Miura

Fiber and Polymer Engineering Technology, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya, Japan

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In order to measure the fourth moment of molecular orientation of poly(vinyl chloride) film a new polarized fluorescent method is examined. The fundamental principle of the method is to employ the polyene and the carbonyl radicals formed in the molecular chain, at the working process or with heat treatment, instead of a fluorescent dyestuff. It is necessary, in this method, to estimate the ratio of polyene to carbonyl in the sample, and the value is found to be 1.5 for unheat treated PVC film or 1.0 for heat treated PVC film. The second moment $\langle \cos^2 \theta \rangle$ and the fourth moment $\langle \cos^4 \theta \rangle$ are evaluated from the fluorescence intensity pattern. The applicability of this method is verified by comparison with the second moment derived from the birefringence. Dependence of deformation mechanism on draw temperature and plasticizer content are also investigated on the basis of a structural model composed of the characterized molecular chain, the practicability of which was already established by observations of the change in birefringence with draw ratio.

INTRODUCTION

There are mainly two methods used to measure the fourth moment on the statistical distribution of amorphous polymer chains; polarized fluorescence method¹ and n.m.r. method².

In the case of the n.m.r. method however a particular knowledge of the structure is necessary in order to determine the position of the nuclei which give rise to the magnetic moment.

Similarly we can evaluate the fourth and the second moments by the polarized fluorescence method, and moreover the principle of the evaluation is similar to the visible dichroism method. Generally, in practice this method is carried out by dyeing with a fluorescent dyestuff^{3,4} and consequently it needs much cumbersome work to evaluate the exact relationship between axis and that of the dyestuff.

On the other hand, if we use fluorescent emission of polyene and carbonyl groups in a polymer chain produced by treating with heat, the results of the experiment may more exactly reflect the actual behaviour of the polymer chain⁵.

Because, with PVC the bifunctional resonance system consisting of polyene-carbonyl can be readily produced by heat treatment we may investigate directly the molecular orientation behaviour of PVC, using the polarized fluorescence method.

In this paper, uniaxially stretched PVC film was selected as an example in order to investigate the orientation behaviour of a non-crystalline chain and the molecular orientation behaviour by the polarized fluorescence method.

ANALYSIS OF POLARIZED FLUORESCENCE INTENSITY WITH A MODEL

Postulation of the orientation distribution function

This method, as well as other methods mentioned above cannot be used directly to estimate the orientation distribution of molecular chains; in order to estimate the value n —the ratio of polyene to carbonyl—molecular distribution function we must, therefore, postulate the function. According to the previous paper⁶ (part 1 in the series), the following molecular orientation distribution functions are considered.

(a) Unplasticized film obeys affine deformation mechanism when drawn below its glass transition temperature T_g , but if the film is stretched above its T_g the deformation mechanism follows from a compound distribution which consist of affine deformation corresponding to a rigid rod-like chain and Langevin chain type distribution, presented by Roe *et al.*⁷, corresponding to flexible chain.

The formulae for the compound distribution is the same as that used in part 1 and the parameters included; viz. the ratio of the two kinds of chain, segment number of Langevin chain, are listed in *Table 1*. For a commercial film, nominally unplasticized, the parameters are determined independently by the same procedure and are tabulated in *Table 2*.

(b) Plasticized film obeys the compound distribution mentioned above and the parameters in this distribution are listed in *Table 1*.

Analysis of fluorescence intensity

It is well-known that when poly(vinyl alcohol) (PVA) or PVC are subjected to annealing or thermal degradation

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Table 1 Characteristic values and deformation mechanisms applied to the calculation of the fluorescence intensity of the plasticized and the unplasticized film. θ_j is the contact angle of the fluorescent group with the chain axis

Sample	Draw temperature (°C)	n	θ_1^0	θ_2^0	Deformation mechanism	Segment number, N	Ratio (affine: Langevin)
D	65	1.5	20	90	affine	—	—
C	65	1.5	20	90	a + L	6	60:40
B	65	1.5	20	90	a + L	6	60:40
A	65	1.5	20	90	a + L	7	60:40
D	110	1.5	20	90	a + L	10	70:30
C	110	1.5	20	90	a + L	10	50:50
B	110	1.5	20	90	a + L	10	50:50
A	110	1.5	20	90	a + L	20	50:50

n = Polyene/carbonyl group; a + L = affine + Langevin

Table 2 The characteristics for the commercial, nominally unplasticized, film heat treated at 175°C for 60 min

Sample	Draw temperature (°C)	n	θ_1^0	θ_2^0	Deformation mechanism	Segment number, N	Ratio (affine: Langevin)
175°C anneal	65, 80	1.0	20	90	affine	—	—
	110, 125	1.0	20	90	a + L	8	50:50

n = Polyene/carbonyl group; a + L = affine + Langevin

polyene and carbonyl groups are formed in the molecular chains⁸⁻¹². It has also been reported that fluorescence emission occurs in the samples containing the above groups.

Considerable differences, however, have been recognized between a drawn film, having polyene and carbonyl groups, and one drawn after dyeing with fluorescence dyestuff¹³. The fluorescence intensity of the former shows a pattern like that of biaxially stretched sample. It has been reported that the perpendicular component in the pattern, $I_{\perp}(90^\circ)$, becomes larger, but an explanation of the cause has not been made. It is reasonable to think that resonance emission occurred between the polyene and carbonyl groups in the film.

On the basis of the above consideration, we have used a model to analyse the fluorescence intensity by summation of the contribution of the carbonyl and polyene groups which are perpendicular to or nearly parallel with the main chain.

According to Roe's method¹⁴, the fluorescence intensity of a uniaxially drawn sample, with cylindrical symmetry about extension axis, is given by:

$$I = 4\pi^2 k \left(\frac{2}{2l+1} \right)^{1/2} \sum_{l=0}^4 N_{l0} W_{l00} \Pi_l(\cos \theta) \quad (1)$$

where

$$\Pi_l(\cos \theta) = \left(\frac{2l+1}{2} \right)^{1/2} P_l(\cos \theta)$$

is the normalized Legendre's function and W_{l00} relates to the orientation factor given by:

$$F_{l00} = \langle P_l(\cos \theta) \rangle = \left(\frac{2}{2l+1} \right)^{1/2} 4\pi^2 W_{l00} \quad (2)$$

Since k is a constant peculiar to the apparatus and measuring method, and the coefficients N_{l0} may be determined

as shown later, the orientation factor may be calculated from the above equation.

If we denote the direction of polarization of a fluorescence radical which absorbs and emits polarized light (the vibration axis of the emission and absorption light), the electric vector of linearly polarized light and the electric vector of polarized light being permitted to pass through the analyser, by the notations A_j , P_1 and P_2 ; the fluorescence intensity of the polarized light is given by^{14,15}:

$$i_A = k \cos^2 \widehat{A_j P_1} \cos^2 \widehat{A_j P_2} \quad (3)$$

for a reference fluorescent radical, where $\widehat{A_j P_1}$ and $\widehat{A_j P_2}$ are angles between A_j and P_1 or A_j and P_2 , respectively.

By expanding i_A in a series of spherical harmonics, we get:

$$i_A = k \sum_{l=0}^4 N_{l0} \Pi_l(\cos \theta_j) \quad (4)$$

from cylindrical symmetry of the orientation distribution, the suffix j indicates the j th fluorescent radical.

If we use equations (3) and (4) and refer to Figure 1, N_{l0} are given as follows:

$$N_{00} = \frac{(2)^{1/2}}{15} (2 \cos^2 \widehat{P_1 P_2} + 1)$$

$$N_{20} = \frac{(10)^{1/2}}{105} [2 \cos^2 \widehat{P_1 P_2} + 1 + 9 \cos(\beta_1 - \beta_2) \times \cos(\beta_1 + \beta_2) + 6 \sin^2 \beta_1 \sin^2 \beta_2 \sin^2(\alpha_1 - \alpha_2)]$$

$$N_{40} = \frac{(2)^{1/2}}{105} [-8 \cos^2 \widehat{P_1 P_2} - 4 + 20 \cos^2 \beta_1 \cos^2 \beta_2 + 10 \sin^2 \beta_1 \sin^2 \beta_2 + 5 \sin^2 \beta_1 \sin^2 \beta_2 \cos 2(\alpha_1 - \alpha_2)] \quad (5)$$

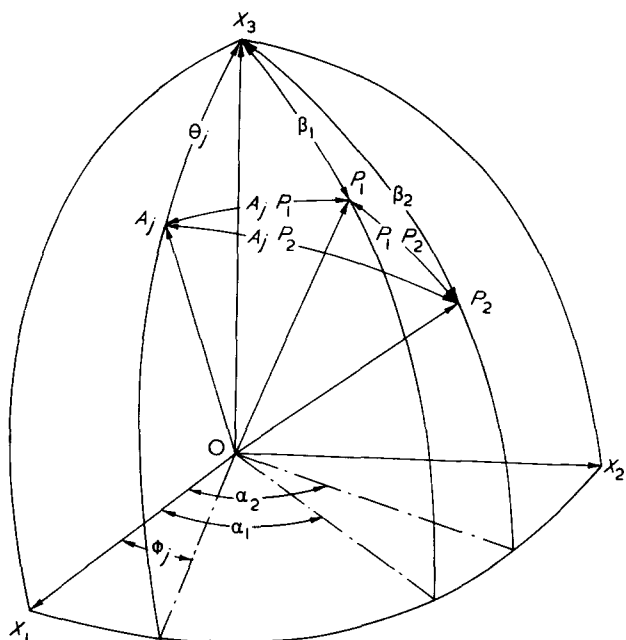


Figure 1 Angular relations between polarizer, analyser and fluorescent radical, relating to the fixed coordinates ($O - X_1, X_2, X_3$) with X_3 axis parallel with the draw axis

Furthermore, W_{l00} are averages of Legendre's functions with respect to the orientation distribution function $w(\theta, \phi, \eta)$ of the structural unit (the chain axis); therefore we can evaluate W_{l00} by assuming $w(\theta, \phi, \eta)$. Accordingly, using equations (1) and (5), we can theoretically estimate the fluorescence intensity for the assumed distribution function. The geometrical meaning of the notations Θ_j , Φ_j , θ , ϕ and η are illustrated in Figures 1 and 2 with respect to the rectangular coordinates $o - X_1, X_2, X_3$ fixed in the sample; u_1, u_2 and u_3 denote the principal axes of the structural unit (axis u_3 being coincident with the chain axis) and $o - X_3$ and $o - X_1$ are parallel with the draw and the thickness direction respectively. Since it is clear that W_{l00} in equation (1) corresponds to the coefficient W_l in Roe's equation⁷ (refer to equation (2) in part 1) from its definition, each segment in the Langevin chain can be regarded as a structural unit and the angle of segment to the extension axis may be treated as being the same as θ .

Calculation of fluorescence intensity on reflection method

The electric vector of the incident polarized light can be split up into two parts, one perpendicular to and the other parallel to the incident plane.

Theoretical calculation shows that the fluorescence intensity patterns obtained from the two components are similar. The calculation is omitted here for brevity and indispensable formulae for the calculation of the perpendicular component are given below.

(a) The intensity distribution $I_{\parallel}(\beta_i)$ for the case of P_1 and P_2 being parallel: since $\beta_1 = \beta_2$ and $\alpha_1 = \alpha_2 = \pi/2$ in Figure 1, the coefficients N_{l0} shown by equation (5) are given by:

$$N_{00} = \frac{(2)^{1/2}}{5}, \quad N_{20} = \frac{(10)^{1/2}}{35} (1 + 3 \cos 2\beta_1)$$

$$N_{40} = \frac{(2)^{1/2}}{105} (-12 + 20 \cos^4 \beta_1 + 15 \sin^4 \beta_1) \quad (6)$$

and then substitution of the above results into equation (1) leads to:

$$I_{\parallel}(\beta_1) = \frac{k}{35} [8P_4(\cos \beta_1)P_4(\cos \Theta_j)F_{400} + 20P_2(\cos \beta_1)P_2(\cos \Theta_j)F_{200} + 7] \quad (7)$$

(b) The intensity distribution $I_{\perp}(\beta_i)$ for the case of P_1 and P_2 being normal:

$$N_{00} = \frac{(2)^{1/2}}{15}, \quad N_{20} = \frac{(10)^{1/2}}{105},$$

$$N_{40} = \frac{(2)^{1/2}}{105} (35 \cos^2 \beta_1 \sin^2 \beta_1 - 4) \quad (8)$$

because

$$\beta_1 + \pi/2 = \beta_2$$

and

$$\alpha_1 = \alpha_2 = \pi/2,$$

and then

$$I_{\perp}(\beta_1) = k \left[-\frac{8}{35} P_4(\cos \beta_1)P_4(\cos \Theta_j)F_{400} + \frac{2}{21} P_2(\cos \beta_1)P_4(\cos \Theta_j)F_{400} + \frac{2}{105} P_4(\cos \Theta_j)F_{400} + \frac{1}{21} P_2(\cos \Theta_j)F_{200} + \frac{1}{15} \right] \quad (9)$$

In these calculations, we have ignored the effect of birefringence and absorption of light. However, as far as the principal values of fluorescence intensity: $I_{\parallel}, I_{\perp}(\beta)$ at $\beta = 0^\circ$ and 90° ; $I_{\parallel}(90^\circ), I_{\perp}(0^\circ)$ and $I_{\perp}(90^\circ)$, are concerned this treatment may be permissible.

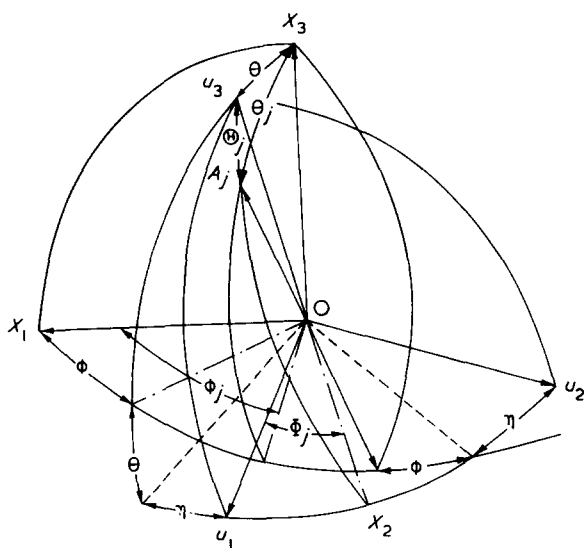


Figure 2 Position of a fluorescent group expressed with respect to the two coordinate systems fixed in the sample and fixed in the structural unit, the main chain direction being specified by unit vector u_3

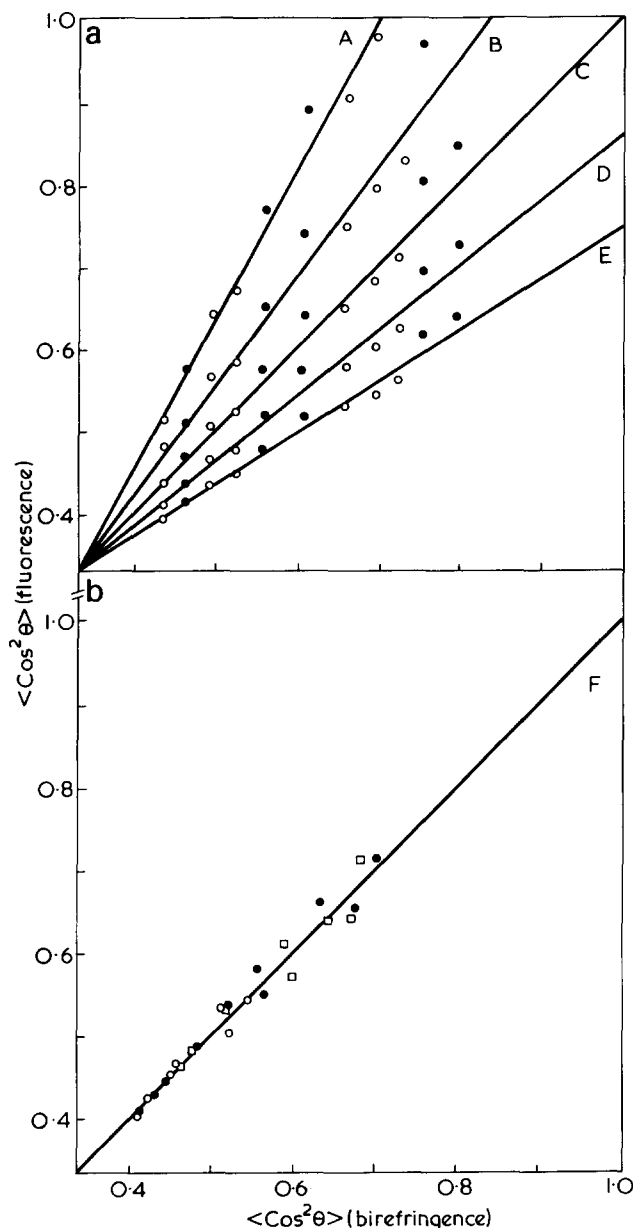


Figure 3 (a) Correlation of $\langle \cos^2 \theta \rangle$ between the values, derived from measured polarized fluorescence intensity with a variable parameter n and the birefringence for the unplasticized films. A, $n = 1.0$; B, $n = 1.2$; C, $n = 1.5$; D, $n = 2.0$; E, $n = 3.0$. Draw temperature: ●, 65°C; ○, 110°C. (b) The correlation between the values of $\langle \cos^2 \theta \rangle$ with a constant parameter $n = 1.5$, for the plasticized film drawn at the different temperature below or above its T_g . Curve F, $n = 1.5$. ○, Sample A; ●, sample B; □, sample C

Actual fluorescence intensity of heat treated PVC film in terms of chemical structure

The structure of polyene, $-(\text{CH}=\text{CH})_n-$, resulting from dehydrochlorination and the formation of carbonyl groups has been observed in the heat treated PVC films used in this experiment by the observation of the infra-red absorption.

It is probably true that the carbonyl radical as well as the conjugate double bond of polyene causes the fluorescence intensity increase until it is detectable because the carbonyl radical acts so as to change electron density to the resonance condition¹⁶. In addition, even all unheat treated samples used in this experiment show enough fluorescence intensity to measure because polyene-carbonyl group may be formed up to about 0.2% in volume during their hot-press procedure. The ratio of polyene to carbonyl, n , alters according to the condition of heat treatment.

In order to obtain the actual fluorescence intensity assuming the applicability of additive property we must modify equations (7) and (9) as follows:

$$I_{\parallel}(\beta_1) = \frac{k}{35} \{ n [8P_4(\cos \beta_1)P_4(\cos \Theta_1)F_{400} + 20P_2(\cos \beta_1)P_2(\cos \Theta_1)F_{200} + 7] + [8P_4(\cos \beta_1)P_4(\cos \Theta_2)F_{400} + 20P_2(\cos \beta_1)P_2(\cos \Theta_2)F_{200} + 7] \} \quad (10)$$

$$I_{\perp}(\beta_1) = k \left\{ n \left[-\frac{8}{35} P_4(\cos \beta_1)P_4(\cos \Theta_1)F_{400} + \frac{2}{21} P_2(\cos \beta_1)P_4(\cos \Theta_1)F_{400} + \frac{2}{105} P_4(\cos \Theta_1)F_{400} + \frac{1}{21} P_2(\cos \Theta_1)F_{200} + \frac{1}{15} \right] + \left[-\frac{8}{35} P_4(\cos \Theta_1)P_4(\cos \Theta_2)F_{400} + \frac{2}{21} P_2(\cos \beta_1)P_4(\cos \Theta_2)F_{400} + \frac{2}{105} P_4(\cos \Theta_2)F_{400} + \frac{1}{21} P_2(\cos \Theta_2)F_{200} + \frac{1}{15} \right] \right\} \quad (11)$$

where Θ_1 and Θ_2 indicate the contact angles of polyene and carbonyl groups with the main chain axis respectively.

We have two unknown parameters, n and F_{100} , in equations (10) and (11). In order to calculate the orientation factor F_{100} , the orientation distribution function of the amorphous chain must be known. Thus, for our samples the distribution function has been postulated as previously described and after calculating F_{200} and F_{400} , these values are substituted into equations (10) and (11).

The value of n probably lies between 1.0 and 1.5¹¹, we first use n as a parameter with value between the above mentioned values, in the calculation of equations (10) and (11) and then determine the best value from the simultaneous equations shown in the Appendix by comparison with the experiment (Figures 3 and 4).

The angles between the polymer chain and fluorescent radicals Θ_1 and Θ_2 are $\Theta_1 = 19.5^\circ$ for polyene, and $\Theta_2 = 90^\circ$ for carbonyl, respectively; these results are obtained by reference to the structural arrangement of the chain. We therefore use the values $\theta_1 = 20^\circ$ and $\theta_2 = 90^\circ$ for the following calculations.

However, since the samples used in this experiment are measured by the reflection method, it is difficult to determine the exact phase angle¹⁷ and we therefore perform the analysis mainly with the principal values; e.g. $I_{\parallel}(0^\circ)$, $I_{\perp}(90^\circ)$ etc. where the effect of birefringence does not occur.

EXPERIMENTAL

Preparation of sample film

Three kinds of PVC film were prepared as samples. The first one was produced without plasticizer by heat pressing

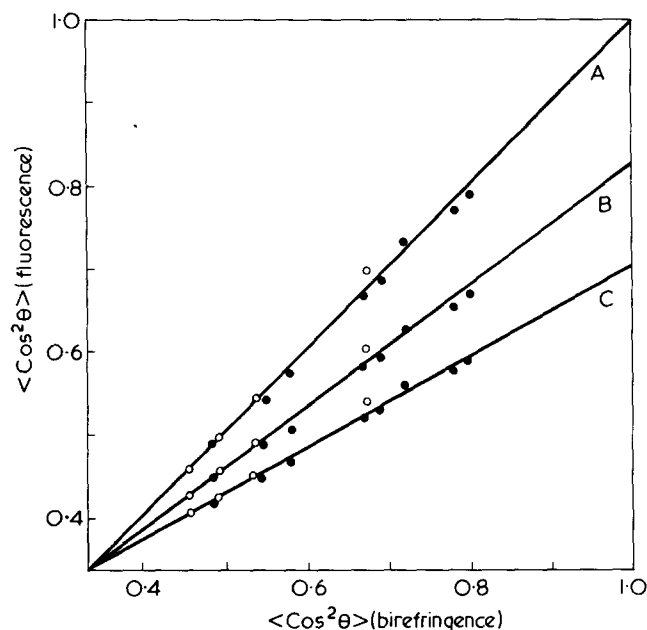


Figure 4 The correlation on $\langle \cos^2 \theta \rangle$ for the heat treated commercial film drawn at the different temperature above or below its T_g . Draw temperature: ●, 65°, 80°C; ○, 110°, 125°C. A, $n = 1.0$; B, $n = 1.2$; C, $n = 1.5$

at $185^\circ \pm 1^\circ\text{C}$. The second samples were produced under the same conditions as the above sample with 20, 30 and 50 parts of plasticizer.

The third film is a commercial film, normally without plasticizer, which is used after heat treatment at $175^\circ \pm 1^\circ\text{C}$ for 60 min. All samples, except the commercial film, are the same as those used for birefringence measurements in part 1.

Uniaxially stretching method of the samples

All samples were drawn at a rate of 10%/min at intervals of 15°C between 50° and 125°C . In order to focus our attention on the effect about T_g , however, the samples drawn at 65° and 110°C were mainly used.

Measurement of polarized fluorescence intensity

Fluorescence intensity was measured by the reflection method with polarized fluorometer FOM-1, produced by Nihon Bunko Industry. The experimental arrangement is shown in Figure 5.

RESULTS AND DISCUSSION

Correlation between fluorescence intensity and the second order optical quantity in plasticized or unplasticized film

To investigate the relationship between birefringence, the second order optical quantity, and fluorescence intensity, we introduce the following simultaneous equations.

Substituting $\beta_1 = 90^\circ$ and 0° into equations (10) and (11) respectively, we obtain simultaneous equations of F_{400} and F_{200} as follows. Replacing $I_{\parallel}(90^\circ)$ and $I_{\perp}(0^\circ)$ on the left hand side of equations (10) and (11) by the ratio of measured or calculated fluorescence intensity:

$$X = \frac{I_{\parallel}(\beta_1 = 90^\circ)}{I_{\parallel}(\beta_1 = 0^\circ)} \quad \text{and} \quad Y = \frac{I_{\perp}(\beta_1 = 0^\circ)}{I_{\parallel}(\beta_1 = 0^\circ)}$$

and taking n (ratio of polyene to carbonyl) as a parameter we construct simultaneous equations of F_{400} and F_{200} as shown in the Appendix; thus $\langle \cos^2 \theta \rangle$ and $\langle \cos^4 \theta \rangle$ can be found from the principal values of the fluorescence intensity. These values of $\langle \cos^2 \theta \rangle$ obtained from measured fluorescence intensity are compared with those obtained from birefringence reported in part 1⁶ as shown in Figures 3a and 3b.

In Figure 3a, each group of points neighbouring the closest line, which is obtained by the method of least squares, is the result of calculations using the corresponding value of n for the fluorescence intensity. It is clear that both values of $\langle \cos^2 \theta \rangle$ obtained from the two methods, birefringence and fluorescence, must be consistent if selection of n is suitable; i.e. correlation coefficient is expected to be 1. From Figure 3a, we can see that the group indicated by $n = 1.5$ satisfies the above condition.

Morikawa¹¹ reported that at the initial stage of thermal degradation the value of n is large but decreases with increasing extent of degradation. Compared with $n = 1.0$ for the sample subjected to heat treatment, the value of $n = 1.5$ may be acceptable.

On the other hand, the difference as to whether the sample was drawn above T_g or below T_g is specified in Figure 3c by using the notations ● and ○. Since it is difficult from Figure 3a to establish the difference exactly the value n is regarded as being constant in both cases. Figure 3b shows that the above facts are also true for the plasticized samples.

Correlation in the heat treated commercial film

The correlation of $\langle \cos^2 \theta \rangle$ is shown in Figure 4 in the same way as previously described. Here, we find $n = 1.0$ to be reasonable and in comparison with $n = 1.5$ this result seems to be due to the increasing formation of carbonyl groups.

Comparison of calculated $\langle \cos^2 \theta \rangle$ vs. $\langle \cos^4 \theta \rangle$ curves with their measured values

Substituting the measured principal values of the fluorescence intensity into the equations shown in the Appendix, we determine the values of $\langle \cos^2 \theta \rangle$ and $\langle \cos^4 \theta \rangle$, and compare the results with the theoretically calculated curves in Figures 6a and 6b.

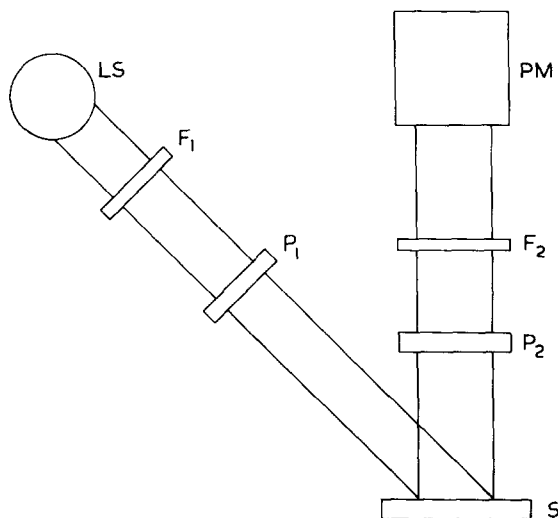


Figure 5 Optical system for polarized fluorescence intensity measurement

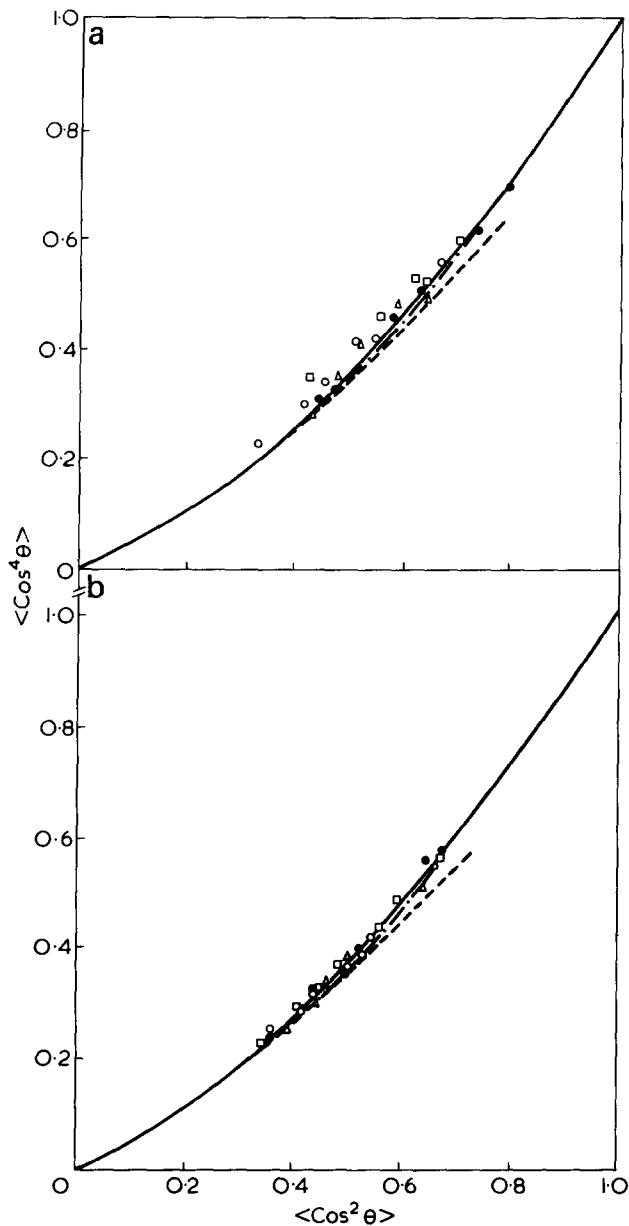


Figure 6 (a) Correlation between $\langle \cos^2 \theta \rangle$ and $\langle \cos^4 \theta \rangle$, where points indicate experimental results obtained from the fluorescence intensity and the two curves are results of calculation by using the parameters listed in Table 1 and affine or Langevin type distribution function; for the unheat treated films drawn at temperature 65°C below T_g . Draw temperature 65°C. \circ , Sample A; \square , sample B; \triangle , sample C; \bullet , sample D. —, Affine; - - -, affine: Langevin (60:40), $N = 6$; — — —, Langevin, $N = 6$. (b) The correlation for the films drawn at 110°C above T_g , the two curves being calculated in the same way as (a). Draw temperature 110°C. \circ , Sample A; \square , sample B; \triangle , sample C; \bullet , sample D. —, Affine; - - -, affine: Langevin (50:50), $N = 10$; — — —, Langevin, $N = 10$

In these Figures we show two extreme curves drawn as a full line and a broken line and one middle curve to show the general tendency of the $\langle \cos^2 \theta \rangle$ vs. $\langle \cos^4 \theta \rangle$ curve. The former curves are derived from affine and Langevin distribution functions and the latter curve for the complex distribution function. The ratio of affine to Langevin being 60:40 or 50:50 and the segment number $N = 6$ or $N = 10$ (sample B).

For the heat treated commercial film the same result was obtained, but it is omitted here for brevity.

Ascertainment of calculated fluorescence intensity

The calculated fluorescence intensity patterns which are derived from the distribution functions and parameters listed in Tables 1 and 2 show good agreement with those of the experiment in the principal directions $\beta_1 = 0^\circ$ and 90° . Figure 7 is for the unplasticized film drawn up to 3 times. This agreement also holds for all samples drawn up to any draw ratio and Figure 8 shows such an example.

It is clear from Figure 8 that we can use as a good approximation the values of parameters with fixed values, shown in Tables 1 and 2, up to the full extent of the draw ratio used in this experiment.

CONCLUSIONS

(a) The value of $\langle \cos^2 \theta \rangle$, derived either from birefringence or fluorescence intensity independently, show good agreement if we use the values of 1.0 or 1.5 for the ratio of poly-

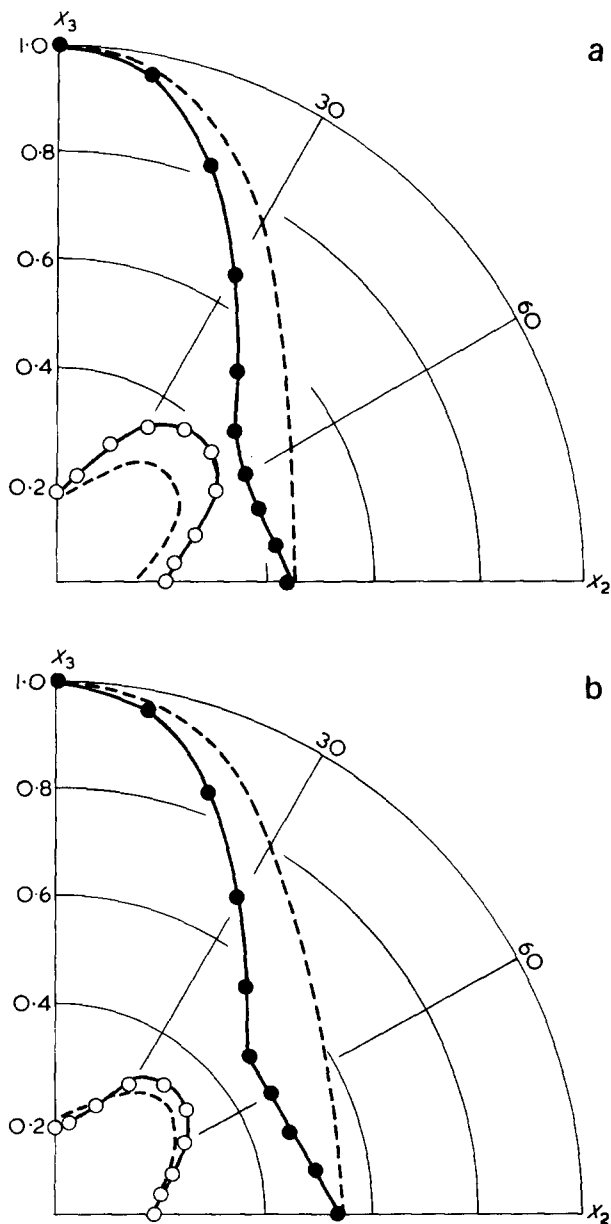


Figure 7 (a) Pattern of the fluorescence intensity of the unplasticized film drawn by 3 times as large as its initial length at 65°C. — — —, Calculated result. (b) The pattern for the unplasticized film drawn by 3 times at 110°C. \bullet , Observed $I_{\parallel}(\beta)$; \circ , $I_{\perp}(\beta)$; — — —, calculated

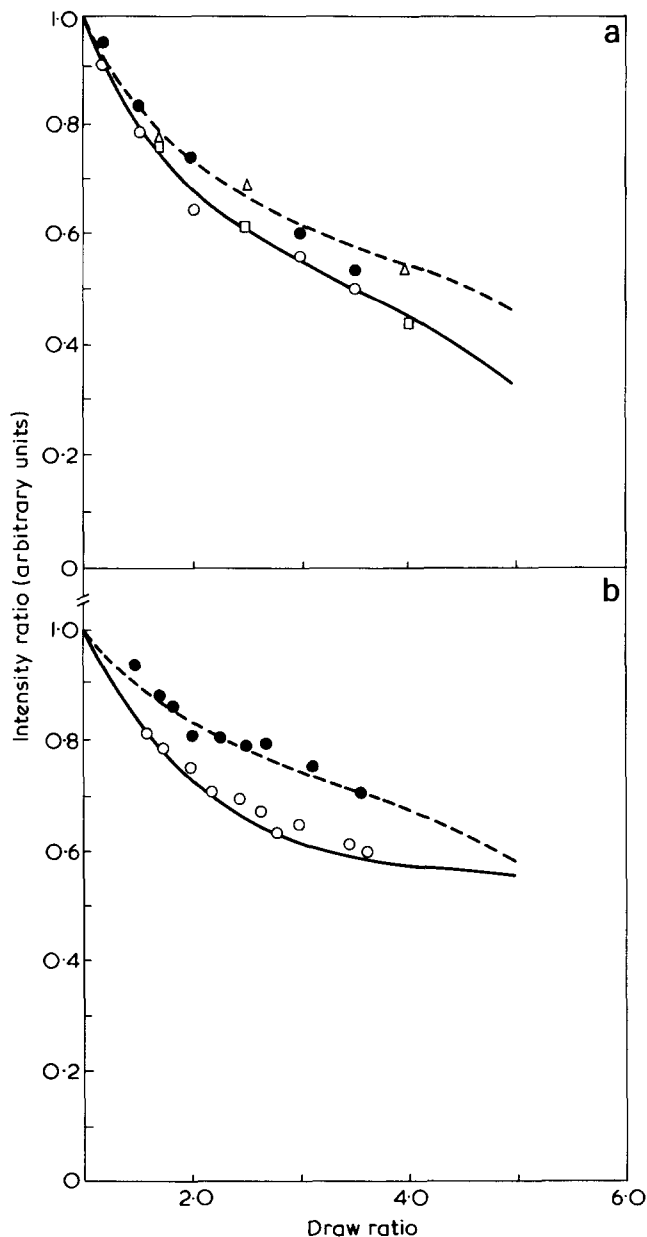


Figure 8 Change of intensity ratio $I_{\parallel}(90^{\circ})/I_{\parallel}(0^{\circ})$ with draw ratio, where points indicate the results of measurement and each curve is the calculated result from equations (10) and (11). (a) Plasticized films B and C. $n = 1.5$. Film B: \circ , 65°C ; \bullet , 110°C . Film C: \square , 65°C ; --- , 65°C , $N = 6(60:40)$; \triangle , 110°C ; --- , $N = 10(50:50)$. (b) Commercial film heat treated at 175°C for 60 min. $n = 1.0$. \circ , 65°C ; --- , 65°C , affine; \bullet , 110°C ; --- , 110°C , $N = 8(50:50)$

ene to carbonyl to estimate $\langle \cos^2 \theta \rangle$ results for the heat treated or the unheat treated film. The values of n are consistent with those values determined by a heat degradation process. Considering this result, we may conclude that although there are differences in origin between birefringence and polarized fluorescence intensity; i.e. the former regards the whole reflection in the sample including the plasticizer as orientation behaviour of the polymer chain, but in the latter case the behaviour of the polymer chain is evaluated from the orientation of the polyene and carbonyl groups, the fact that the values of $\langle \cos^2 \theta \rangle$ derived from the two methods are the same suggests that a fundamental postulation of this experiment; i.e. orientation of the fluorescent group present in the main chain reflects the orientation behaviour of the molecular chain, is correct.

(b) As the result of the analysis of the fourth-optical quantity $\langle \cos^4 \theta \rangle$ from the patterns of fluorescence intensity, using the orientation distribution functions and the characteristic constants whose applicabilities were verified already, we can see that the value of $\langle \cos^4 \theta \rangle$ can be estimated quantitatively from the fluorescence intensity pattern.

(c) We regard the morphologic consideration of PVC as a problem for the future. However, comparing measured and calculated fluorescence intensity supports the assumption that rigid chain and flexible chains co-exist in PVC film and the coincidence of the results enables us to postulate *a priori* an orientation distribution function for PVC. Furthermore, it becomes clear that existence of plasticizer raises the portion of soft part consisting flexible chain and increases the mobility of molecular chain.

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APPENDIX

For the ratio of the measured principal values we first put:

$$X = I_{\parallel}(\beta_1)/I_{\parallel}(\beta_1 = 0^{\circ}) \quad (\text{A1})$$

$$Y = I_{\perp}(\beta_1)/I_{\parallel}(\beta_1 = 0^{\circ}) \quad (\text{A2})$$

and if we use equations (10) and (11), X and Y can be expressed as follows:

$$X = A/B \tag{A3}$$

$$A = n [8P_4(\cos \beta_1)P_4(\cos \Theta_1)F_{400} + 20P_2(\cos \beta_1)P_2(\cos \Theta_1)F_{200} + 7] + [8P_4(\cos \beta_1)P_4(\cos \Theta_2)F_{400} + 20P_2(\cos \beta_1)P_2(\cos \Theta_2)F_{200} + 7]$$

$$B = n [8P_4(\cos \Theta_1)F_{400} + 20P_2(\cos \Theta_1)F_{200} + 7] + [8P_4(\cos \Theta_2)F_{400} + 20P_2(\cos \Theta_2)F_{200} + 7] \tag{A4}$$

$$Y = C/D \tag{A5}$$

$$C = n [-24P_4(\cos \beta_1)P_4(\cos \Theta_1)F_{400} + 10P_2(\cos \beta_1)P_4(\cos \Theta_1)F_{400} + 2P_4(\cos \beta_1)F_{400} + 5P_2(\cos \Theta_1)F_{200} + 7] + [-24P_4(\cos \beta_1)P_4(\cos \Theta_2)F_{400} + 10P_2(\cos \beta_1)P_4(\cos \Theta_2)F_{400} + 2P_4(\cos \Theta_2)F_{400} + 5P_2(\cos \Theta_2)F_{200} + 7]$$

$$D = 3\{n [8P_4(\cos \Theta_1)F_{400} + 20P_2(\cos \Theta_1)F_{200} + 7] + [8P_4(\cos \Theta_2)F_{400} + 20P_2(\cos \Theta_2)F_{200} + 7]\} \tag{A6}$$

Substituting equations (A4) and (A6) into equation (A3) and (A5) respectively, and then modifying, we obtain

F_{200} and F_{400} as the solution of the results i.e.:

$$F_{200} = \frac{7(n+1)[(3Y-1)(8X-3)]}{[nP_2(\cos \Theta_1) + P_2(\cos \Theta_2)][24(2Y+1)(2X+1) - 12(X-1)(2Y+1)]} \times \frac{-12(X-1)(2Y+1)}{-5(8X-3)(12Y-1)} = \frac{(n+1)(3Y-4X+3)}{[nP_2(\cos \Theta_1) + P_2(\cos \Theta_2)](8X+12Y+3)} \tag{A7}$$

$$F_{400} = \frac{7(n+1)[10(3Y-1)(2X+1)]}{[nP_4(\cos \Theta_1) + P_4(\cos \Theta_2)][5(8X-3)(12Y-1) - 5(X-1)(12Y-1)]} \times \frac{-5(X-1)(12Y-1)}{-120(2Y+1)(2X+1)} = \frac{3(n+1)(X-6Y+1)}{[nP_4(\cos \Theta_1) + P_4(\cos \Theta_2)](8X+12Y+3)} \tag{A8}$$

and additionally the values $\langle \cos^2 \theta \rangle$ and $\langle \cos^4 \theta \rangle$ can readily be derived from the relation:

$$\langle \cos^2 \theta \rangle = \frac{1}{3} (1 + 2F_{200}) \tag{A9}$$

$$\langle \cos^4 \theta \rangle = \frac{1}{35} (8F_{400} + 20F_{200} + 7) \tag{A10}$$

There, if we substitute $\Theta_1 = 20^\circ$ or $\Theta_2 = 90^\circ$ for $P_i(\cos \Theta_i)$ in equations (A7) and (A8) the values of $\langle \cos^2 \theta \rangle$ and $\langle \cos^4 \theta \rangle$ can be obtained through equations (A9) and (A10), with parameter n .