Molecular orientation behaviour of uniaxially stretched poly(vinyl chloride) film: 1. Birefringence: effect of plasticizers and draw ratio above and below T_g

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In order to investigate the orientation behaviour of a non-crystalline chain polymer, plasticized and unplasticized poly(vinyl chloride) films (PVC) are chosen for investigation. The following two orientation distribution functions are postulated to calculate the second moment of the molecular orientation: (a) for the unplasticized film drawn below the glass transition temperature the distribution function derived from an affine deformation mechanism is applied; (b) for the all plasticized films or for the films drawn above the glass transition temperature a compound distribution function derived from the affine deformation mechanism and that of a rubber-like chain (Langevin model) proposed by Roe *et al* is applied. The parameters which are included in the distribution function, viz. the ratio of the affine part to the Langevin part, the ratio of polyene to carbonyl in a heat treated film and the segment number of the Langevin chain, can be evaluated experimentally. The intrinsic birefringences of normal and heat treated unplasticized and plasticized films are estimated theoretically on the basis of additivity of band polarizabilities. The calculated birefringences and orientation distribution functions show good agreement with measured values.

INTRODUCTION

There are many studies of the mechanical behaviour of poly(vinyl chloride) (PVC). Rider *et al.*[1] and Matsumoto *et al.*[2] analysed the molecular orientation behaviour of stretched PVC films by birefringence. Hennig[3] and Kausch[4] carried out the comparison of experimental results of thermal expansion or isothermal compression with orientation mechanism subject to affine deformation or segment movements in a rubber-like network.

As is well known, the mechanical behaviour of PVC is very sensitive to its plasticizer content and glass transition temperature. How these factors affect the deformation mechanism, however, is not clear from the previous studies. In this paper, by considering the change of orientation factor, $\langle\cos^2\theta\rangle$, of the uniaxially stretched PVC film, we analyse the mechanism by which the plasticizer content and draw temperature affect the deformation process.

With regard to draw temperature it is found that the draw ratio dependence of birefringence changes at the glass transition temperature, 85°–90°C, a fact already recognized by Rider *et al.*[1]. They estimated the intrinsic birefringence of a commercial PVC film, nominally unplasticized, drawn at 20°C by using the orientation function obtained on the assumption that the deformation is to be affine deformation. Our examination, reveals however, that all commercialized, unplasticized PVC films usually contain about 10–15 parts of plasticizer. Accordingly we first produced stabilized PVC films without plasticizer, measured the change of the birefringence with draw ratio and then estimated the intrinsic birefringence.

MODELS FOR CALCULATION OF MOLECULAR ORIENTATION, AND ITS CORRELATION WITH THE GLASS TRANSITION TEMPERATURE

The effect of the glass temperature on the deformation mechanism for unplasticized film was investigated for plasticized film.

When an unplasticized PVC film is drawn below the glass temperature T_g we may regard the structural unit as a rigid body because all molecular chains in PVC are probably frozen. We assume therefore that under this condition the molecular chains are oriented in accordance with affine deformation.

On the contrary, in the case of extension above its T_g, it will be expected that the mobility of the molecular chain increases and the entanglement becomes loose because the molecular chain may be already released from a frozen state. The cohesion resulting from polar attraction however, may remain at the drawing above its T_g. Taking this into account we postulate the following model for the sample drawn above its T_g.

We assume that above T_g PVC solid consists of two parts; i.e. one is composed of rigid rod-like chains which follow affine deformation because the entanglement serves as a crosslink, and the other part is an assembly of a chain—Langevin chain—consisting of N segments with a great deal of freedom in deformation.

Another problem is how does the content of plasticizer affect the deformation mechanism? In general, since the polar attraction decreases with addition of the plasticizer the freedom of the molecular chain movement will become larger. Therefore, in the case of drawing below T_g, if we add plasticizer the number of chains with mobility will increase and the distance between adjacent crosslinks

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may grow larger with increasing plasticizer content.

On the other hand, for the plasticized samples subjected to extension above the T_g, the part consisting of the chain with freedom (Langevin chain) may be increased as well as increasing the number of segments in the chain compared with the state below T_g.

Thus, we adopt two types of distribution function for the two kinds of chain. For the rigid rod-like chain the well-known distribution function which follows affine deformation is applied[5] and for the non-rigid chain the following distribution function presented by Roe *et al.*[6] is adopted:

$$
\begin{aligned}
(2)^{1/2} W_0 &= 1 \\
(2/5)^{1/2} W_2 &= (1/5N)(\lambda^2 - 1/\lambda) + (36/875N^2) \\
&\quad \times (\lambda^4 + \lambda/3 - 4/3\lambda^2) \\
&\quad\quad + (108/6125N^3)(\lambda^6 + 3\lambda^3/5 - 8/5\lambda^3) \\
(2/9)^{1/2} W_4 &= (3/175N^2)(\lambda^4 - 2\lambda + 1/\lambda^2) \\
&\quad + (216/13475N^3) \\
&\quad \times (\lambda^6 - 4\lambda^3/5 - 7/5 + 6/5\lambda^3) \\
(2/13)^{1/2} W_6 &= (27/35035N^3)(\lambda^6 - 3\lambda^3 + 3 - 1/\lambda^3)
\end{aligned}
\tag{1}
$$

and

$$
w(\cos\chi) = \sum_{l=0}^{6} W_l P_l(\cos\chi) \tag{2}
$$

where $w(\cos\chi)$ is given in a series of Legendre's polynomial (summation to the 6th order was numerically sufficient), N is the number of segments, λ is the extension ratio and χ is the angle between the axis of the segment and the extension axis.

EXPERIMENTAL

Preparation of sample film

After premixing a stabilizer with PVC powder without plasticizer (P_η = 1300, produced by Mitsui–Toatsu Chemical Industry) sample sheets were made by extrusion, and then pressed at 185° ± 1°C into film. Films containing 20, 30 or 50 parts of DOA and DOP etc. were produced under the same conditions. Unplasticized film heat treated at 190°C for 60 min was used as the heat treated, unplasticized sample.

Uniaxial stretching of the samples

Uniaxial stretching of the films were made under the following conditions.

In order to focus our attention on the glass transition temperature we selected intervals of 15°C between 50° or 65°C and 125°C as the drawing temperature and used a draw rate of 10%/min. The extensometer used was Tensilon III (produced by Toyo Mesuring Instrument Company), equipped with an air oven.

Measurement of birefringence and refractive index

The polarizing microscope POM-II (Nihon Kogaku Co.), equipped with a Berek-type compensator was used to measure birefringence and the values were evaluated from the retardation.

Abbe's refractometer with monochromatic sodium light was used for the measurement of the refractive index of the sample at a temperature 20° ± 1°C.

RESULTS AND DISCUSSION

Effect of plasticizer and glass transition temperature on birefringence

The change of birefringence with draw ratio for plasticized and unplasticized films, for the sample drawn at 65°C (below its T_g) and for the sample drawn at 110°C (above its T_g) are shown in *Figure 1*.

These results show that the birefringence decreases with increasing plasticizer content both above and below the T_g.

Assuming an affine deformation we can calculate the intrinsic birefringence of the molecular chain for the uniaxially stretched unplasticized film, drawn below T_g, by using the intrinsic values of the bond polarizabilities.

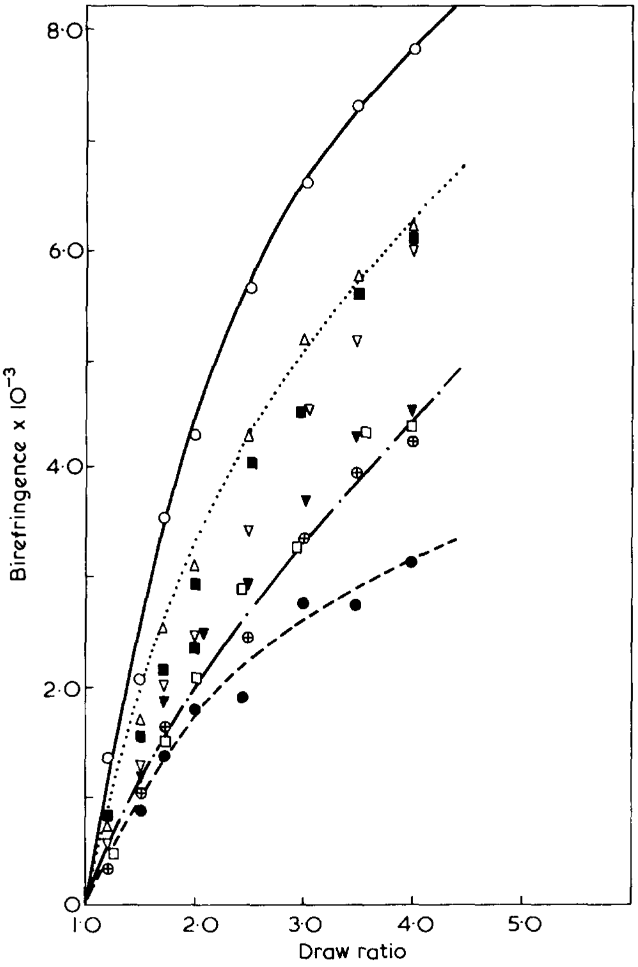

Figure 1 Relation between birefringence and draw ratio for plasticized and unplasticized films at the temperatures above and below T_g. Films A, B and C contain 50, 30 and 20 parts plasticizer, respectively; D, unplasticized film. Draw temperatures for film A; ⊕, —·—·, 65°C; ●, – – –, 110°C. Draw temperatures for film B: ▽, 65°C; □, 110°C. Draw temperatures for film C: ■, 65°C; ▼, 110°C. Draw temperatures for film D: ○, ——, 65°C: △, ·····, 110°C

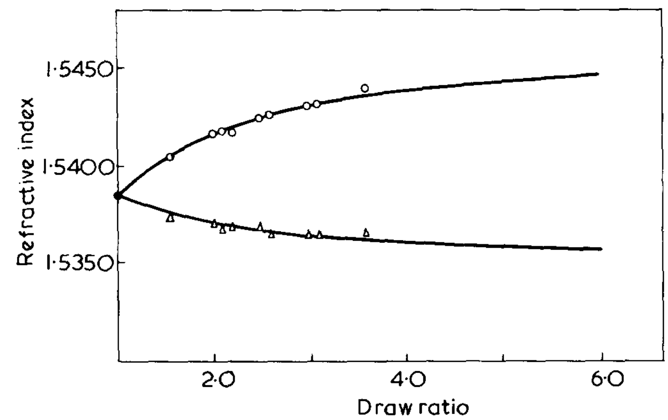

Figure 2 Correlation between measured refractive indices and refractive index vs. draw ratio curves calculated under the assumption that deformation mechanism obeys affine deformation with intrinsic bond polarizabilities $b_{\parallel}^{C-Cl} = 32.8 \times 10^{-25}$ and $b_{\perp}^{C-Cl} = 21.4 \times 10^{-25}$ for the unplasticized sample stretched at 65°C. $n_{\parallel}$ (○) and $n_{\perp}$ (△) are the refractive indices parallel and perpendicular to the extension direction; $\bar{n} = 1.5386$ (●). $\Delta_t^0 = 10.4 \times 10^{-3}$

As the value of bond polarizability of the C–Cl bond is uncertain, we, first of all, calculated the refractive indices vs. draw ratio curves by using the distribution function for the affine deformation and the values of bond polarizability of C–Cl bond as parameters, e.g. the two curves shown in *Figure 2*, where points are measured refractive indices. In this calculation the bond polarizabilities, obtained as averages of Bunn's[7] and Vulk's[8] viz. $b_{\parallel} = 12.29 \times 10^{-25}$ cm^2, $b_{\perp} = 1.615 \times 10^{-25}$ cm^2 for C–C bond and $b_{\parallel} = 7.65 \times 10^{-25}$ cm^2, $b_{\perp} = 6.10 \times 10^{-25}$ cm^2 for C–H bond parallel and perpendicular to their bond axes were used.

Comparing with the measured values of refractive index, we can determine the bond polarizability of the C–Cl bond as the values on the curve closest to the measurement points; these values are shown in *Figure 2*. Consequently, by using the values of bond polarizability the intrinsic birefringence is given by $\Delta_t^0 = 10.4 \times 10^{-3}$.

The detailed calculation of Δ_t^0 is as follows. Polarizability of a molecular chain which consists of n bonds having cylindrical symmetry about the bond axis can be obtained by:

$$P_j = \sum_i^n b_{i\parallel} \cos^2\theta_{ij} + \sum_i^n b_{i\perp} \sin^2\theta_{ij} \qquad (j = 1, 2, 3) \quad (3)$$

with respect to the principal directions of the molecular chain; where $b_{i\parallel}$ and $b_{i\perp}$ are the bond polarizabilities parallel and perpendicular to the bond axis, and θ_{ij} indicates the angle between the principal direction and the bond axis with relation to the ith bond. The spacial arrangement of the bonds in a PVC chain is shown in *Figure 3*. Using the bond polarizability of the C–Cl bond and those of C–C and C–H mentioned previously, we can calculate P_j from equation (3). The values are listed in *Table 1* together with the polarizabilities of PVC chain $P_{\parallel}^0$ and $P_{\perp}^0$, in the molecular chain and in the perpendicular direction.

In *Table 1*, the value of $\bar{n}$ derived from $(P_1 + P_2 + P_3)/3$ corresponds to the state of random molecular orientation, and this is also indicated in *Figure 2* as the origin of the refractive index vs. draw ratio curves.

If we use Lorentz–Lorenz's formula and substitute the molecular weight $M = 62.5$ and the density $\rho = 1.390$, the polarizabilities are translated into the refractive indices $n_{\parallel}^0$ and $n_{\perp}^0$. We can finally determine the intrinsic birefringence value of 10.4×10^{-3} from $\Delta_t^0 = n_{\parallel}^0 - n_{\perp}^0$ as shown in *Table 1*.

This value is rather larger than that of 7.2×10^{-3} proposed by Rider *et al.*[1] for an unplasticized, commercial film. However when we allow for the fact that commercial film still contains a few % plasticizer, the above difference is thought to be reasonable.

On the other hand, the value of 10.4×10^{-3} is smaller than 12.6×10^{-3} proposed by Kashiwagi and Ward[9]. The films used in the latter experiment were drawn at temperatures neighbouring their T_g and at the extension ratios used it was difficult to obtain an accurate value of Δ_t^0 by extrapolation.

Whether it is above T_g or below T_g, the value of intrinsic birefringence may be fixed. We thus assign the value of 10.4×10^{-3} to the sample drawn above T_g. The values of birefringence of the unplasticized samples drawn at temperature above T_g are smaller than those for the samples drawn below T_g, and as will be described later the variation of birefringence with increasing draw ratio cannot be explained through affine deformation mechanism alone. If we consider these results, we must take into account that there are some differences in the deformation behaviour on the molecular chain between the states above and below T_g.

For the case above its T_g we assume existence of two kinds of molecular chain mentioned previously and then

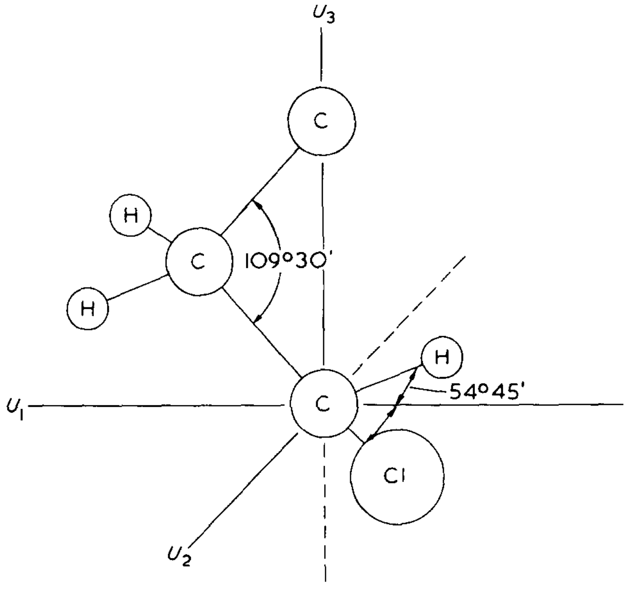

Figure 3 Geometrical arrangement of the chemical bonds in a PVC monomer

Table 1 Intrinsic polarizabilities and birefringence of a molecular chain in unplasticized PVC film

P_3	56.42 ($\times 10^{-25}$ cm^3)
P_1	55.82 ($\times 10^{-25}$ cm^3)
P_2	55.25 ($\times 10^{-25}$ cm^3)
$P_{\parallel}^0 = P_3$	56.42 ($\times 10^{-25}$ cm^3)
$P_{\perp}^0 = (P_1 + P_2)/2$	55.54 ($\times 10^{-25}$ cm^3)
$n_{\parallel}^0$	1.5455
$n_{\perp}^0$	1.5351
$\bar{n}$	1.5386
Δ_t^0	10.4×10^{-3}

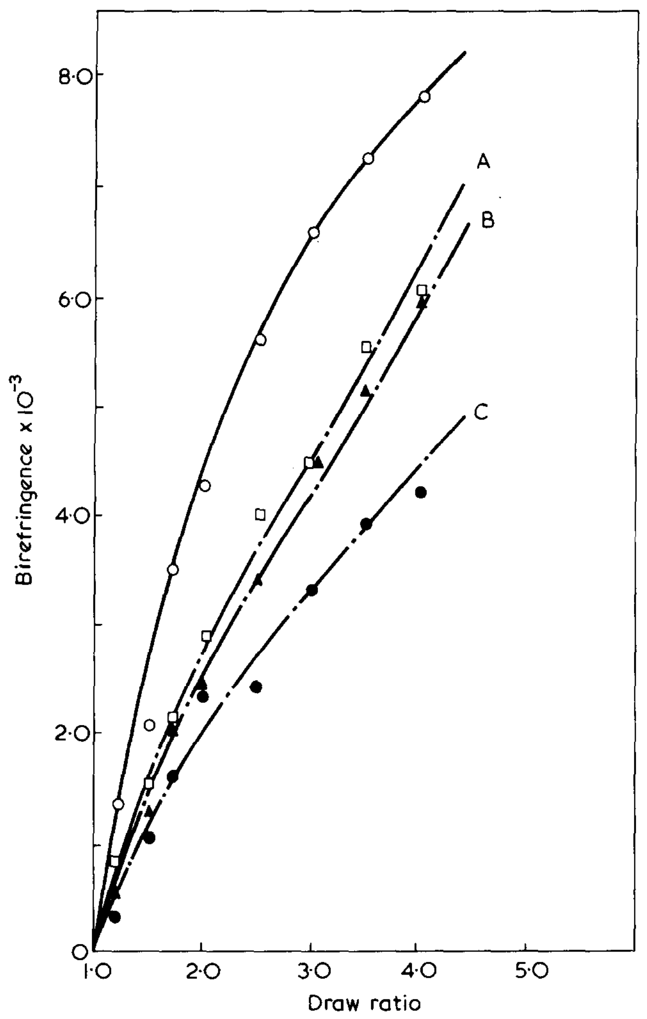

Figure 4 Dependence of birefringence vs. draw ratio curve on the change of plasticizer content at a draw temperature below T_g. Draw temperature 65°C. Curve A, N = 6 (60:40); B, N = 6 (60:40); C, N = 7 (60:40). Δ_t^0 values: ○, 10.4 × 10^{-3} (film D); □, 9.6 (film C); ▲, 9.0 (film B); ●, 7.3 (film A). ——, Affine; — · — · —, affine + Langevin

calculate the distribution function from equation (1) and the formula of affine deformation.

Two parameters must be considered, one is the extension ratio of the chains which belong to the affine part or the Langevin part, and the other is the segment number N forming a molecular chain in the Langevin part.

Thus to determine the values of the parameters, we postulated nine values of the extension ratio of affine part (every 10% from 10 to 90%) and six segment numbers ($N = 6, 8, 10, 12, 15$ and 50).

Birefringence vs. draw ratio curves were calculated for each combination selected from the above two groups. We estimate that N = 10 and the extension ratio of 30% were closest to the measured points.

The intrinsic birefringence of the plasticized film was determined as follows. Firstly, the average value of refractive index of the plasticizers used in the sample, n_p^0, was calculated from those of measured values for the each plasticizer and stabilizer of the sample under the assumption that these are optically isotropic and additive property of refractive index* holds.

The values of the intrinsic refractive indices of the plasticized film, $n_{p\parallel}^0$ and $n_{p\perp}^0$ were deduced by means of averaging $n_\parallel{}^0$ and n_p^0 or $n_\perp^0$ and n_p^0 for each volume fraction. The values of the intrinsic birefringence of the plasticized film obtained by subtraction $n_{p\parallel}^0 - n_{p\perp}^0 = \Delta_t{}^0$, were: 9.6 x 10^{-3} (for the film C), 9.0 x 10^{-3} (for the film B) and 7.3 x 10^{-3} (for the film A).

In other words, the basis of the above calculation consists of an assumption that PVC film is an aggregation of a structural unit composed of pure PVC surrounded by the plasticizer. Thus we imagine a structural unit of PVC with principal polarizabilities $P_\parallel{}^0$, $P_\perp$ and $P_\perp{}^0$ surrounded by plasticizer having isotropic polarizability P_p^0.

Using the same method as for the unplasticized film the birefringence vs. draw ratio curves were compared with the measured values and the two parameters included in the curves were determined. *Figures 4* and *5* show the final results and from the Figures it follows that for the films drawn below T_g, the ratio 60:40 and N = 6–7 are the most suitable and the values of both parameters do not show any noticeable change with increasing plasticizer content.

These results show that in the mixing of plasticizer and PVC the plasticizer softens the PVC film but it is also supposed that the plasticizer still remains dispersed in the massive state because its microscopic dispersion hardly occurs at all.

Above T_g, on the other hand, the ratio of affine to Langevin is small in comparison with that below T_g because frozen polymer chain may be released. Since this releasing makes dispersion of plasticizer into entangled

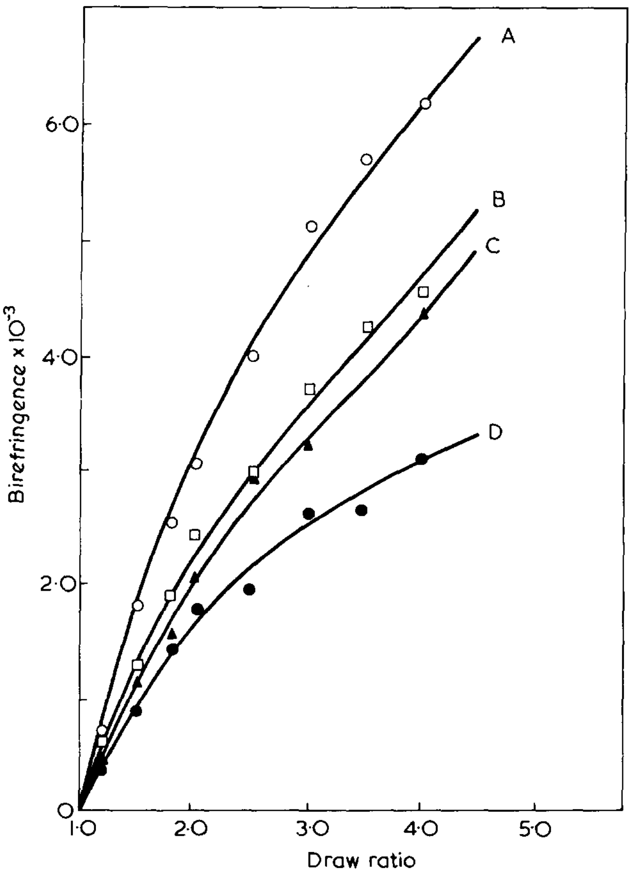

Figure 5 Dependence of the birefringence vs. draw ratio curve on the change of plasticizer content at a draw temperature above T_g. Draw temperature 110°C. Curve A, N = 10 (70:30); B, N = 10 (50:50); C, N = 10 (50:50); D, N = 20 (50:50). Δ_t^0 values as for *Figure 4*. ——, Affine + Langevin

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* Strictly, average polarizabilities should be used but in view of the structural complexity of the plasticizer we consider that the additive property of refractive index is more practical.

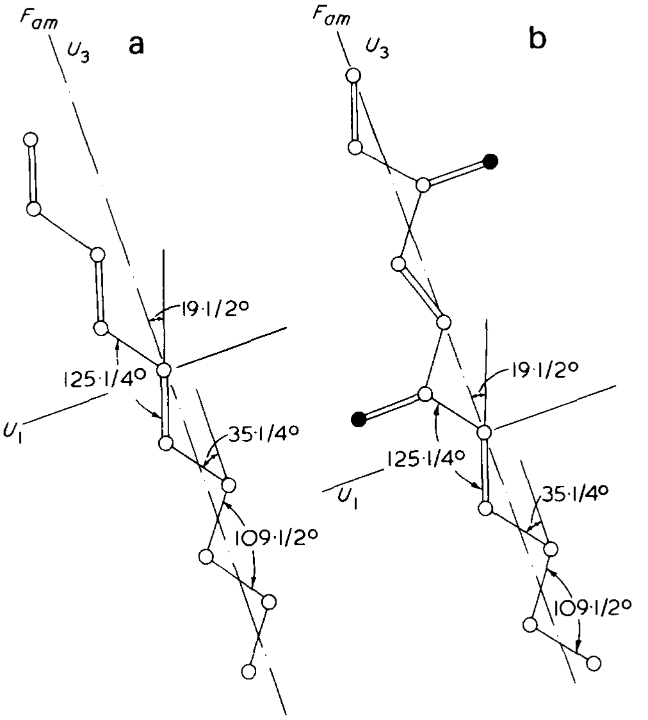

Figure 6 Geometrical arrangement of polyene and carbonyl groups in a molecular chain of PVC

Table 2 Intrinsic polarizabilities and birefringences of the molecular chain with polyene group or polyene and carbonyl groups

Type 1		Type 2	
P_3	44.55×10^{-25} cm^3	P_3	63.54×10^{-25} cm^3
P_1	32.25×10^{-25} cm^3	P_1	61.62×10^{-25} cm^3
P_2	24.02×10^{-25} cm^3	P_2	35.38×10^{-25} cm^3
$P_{\parallel}^0$	44.55×10^{-25} cm^3	$P_{\parallel}^0$	63.54×10^{-25} cm^3
$P_{\perp}^0$	28.13×10^{-25} cm^3	$P_{\perp}^0$	48.75×10^{-25} cm^3
$n_{p\parallel}^0$	1.4137	$n_{p\parallel}^0$	1.6312
$n_{p\perp}^0$	1.2497	$n_{p\perp}^0$	1.4591
$\bar{n}$	1.3043	$\bar{n}$	1.5165
Δ_{pol}	164.0×10^{-3}	Δ_{pol}	172.1×10^{-3}

chains easier the free volume increases and the value of N increases to 10–20.

Behaviour of birefringence of the film subjected to heat treatment

A small amount of polyene and carbonyl radicals are produced through thermal hysteresis during the processing (it may be thought to be 0.2%) in the samples used but their effect on the birefringence may be small and negligible.

In the case of heat treated PVC film, however, the effect cannot be ignored. In order to calculate the intrinsic birefringence, we must determine the volume fraction and the ratio of polyene to carbonyl. Polyene and carbonyl radicals lie in the PVC film in two extreme types shown in *Figure 6*; the one has polyene at every two bonds and the other has polyene or carbonyl alternately at every two bonds, and the ratio of the two types can be determined for that of polyene to carbonyl.

However, we can estimate the ratio n, polyene to carbonyl, as 1.0–2.0 from previously published measurements[10] and the intrinsic birefringence of the typical chains shown in *Figure 6* has values, $\Delta_{pol}^0 = 164 \times 10^{-3}$ and $\Delta_{pol}^0 = 172 \times 10^{-3}$ corresponding to the each type (*Table 2*). In calculating Δ_{pol}^0 it is assumed in view of the small volume fraction of polyene groups that the polyene bonds are randomly distributed along the PVC chain and that the angle between the polyene bond axis and the main chain axis retains a definite value.

Considering the fact that difference of Δ_{pol}^0 is small, we assume the value $n = 1.5$ and this value is verified by polarized fluorescence method described in part 2.

The volume fraction of the polyene–carbonyl groups derived on the basis of additive property of density and as a result of measurements of the density of the sample[10] is 1.5%.

Thus, using the values of n and the volume fraction of polyene–carbonyl groups together with the additive property of birefringence, we obtain the value of $\Delta_f^0 = 12.7 \times 10^{-3}$ for the intrinsic birefringence of the film. Using this value for a sample drawn below T_g, birefringence vs. draw ratio curves plotted according to their orientation distribution function are shown in *Figure 7*. The full line showing the calculated result is in agreement with the measured values.

Above T_g, on the other hand, we postulate two ratios (affine: Langevin); 60:40 and 50:50 in *Figure 7* and it may be seen that $N = 9$ and 55:45 are the closest parameters to the measured points.

In the transient temperature region adjacent to T_g, which is represented by the notations △ and ⊕ in *Figure 7*

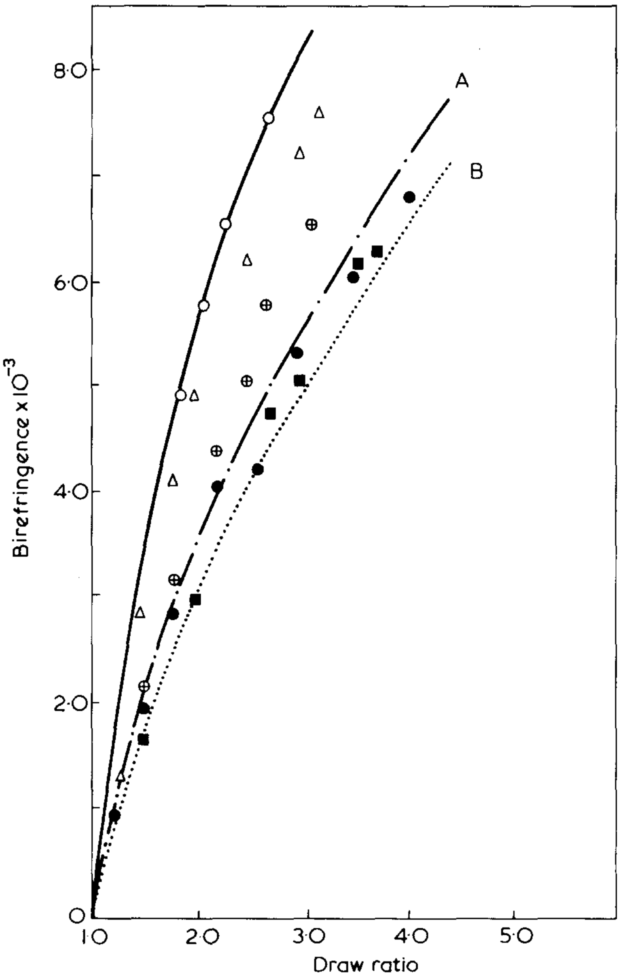

Figure 7 Change of birefringence vs. draw ratio curves with the draw temperature for the heat treated unplasticized film. $\Delta_f^0 = 12.7 \times 10^{-3}$. Draw temperature: ○, 65°; △, 80°; ⊕, 95°C; ●, 110°; ■, 125°C. ——, Affine; — · — and – – –, affine + Langevin. Curve A, $N = 9$ (60:40); B, $N = 9$ (50:50)

the compound distribution function with a different ratio of affine to Langevin may be adapted.

CONCLUSIONS

(a) intrinsic birefringence of unplasticized PVC film is given by 10.4×10^{-3}. However, this value is rather larger than that of Rider, which corresponds to a commercial unplasticized film. The reason for this difference is the fact that plasticizer incorporated in commercial materials reduces the birefringence.

(b) A structural model consisting of affine part (rigid part) and Langevin part (soft part) seems to be applicable to the analysis of the optical anisotropy of PVC film and the ratio of the two parts depends on draw temperature and plasticizer content because of the change in freedom of the molecular chains.

(c) For the plasticized film, an aggregate model consisting of a structural unit of unplasticized PVC with principal polarizabilities P_p^0, ${P_\parallel}^0$, ${P_\perp}^0$ and ${P_\perp}^0$ in the three orthogonal directions surrounded by plasticizer having isotropic polarizability P_p^0 is considered to be of good practical use for the calculation of its intrinsic birefringence.

(d) If PVC film is subjected to heat treatment its intrinsic birefringence becomes larger than that of unheat treated film owing to polyene–carbonyl groups formed in the film. Furthermore, the number of Cl bonds decreases with treatment and the soft part represented by the Langevin chain increases.

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