Infrared Dichroism and Orientation of Plasticizers in Stretched Polyvinylchloride Films

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Infrared dichroic measurements were made of stretched polyvinylchloride (PVC) films containing dioctyl phthalate and diethyl phthalate as plasticizer. It was concluded that dioctyl phthalate molecules added less than about 15 % were oriented keeping their relative orientation to PVC chain constant, and that those added more than about 15 % were dispersed freely in PVC medium. For the former case, the angles between PVC chain axis and three mutually orthogonal axes of benzene ring in phthalates were caluculated from the orientation functions for the benzene absorption bands. The effect of alkyl chain length of phthalates on the orientation was discussed by comparing the results obtained for dioctyl phthalate and diethyl phthalate.

INTRODUCTION

Many studies have been made of the nature and mechanism of plasticizing action. It is reported that the polar plasticizer such as phthalates, added to polyvinylchloride (PVC), make solvation with some active point of PVC[1]. In order to confirm this, it is worthwhile to have informations about the orientation of plasticizer with respect to the PVC chain. Studies along this line, however, have been very limited in number.

On the other hand, in connection with the relative orientation between the polymer and the molecules added to the polymer, there are studies of the amorphous orientation by means of the visible dichroism of dyes incorporated into the polymer, and the polarization of fluorescence emitted from fluorescent molecules added or bonded to the polymer. These methods suffer from the disadvantage that the orientation of the added molecules with respect to the polymer chain segments is generally unknown, so that the accurate estimates of amorphous chain orientations have not yet been possible. The polarized infrared method has the advantage that one can measure the dichroism not only of the polymer but also of the added molecules, simultaneously.

In the present work, the infrared dichroism was measured for the stretched PVC films containing di-2-ethyl-hexyl phthalate (DOP) or diethyl phthalate (DEP). Besides ordinary polarized infrared spectra, use was made of the differential polarized spectra which were proposed by some of the present authors for precise measurement of low dichroism[2]. From the results of dichroic measurements,

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the relative orientation with respect to PVC chain was argued. The effect of the alkyl chain length on the orientation is also discussed by comparison of the results obtained for DOP and DEP.

EXPERIMENTAL

The PVC sample used is commercial *KANEVINYL S1001* from Kanegafuchi Chemical Industry Co., having the degree of polymerization of 1050 in average. It is said that the sample consists of nearly the same amount of syndiotactic and isotactic diads[3]. DEP and DOP are of chemical grade. The mixture of PVC and DEP or DOP was dissolved into tetrahydrofuran to form 3-5 % solution of PVC at room temperature, then casted so that the film thicknesses were between 8 and 40 μ depending on the intensity of the absorption band used, except for the very weak bands between 2000 and 1800 cm^{-1} for which about 1000 μ films were used. The concentration of DEP or DOP in PVC was chosen to be various values less than 35 weight per cent. After full removal of the solvent at about 4°C in a refrigerator, the film obtained was stretched to various degrees of elongation in boiling water, and then quenched in cold water.

Infrared spectra were recorded by a Perkin-Elmer model 521 grating spectrophotometer. Two silver chloride polarizers were used for polarization measurements, being tilted 45° with respect to the entrance slit of the monochromator to eliminate the effect of polarization characteristics of the grating on the measurements. In the measurements of differential polarized spectra, the two polarizers and the sample were arranged with respect to the monochromator as described before[2,4]. Such arrangement gives the quantity T shown by

$$T = I_s/I_r = 10^{-(A_{//} - A_{\perp})} \tag{1}$$

on the recording paper, where I_s and I_r are the intensities of the sample beam and reference beam, respectively, transmitted through the sample, and $A_{//}$ and $A_{\perp}$ are absorbances of the sample for the polarized radiations with the electric vectors pararell and perpendicular, respectively, to the stretching direction. Eq. (1) means that a pararell band ($A_{//} > A_{\perp}$, and $T < 1$) gives a downward peak in the differencial polarized spectrum, whereas a perpendicular band ($A_{//} < A_{\perp}$, and $T > 1$) gives an upward peak.

Corrections were carried out for the imperfection of polarization in the transmitted beam of silver chloride polarizer used[5].

RESULTS AND DISCUSSIONS

1. Ordinary polarized and differential polarized infrared spectra and band assignments

The ordinary polarized and differential polarized infrared spectra of the PVC film, containing 10 wt% DOP and stretched by 250 % are shown in Figs. 1(a) and (b), respectively. Almost all the bands shown in Fig. 1 could not be used for evaluating the orientation of PVC and DOP because of overlap of the absorption
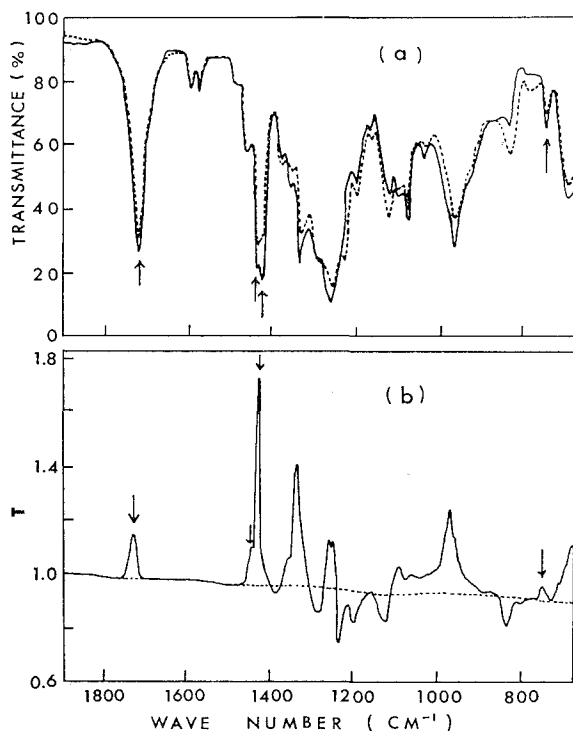
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Fig. 1. (a) Polarized infrared spectra of a PVC film containing 10 % DOP and
stretched by 250 %.
—— electric vector perpendicular to elongation
······ electric vector pararell to elongation
(b) Differential polarized infrared spectra of the same sample as (a).
The broken line is for no sample.

bands in both molecules. Only two bands of PVC and two bands of DOP shown
by arrows in Fig. 1 were found to be free from the overlap and were used for
the quantitative treatments. The situation was the same for the PVC film con-
taining DEP.

Infrared absorption spectra of PVC having various conformations have been
studied by many authors[6~11]. According to Germar et al[11], the 1426 cm^{-1} band
was attributed to the bending mode of the CH$_2$ group of the syndiotactic TT con-
formation, whereas the 1435 cm^{-1} band to the same mode of the isotactic TG and
syndiotactic GG conformations*.

Pure DEP and DOP have the C=O stretching vibration band at 1729 and 1730
cm^{-1}, respectively. When the molecules are dispersed into PVC medium, these
bands shift to 1725 and 1723 cm^{-1}, respectively. This frequency shift may be due
to some interaction between carbonyl groups of phthalates and some active parts
of PVC chain as was pointed out by Luther et al[12].

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* The conformations of linear polymer molecules can be expressed by the consecutive ar-
rangement of T (*trans* form) and G (*gausch* form) in a main chain. See S. Mizushima :
"Structure of Molecules and Internal Rotation", p. 98, Academic Press, New York (1954).
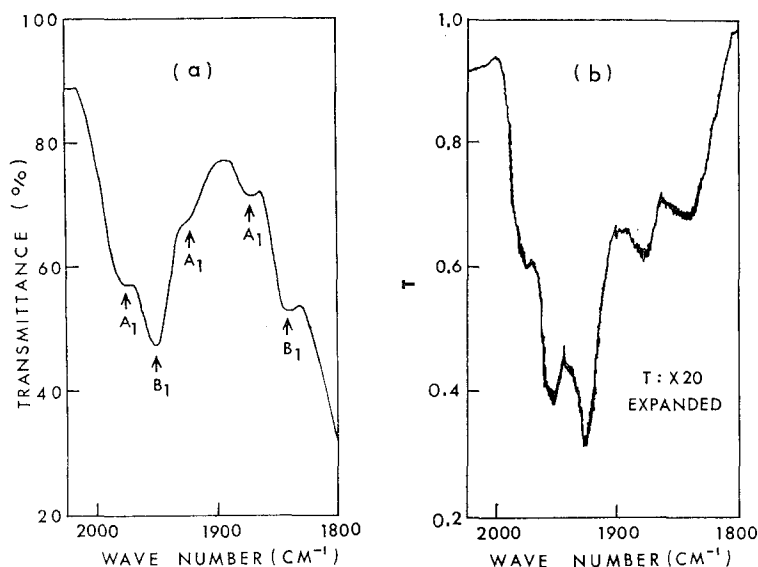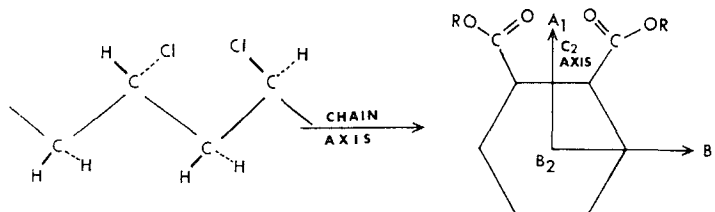
Fig. 2. Unpolarized (a) and differential polarized (b) infrared spectra of a PVC film
containing 15 % DOP and stretched by 650 %.

Table 1. Assignments of bands used.

Wave number		Assignment	Symmetry species of C_{2v}		Transition moment
PVC	1426	CH₂ scissoring of syndiotactic TT unit			Perpendicular to chain axis
	1435	CH₂ scissoring of isotactic TG unit and syndiotactic GG unit			See the text
DEP	**DOP**				
745	743	CH out-of-plane deformation of benzene		(B_2)	Perpendicular to benzene plane
1725	1723	C=O stretching			————
1855	1840	Overtones and combinations of CH out-of-plane deformations (b, c & d) of benzene	b+c	(B_1)	In-plane, perpendicular to C₂ axis
1886	1868		c+d	(A_1)	In-plane, pararell to C₂ axis
1936	1918		2b	(A_1)	In-plane, pararell to C₂ axis
1956	1946		b+d	(B_1)	In-plane, perpendicular to C₂ axis
1984	1973		2d	(A_1)	In-plane, pararell to C₂ axis

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On the other hand, it is reasonable to consider that the CH out-of-plane deformation vibration at 745 cm⁻¹ (DEP) and 743 cm⁻¹ (DOP) belong to the B_2 symmetry species having their transition moments perpendicular to the benzene ring, if the DEP and DOP molecules are assumed to have the symmetry of the point group C_{2V}. This assumption may not be strictly true for whole molecules, because the geometry of the substituents in these molecules is not known. But it may be virtually true as far as only the absorption bands of the benzene ring are discussed.

Figure 2(a) represents the unpolarized spectrum between 2000 and 1800 cm⁻¹ of a PVC film, containing 15 % DOP and stretched by 650 %. Five absorptions are observed in this region. As the intensity of these bands is much weaker than that of the bands shown in Fig. 1, thicker films were used in this case as compared with the previous case. Since dichroism of these bands is very small, it could hardly be detected by the ordinary polarized spectrum. Therefore the differential polarized spectrum was recorded as is shown in Fig. 2(b) with the ordinate scale expantion of twenty fold. According to Kakiuchi[13] these bands can be assigned to the overtone or combination bands (the A_1 or B_1 species of the point group C_{2V}) of the CH out-of-plane deformation vibrations of the substituted benzene ring.

The assignments of the bands shown in Figs. 1 and 2 are summarized in Table 1. Since the transition moments of the A_1, B_1 and B_2 species bands are mutually orthogonal as shown in the figure in Table 1, the orientation of the benzene ring in phthalates could be completely evaluated using the A_1, B_1 and B_2 species bands.

2. Evaluation of orientation : orientation function

In order to evaluate the orientation of PVC chain axis with respect to the stretching direction, a orientation function F defined by[14,15]

$$F = f_a \cdot f_\theta \tag{2}$$

$$f_a = \frac{3 <\cos^2 \alpha> - 1}{2} \tag{3}$$

$$f_\theta = \frac{3 <\cos^2 \theta> - 1}{2} \tag{4}$$

was used under the assumption of uniaxial orientation, where α is the angle between the stretching direction and the PVC chain axis, and θ between the PVC chain axis and the transition moment of the infrared absorption band.

For the 1426 cm⁻¹ band θ can reasonably be assumed to have the value of $\pi/2$, so that the orientation function of this band is given by

$$F(1426) = -f_a/2 \tag{5}$$

Eq. (2) holds also for the bands of DOP and DEP, if θ is replaced by γ, δ or ε, which is the angle between the PVC chain axis and the transition moment of the A_1, B_1 or B_2 species band, respectively, of DOP and DEP molecules, as shown in Fig. 3, that is,
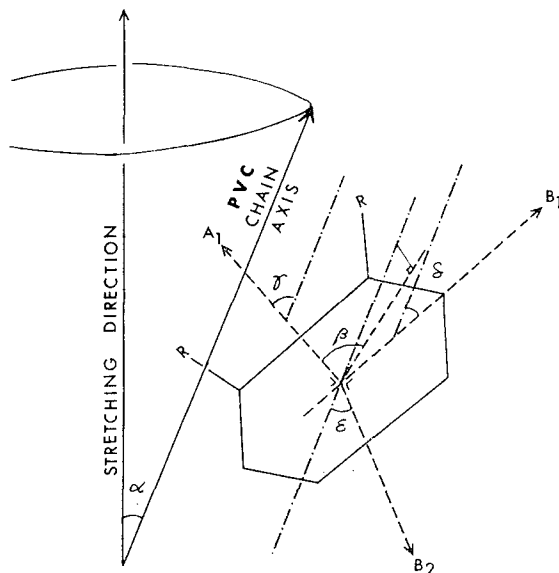
$$F(A_1) = f_a \cdot f_\gamma \tag{6}$$

Fig. 3. Orientation of a phthalate molecule with respect to a uniaxially oriented PVC chain axis.

$$F(B_1) = f_\alpha \cdot f_\delta \qquad\qquad (7)$$

$$F(B_2) = f_\alpha \cdot f_\varepsilon \qquad\qquad (8)$$

As the transition moment of the A_1, B_1 and B_2 species bands are mutually orthogonal, we have

$$f_\gamma + f_\delta + f_\varepsilon = 0 \qquad\qquad (9)$$

It should be noticed that the orientation function gives the mean value of cosine of angles, but not the distribution of angles. Therefore it is useful, in some cases, to employ α_M *etc.* which satisfy $\cos^2 \alpha_M = \langle \cos^2 \alpha \rangle$ *etc.*. If the distribution of the angles is narrow or sharp, α_M is virtually equal to $\langle \alpha \rangle$.

The orientation function can be obtained from infrared dichroism of the band by

$$F = (A_{/\!/} - A_\perp)/(A_{/\!/} + 2A_\perp) \qquad\qquad (10)$$

For an uniaxially oriented sample we may define the absorbance A by

$$A = (A_{/\!/} + 2A_\perp)/3 \qquad\qquad (11)$$

A is independent of the state of orientation within the sample and is proportional to the amount of absorbing centers in the oriented sample. We may note that in general A is not equal to the absorbance A' of the oriented sample for unpolarized beam[16]. If the dichroism is very small, A is nearly equal to A'. In this case, the orientation function is expressed from Eqs. (10) and (11) as

$$F \approx (A_{/\!/} - A_\perp)/3A' \qquad\qquad (12)$$

where $A_{/\!/} - A_\perp$ can be obtained from T given by Eq. (1).

3. Variations in the orientation function with elongation

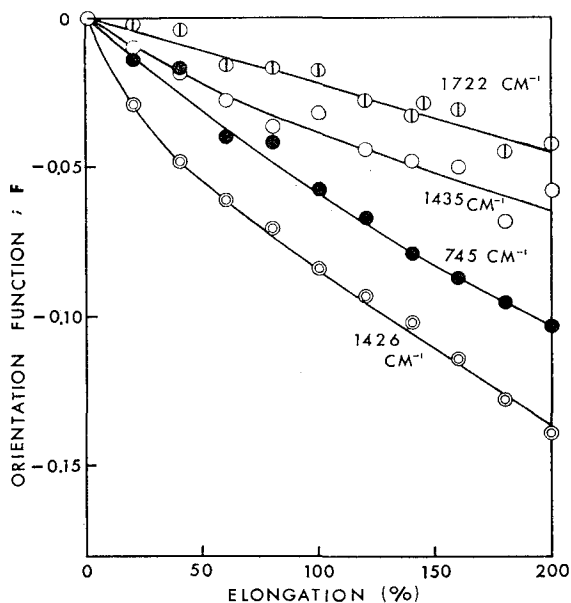Junzo UMEMURA, Tohru TAKENAKA, Soichi HAYASHI and Rempei GOTOH

Fig. 4. Variations in orientation functions with elongation of PVC films containing 6.3% DEP.
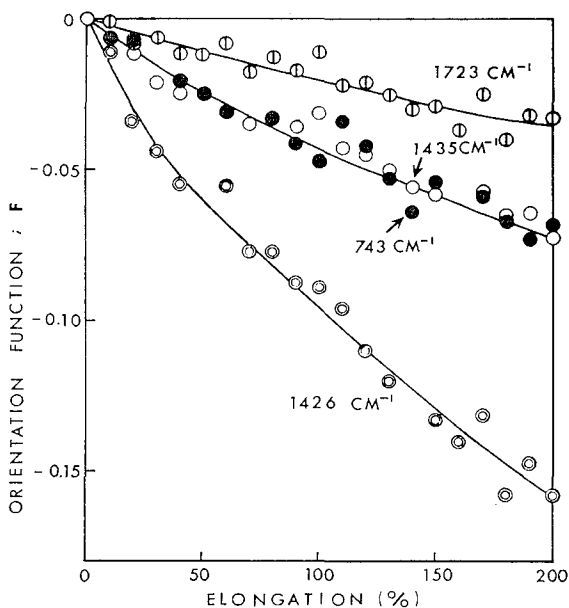

Fig. 5. Variations in orientation functions with elongation of PVC films containing 10% DOP.

Figs. 4 and 5 show variations in the orientation functions with elongation of PVC films containing 6.3 wt. % DEP and 10 wt. % DOP (equivalent in molar per cent), respectively. The F values decreases smoothly with elongation. The ratios of F values of DEP and DOP to those of PVC are constant throughout the whole degree of elongation examined. This fact suggests that the plasticizer
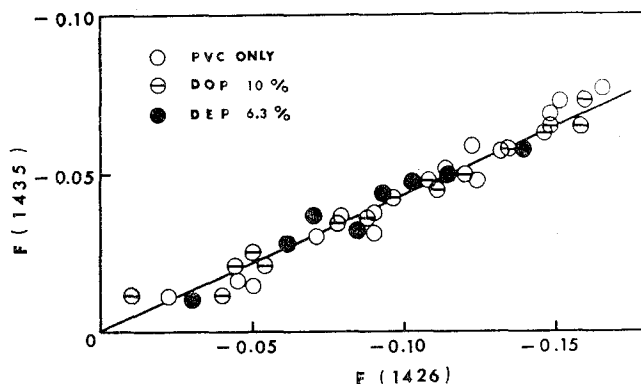
Fig. 6. Correlation between $F(1435)$ and $F(1426)$ of PVC.

molecules follow closely the orientation of PVC chains when PVC films are stretched.

The absolute value of $F(1426)$ is always larger than that of $F(1435)$ as is seen in Figs. 4 and 5. In Fig. 6 the values of $F(1435)$ at various degrees of elongation are plotted against the corresponding values of $F(1426)$, including the case of pure PVC films. All points lie on a straight line. As is described before, the 1426 cm^{-1} band is assigned to the CH$_2$ bending mode of the syndiotactic TT conformation (trans zigzag carbon skeleton) with its transition moment perpendicular to the chain axis. On the other hand, the 1435 cm^{-1} band is mainly ascribed to the CH$_2$ bending mode of the isotactic TG conformations and partly to that of the syndiotactic GG conformations (the bent part of the zigzag carbon chain). The sequence of isotactic TG units forms three-fold helix, and the transition moment of CH$_2$ bending vibration band (1435 cm^{-1}) of this conformation is not perpendicular to the helix axis. It is therefore expected that the absolute value of the orientation function for the 1435 cm^{-1} band is smaller than that for the 1426 cm^{-1} band, even if the orientation of the helix axis of the isotactic TG conformation is the same as that of the chain axis of the syndiotactic TT conformation. Assuming that this is the case and neglecting the contribution of syndiotactic GG units and isolated TG units to 1435 cm^{-1} band, the transition moment of the isotactic TG units is determined to form the angle of about 64° with the helix axis from the slope of the line in Fig. 6. This means that the C—C—C angles of the three-fold helix is about 128° which is somewhat larger than tetrahedral angle 109°28′.

Hereafter, $F(1426)$ will be used to evaluate the orientation of PVC chains under the assumption that the orientation of the helix axis of the isotactic TG units are nearly the same as that of the chain axis of the syndiotactic TT units.

4. The relative orientation between phthalates and PVC

In Fig. 7, the values of $F(745)$ of DEP and $F(743)$ of DOP are plotted against those of $F(1426)$, showing the linear relationships. This fact suggests that the values of f_ε is constant independent of the degree of elongation. Putting this slope equal to the ratio of Eqs. (8) to (5), the values of f_ε, $<\cos^2 \varepsilon>$ and ε_M can be obtained as is shown in Table 2. The difference in $<\cos^2 \varepsilon>$ or ε_M can be
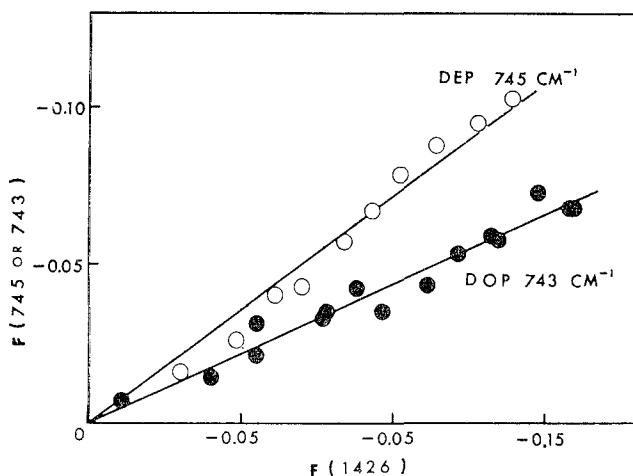
Fig. 7. Correlation between $F(745)$ of DEP or $F(743)$ of DOP and $F(1426)$ of PVC.

Table 2.

	DEP	DOP
f_ε	-0.36	-0.22
$\langle \cos^2 \varepsilon \rangle$	0.093	0.187
ε_M	71°	64°
$F(A_1)^*$	0.094	0.065
$F(B_1)^{**}$	0.043	0.023
f_γ	0.24^8	0.16^2
$\langle \cos^2 \gamma \rangle$	0.49^8	0.44^1
γ_M	45°	48°
f_δ	0.11^3	0.058
$\langle \cos^2 \delta \rangle$	0.40^8	0.37^2
δ_M	50°	52°
β_M	39°	40°

* The avarage value of three $F(A_1)$.
** The avarage value of two $F(B_1)$.

seen between DEP and DOP. Larger value of ε_M in DEP shows that the benzene plane of DEP orients more pararell to the PVC chain than that of DOP does. The ethyl-hexyl groups in DOP is bulkier than the ethyl groups in DEP, and this bulkiness of the ethyl-hexyl groups seems to reduce the pararellism of the benzene plane to the PVC chains.

The next step is to obtain the values of f_γ and f_δ by the use of the results shown in Figs. 2(a) and 2(b). As the dichroism of these bands is small, Eq. (12) in stead of Eq. (10) was used to get the orientation function F. This film was so thick that the dichroism of the 1426 cm^{-1} band could not be measured. Therefore, f_γ and f_δ could not be obtained from Eqs. (5), (6) and (7). The values of f_γ and f_δ were obtained from the ratio of $F(A_1)$ to $F(B_1)$, i.e., f_γ/f_δ and Eq. (9). In this case, f_ε in Eq. (9) was assumed to be the same as that in the elongation less than 200 %. The results are listed in Table 2.

The differences in γ_M and δ_M between DEP and DOP are not so large. This fact and the above-mentioned frequency shift for the C=O stretching vibration seem to mean that the ester groups of substituents in phthalates play the important part in the stable orientation of phthalates to PVC chain.

The angle β_M between the A_1 direction and the projection of the PVC chain axis on the benzene plane can be obtained from already-known γ_M and ε_M, using the next relationships,

$$\cos \gamma_M = \cos\left(\frac{\pi}{2} - \varepsilon_M\right) \cdot \cos \beta_M \qquad (13)$$

The result is listed in Table 2. Little difference in β_M between DEP and DOP also suggests the role of the ester groups in the phthalate orientation described above.

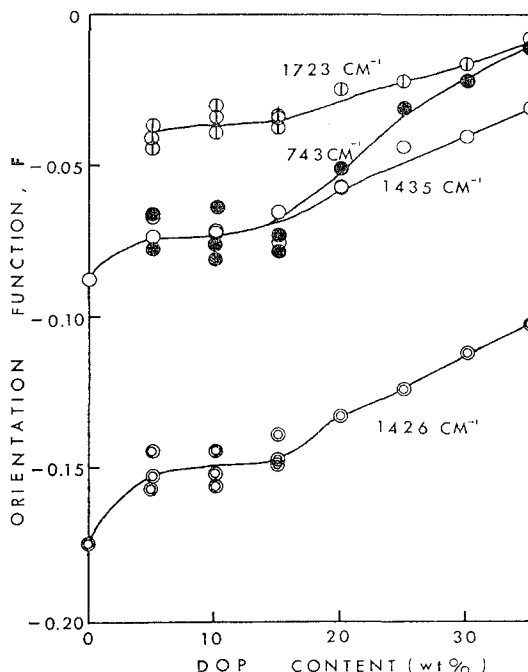## 5. Variations in orientation functions with DOP content

Fig. 8. Variations in orientation functions with DOP content in PVC films stretched by 200%.

Figure 8 shows variations in orientation functions with DOP content in PVC films stretched by 200 %. As the DOP content increases, the values of orientation functions of all the PVC and DOP bands examined increase slowly till about 15 % content, and rapidly thereafter. At the same time the coincidence of $F(1435)$ and $F(743)$ observed at less than about 15 % content disappears at higher content, where $F(743)$ increases more rapidly than $F(1435)$ does. This seems to show that the limit of so-called "solvation" of DOP to PVC is about 15 % content and that DOP molecules added more than about 15 % content are dispersed comparatively freely in the PVC medium. The same results have been obtained by other methods such as broad line NMR[17], and dielectric[17] and mechanical losses[18].

The increase of the value of $F(1435)$ or $F(1426)$ at more than about 15 % content seems to be due to the release of entanglements between PVC chains themselves by the presence of the free DOP molecules. The release of entanglements may increase the freedom of PVC chains, so that the degree of orientation may be lowered.

6. Variation in the conformation of PVC with elongation

Figure 9 shows the variation in the ratio $A(1426)/A(1435)$ with elongation. It is seen that the relative intensity of 1426 cm^{-1} band to that of 1435 cm^{-1} band increases slightly with elongation regardless of the concentration of DOP. This fact suggests the partial interconversion from syndiotactic GG conformation into TT conformation by stretching, that is, the interconversion from bent syndiotactic chain into straight zigzag chain. In this process, the degree of crystallinity may be
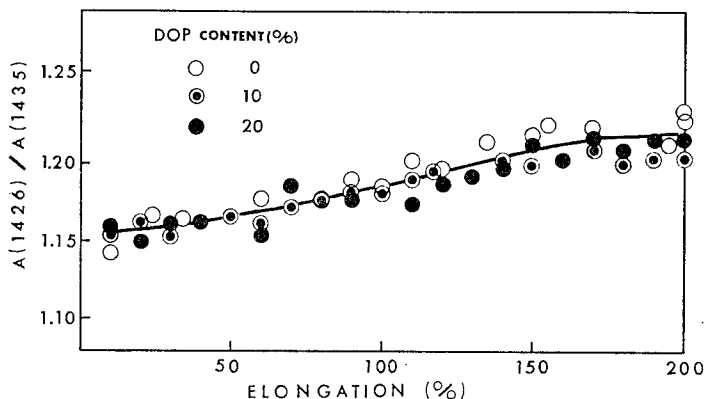
Fig. 9. Variation in the ratio of $A(1426)/A(1435)$ with elongation of PVC films.

increased slightly.

ACKNOWLEDGEMENT

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