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## Polymer Spectra of a Cyanine Dye

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In dilute aqueous solutions the dye 1,1'-diethyl-2,2'-cyanine chloride, a photographic sensitizer, has two broad molecular absorption bands with maxima at 4900 and 5230Å. For a  $10^{-2}$  molar water solution at room temperature, which is a gel, a new, intense, and exceedingly narrow absorption and fluorescence band has been found at 5730Å by G. Scheibe, and by E. Jelley by other methods. The electric polarization of this "*P* band" were studied for thin dye films deposited on glass from solutions containing water. The *P* band shifts about 50Å to greater wavelength, becomes broader and weaker, and finally disappears as the water is removed by pumping and/or by increasing the temperature. This behavior is reversible if water vapor is readmitted. The position of the *P* band enables a measurement of the humidity of the atmosphere surrounding the film. The effect of temperature from  $-195$  to  $+100^{\circ}\text{C}$  is described. The *P* band can be made to appear starting with water solutions as dilute as  $10^{-5}$  *M* by freezing the water, locally concentrating the solution. For dye films, there is observed a second, weaker absorption band

(called the *P*<sub>M1</sub> band) at 5430Å similar to the *P* band in structure and behavior but polarized perpendicular to the polymer chains and requiring a higher dye concentration before appearing. Reasons discussed in the paper indicate that the *P* band is due to single dye polymer chains while the *P*<sub>M1</sub> band should belong to a system of coupled chains lying mutually parallel and forming threads. These threads were observed microscopically. A dehydrated film may contain a fraction of the dye molecules in monomeric form, another fraction (showing only the molecular bands much broadened) in an array anchored to the supporting surface such that the mere addition of water *vapor* immediately produces the polymer chains with the *P* and *P*<sub>M1</sub> bands, and the remainder in crystalline form with a broad absorption band at 5650 and a broad fluorescence band at 6200Å. Experiments undertaken to determine the number of water molecules per dye molecule necessary for polymerization were only sufficient to determine that the order of magnitude of the ratio is from 1:2 to 10:1. An attempt is made to interpret the absorption and fluorescence bands of the polymer chains by the hypothesis of exciton migration.

### 1. INTRODUCTION

THE dye 1,1'-diethyl-2,2'-cyanine chloride is one of a class used for sensitizing photographic emulsions for longer wave-lengths when adsorbed on the surface of the silver halide grains.<sup>1</sup> This red dye shows two normal molecular absorption bands each several hundred angstroms wide with maxima<sup>2</sup> at 4900 and 5230Å, characteristic of the molecules when dissolved in polar solvents such as alcohol.

However, if the solvent is water some unusual phenomena occur. As the concentration of the dye is increased, the 5230Å molecular absorption band becomes weaker, a new absorption band

begins to appear (E. E. Jelley<sup>3</sup> and G. Scheibe<sup>4</sup>), and at the same time the viscosity of the solution increases.<sup>5</sup> [A "saturated solution" at room temperature<sup>6</sup> is about  $3(10)^{-2}$  mole/liter.] At a concentration of about  $10^{-2}$  *M* the viscosity is so high that the solution is a gel<sup>4</sup> while the new absorption band with its maximum at about 5730Å is intense and unusually narrow as compared with normal absorption bands of polyatomic molecules. It actually resembles a broadened atomic absorption line. Diluting or heating the gel causes the new band and the gel state to disappear,<sup>5-8</sup> and these effects are indefinitely reversible. They are explained<sup>8</sup> as the result of a reversible polymerization in which the dye molecules are coupled together through the medium of the water molecules to form long

<sup>1</sup> For the average areal density distribution of the adsorbed dye see, for instance, S. E. Sheppard, R. H. Lambert, and R. D. Walker, *J. Chem. Phys.* **7**, 265 (1939). For the spectral region where the iodide of this dye sensitizes emulsions see C. E. Kenneth Mees, *The Theory of the Photographic Process* (The Macmillan Company, New York, 1942), p. 980.

<sup>2</sup> L. G. S. Brooker and G. H. Keyes, *J. Am. Chem. Soc.* **58**, 659 (1936). This reference is for the iodide compound the molecular spectrum of which is essentially identical to that of the chloride compound.

<sup>3</sup> E. E. Jelley, *Nature* **138**, 1009 (1936).

<sup>4</sup> G. Scheibe, *Zeits. f. angew. Chemie* **50**, 51 (1937).

<sup>5</sup> G. Scheibe, *Kolloid Zeits.* **82**, 1 (1938).

<sup>6</sup> H. Ecker, *Kolloid Zeits.* **92**, 35 (1940).

<sup>7</sup> G. Scheibe, L. Kandler, and H. Ecker, *Naturwiss.* **25**, 75 (1937).

<sup>8</sup> G. Scheibe, A. Mareis, and H. Ecker, *Naturwiss.* **25**, 474 (1937).

polymer chains. The presence of  $\text{H}_2\text{O}$  (or  $\text{D}_2\text{O}$ ) mixed in other solvents is sufficient to bring out this polymer band, but without water it is absent.<sup>6</sup> The gel state has been called a "nematic phase",<sup>9</sup> or a "Z state",<sup>10</sup> or a "mesophase",<sup>11</sup> and the band characteristic of this polymerized state has been called a "*P* band",<sup>6</sup> or a "*Z* band",<sup>10</sup> or a "*J* band".<sup>11</sup> The terms "gel" and "*P* band" (*P* for polymer) will be used in this report, and "gel" will mean about a  $10^{-2}$  *M* solution of dye in water at room temperature.

The structure of the dye molecule is shown in Fig. 1.<sup>12-14</sup> The dimethyl iodide compound was first synthesized many years ago by O. Fischer and G. Scheibe;<sup>15</sup> subsequently improvements in synthesis have been made on the diethyl chloride compound by F. M. Hamer,<sup>16</sup> and by L. G. S. Brooker and collaborators.<sup>17</sup>

The dye in a dilute aqueous solution at room temperature does not fluoresce. However, irradiation of the *gel* with light of the same wave-length as the polymer absorption band (5730Å) causes fluorescence in this *P* band<sup>3,18,19</sup> (*P* for polymer), analogous to the resonance fluorescence of atoms. Irradiation of the gel with light of the wave-lengths of one of the two molecular absorption bands (5230 or 4900Å), or with shorter wave-lengths, does not produce fluorescence in these molecular bands, but again causes fluorescence only in the *P* band.

If the amount of water in the gel is further reduced, new optical and mechanical properties are observed. Scheibe and L. Kandler<sup>13</sup> state that under these conditions both molecular bands shift their positions to longer wave-lengths. Jelley<sup>9</sup> finds that comparable dye concentrations give a thread-like but non-crystalline structure (third phase\*). Further, when all the water is removed it is possible to obtain dye crystals

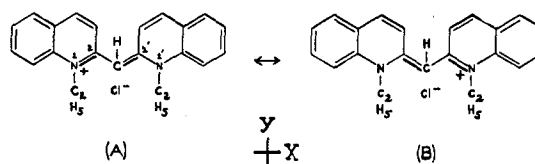


FIG. 1. The dye 1,1'-diethyl-2,2'-cyanine chloride,  $\text{C}_{23}\text{H}_{23}\text{N}_2\text{Cl}$ , shows resonance between several configurations. One of these combinations ( $\text{A} \leftrightarrow \text{B}$ ) is shown above. (The identical dye is called *N,N'*-Diäthyl-Pseudo-Isocyanin-Chlorid in the German literature, and 1:1'-diethyl- $\psi$ -cyanine chloride in the British literature. Eastman Kodak Company's designation is Dye V a. The notation used here in the text seems the least ambiguous.) The electric polarization of the 4900Å molecular absorption band is along the *y* direction; that of the 5230Å molecular absorption band is along *x*. The single polymer consists of dye molecules piled one on top of the other, like a pack of cards, extending in the *z* direction. The electric polarization of the 5730Å polymer absorption and fluorescence band is along *z*, determined by aligning the single polymer chains of the gel by streaming orientation.

(fourth phase), which do not show the narrow *P* band but do show a different absorption and fluorescence spectrum.

J. Franck and E. Teller<sup>20</sup> have presented a theory in which the shape and behavior of the polymer band, the resonance fluorescence, and other spectroscopic and photochemical properties are explained. This *P* band has all the properties expected from an electronic transition in a giant polymer in which the single resonators are so strongly coupled in the excited state that the energy remains in one molecule of the polymer a very short time compared with an oscillation period of that molecule (exciton<sup>21</sup> migration).

Scheibe and co-workers<sup>13,18</sup> have suggested that the dye molecules are coupled together by the inductive forces of the *p* electrons of the dye molecules, and also that the water molecules and conjugation play a role in forming the polymer. On the other hand, Sheppard<sup>10,11,22</sup> has proposed that the intermolecular coupling is due to the linkage of two water molecules with the two pairs of corresponding nitrogen atoms of any two adjacent dye molecules along the polymer.

Many more observations have been enumerated in a survey by Sheppard.<sup>11</sup> The present investigation is devoted to a further experimental study of the dye polymerization.

<sup>9</sup> E. E. Jelley, *Nature* **139**, 631 (1937).

<sup>10</sup> S. E. Sheppard, *Science* **93**, 42 (1941).

<sup>11</sup> S. E. Sheppard, *Rev. Mod. Phys.* **14**, 303 (1942).

<sup>12</sup> G. Scheibe, *Zeits. f. angew. Chemie* **52**, 631 (1939).

<sup>13</sup> G. Scheibe and L. Kandler, *Naturwiss.* **26**, 412 (1938).

<sup>14</sup> G. Scheibe, A. Schöntag, and F. Katheder, *Naturwiss.* **27**, 499 (1939).

<sup>15</sup> O. Fischer and G. Scheibe, *J. prakt. Chemie* **100**, 86 (1920).

<sup>16</sup> Frances M. Hamer, *J. Chem. Soc.*, p. 206 (1928).

<sup>17</sup> L. G. S. Brooker and G. H. Keyes, *J. Am. Chem. Soc.* **57**, 2488 (1935).

<sup>18</sup> G. Scheibe, *Zeits. f. angew. Chemie* **50**, 212 (1937).

<sup>19</sup> G. Scheibe, *Naturwiss.* **25**, 795 (1937).

\* The first phase is a molecularly dispersed solution; the second corresponds to the gel with primary polymerization.

<sup>20</sup> J. Franck and E. Teller, *J. Chem. Phys.* **6**, 861 (1938).

<sup>21</sup> J. Frenkel, *Physik. Zeits. Sowjetunion* **9**, 158 (1936).

<sup>22</sup> C. E. Kenneth Mees, *The Theory of the Photographic Process* (The Macmillan Company, New York, 1942), p. 1076.

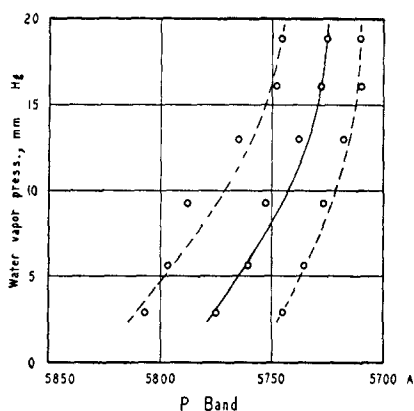


FIG. 2. — position of maximum absorption. --- position of the edges at estimated half-maximum absorption. With increasing water vapor pressure in the environment of a dye film at room temperature (21.4°C for the above data, and using Method 1 mentioned in the text), the wave-length of the maximum absorption of the *P* band continuously decreases, the width at half-maximum decreases, and the intensity of the maximum increases. Any new position is attained rapidly and reproducibly.

## 2. DEPENDENCE OF THE *P* BAND AT ROOM TEMPERATURE ON WATER VAPOR PRESSURE

For dye films made by the evaporation of a solvent from a solution, Scheibe and co-workers<sup>13,23</sup> have shown that the *P*-absorption band becomes weaker and broader and shifts to somewhat longer wave-lengths as water is removed from the film by pumping. Jelley<sup>9</sup> has also noticed such a shift with aging. In the present work this observation has been studied by several methods.

Most of the experiments were done with thin films of dye on glass; in a few cases polished metal surfaces were used. To make these films a dye solution of 1 mg per cc of solvent, or  $2.76 (10)^{-3} M$ , is placed on clean glass and the solvent is allowed to evaporate. Water is a poor solvent for this purpose because it does not evaporate uniformly and quickly, but the lower alcohols and chloroform in humid air behave more satisfactorily. Ethyl alcohol (95 percent) is preferable. The best thickness for observing the *P* band is about  $5 (10)^{-6}$  g of dye per  $\text{cm}^2$ . A thinner film shows the *P* band too weakly; a thicker film acts as a red filter with a fairly sharp cut-off at about 5850Å.

<sup>23</sup> G. Scheibe, A. Schöntag, J. Kopske, and K. Henle, *Zeits. f. wiss. Photographie, Photophysik, u. Photochem.* **38**, 1 (1939).

Even if absolute ethyl alcohol, used as the solvent, evaporates from the glass in ordinary air, the *P* band appears since water vapor from the atmosphere immediately enters the alcohol and also condenses on the film due to cooling by evaporation. When the gel state is reached the *P* band appears suddenly, intense, and narrow at 5730Å. The gel film appears red by reflected light. Further drying reduces the intensity of the *P* band, broadens it, and shifts it continuously to longer wave-lengths (depending upon the humidity of the environment). The film now looks solid and appears golden by reflected light.

Such dye films on glass show the *P*-absorption band nicely when placed before the slit of a spectroscope with a white light continuous background. The instrument used was a direct vision Schmidt and Haensch (three-prism) spectroscope with a resolving power which permitted estimation of the position of the maximum absorption of the *P* band with an accuracy of about  $\pm 3\text{Å}$ .

Measurements of the dependence of the *P* band at room temperature on water vapor pressure were made by many methods, three examples of which follow:

1. In a closed box with glass windows the films were mounted over large flat trays in which was spread out a slushy mixture of water saturated with various salts, with an excess of salt. The air in the box was circulated. Each salt maintains its own characteristic constant water vapor pressure (depending upon temperature), and the values used were taken from the data of the U. S. Bureau of Standards.

2. The dye films were put in a closed glass vessel which was connected by a large tube to a remote reservoir of liquid water kept at various temperatures. In this way the water vapor pressure of the environment of the films could be controlled.

3. Water-saturated air at room temperature and dehydrated air were mixed in various proportions at various total pressures for the environment of the films.

These methods gave the same behavior of the *P* band; the presence or absence of dehydrated air made no difference.

The results are shown in Fig. 2. The total shift of the *P* band from the lowest water vapor pressure at which it is observable to saturation is about 50Å. The position of the *P* band at all water vapor pressures remains distinct from that of each of the two molecular bands. The *P*-band behavior is understandable if one assumes that the polymer chains become longer as more water

is taken up (see, for instance, the discussion by Franck and Teller<sup>20</sup>).

The position of the *P*-absorption band of such dye films on glass can be used to measure water vapor pressure. This is a hygrometer\* based on a new principle.

After remaining a long time in ordinary air (where water vapor is always available), films of dye often develop a "permanent" disappearance of the *P* band. This disappearance can usually be attained quickly by heating normal polymerized films to about 100°C in an environment of very low water vapor pressure. These films when cooled to room temperature in ordinary air usually do not show the *P* band, but instead show a weak absorption band with its maximum at about 5650Å and an estimated full width at half-maximum of about 200Å. Placing these films in water-saturated air at room temperature, or even at temperatures as high as 100°C where the water vapor pressure is one atmosphere, usually does not cause the *P* band to reappear. Only if *liquid* water is condensed on the surface of the film (for instance, by strong exhalation), so that for a time the dye is dissolved in water, does the 5650Å band disappear and the *P* band reappear. After the surplus water has evaporated the dye film shows the normal reversibly polymerized *P*-band phenomena. It has been concluded, therefore, that another solid modification<sup>24</sup> of the dye is possible (Jelley's<sup>9</sup> fourth phase). As will be shown, this is a crystalline state of the dye which must be distinguished from the polymerized state. Consequently, dye molecules deposited on glass in a way which excludes water molecules during the formation of the film should give this crystalline state, which cannot be converted into the polymerized state by the mere presence of water *vapor* if liquid water is excluded.

To prove this, the following arrangement was used. A gas-tight glass box was fitted with sealed-on rubber gloves for manipulation. The box contained an atmosphere of CO<sub>2</sub> kept free from water vapor by the use of P<sub>2</sub>O<sub>5</sub>. The dye was

deposited on the surface of glass in the manner described above, but great care was taken that the solvent, absolute ethyl alcohol or chloroform, was free from water. The evaporation of the solvent from the surface of the glass took place inside the dry box. In this way films were made which did not show the *P* band in the dry box nor after transfer to normal humid air. However, these films did show the 5650Å crystal absorption band. Scheibe and collaborators<sup>23</sup> have used anhydrous amyl alcohol to get solid films not showing the *P* band.

The same effect was obtained in experiments originally carried out to study the formation of monomolecular films of dye on the surface of mercury. Inside the dry box mentioned above glass slides were dipped through the dye film on mercury, in the manner of the Langmuir and Blodgett<sup>25</sup> built-up film technique. These films, which were non-uniform after about 50 dips, again did not show the *P* band in the dry box nor after transfer to normal humid air. However, both these films and those mentioned in the previous paragraph showed the normal reversibly polymerized *P*-band phenomena when droplets of water dissolved the dye and the excess water evaporated.

Macroscopic crystals of the dye obtained by standard crystallization methods do not show the *P* band even when put in a water-saturated atmosphere at room temperature, but do show the 5650Å crystal absorption band.

These results do not contradict the observation that dye films deposited in normal humid air, or from a solution containing water, or both, can be dehydrated and rehumidified reversibly and repeatedly at room temperature in the manner previously described. The removal of the water links permits the molecular planes to acquire new positions with respect to each other (probably a perfect disorder) but not to change the positions of their anchor points on the supporting surface; these molecules are therefore prevented from grouping themselves into the crystalline state but remain in the right array to be aligned again into polymer chains as soon as water vapor is admitted. A dehydrated film may contain a fraction of the dye molecules in dispersed

\* To make a practical instrument the temperature must be accounted for and the dye sample has to be replaced after several months. The design of such a practical instrument was not completed, but its feasibility was demonstrated.

<sup>24</sup> J. A. Leermakers, B. H. Carroll, and C. J. Staud, J. Chem. Phys. 5, 878 (1937).

<sup>25</sup> Katharine B. Blodgett and Irving Langmuir, Phys. Rev. 51, 964 (1937).

TABLE I. Effect of low temperature on the *P* band.  
2.76 (10)<sup>-4</sup> *M* dye in water, 3 mm thick.

Temp.	$\lambda_{\text{max. abs.}}$	Estimated full width at half-max.
20°C	no band	
-10	5730A	50A
-20	5720	40
-78	5712	30
-183	5700	25
-195	5685	20

The intensity of the maximum absorption increases with decreasing temperature. With liquid oxygen (-183°C) or aged liquid air the *P* band must be distinguished from the broader molecular absorption band of liquid oxygen from 5740 to 5800 with its maximum at about 5780A.

monomeric form, another fraction in this particular array ready to be polymerized by water vapor, and the remainder in crystalline form.

### 3. DEPENDENCE OF THE *P* BAND AT VARIOUS TEMPERATURES ON WATER VAPOR PRESSURE

Warming the gel to about 60°C causes the gel state and the associated *P* band to disappear.<sup>5,6</sup> From such observations one can conclude that even at room temperature the lengths of the polymer chains are reduced by heat movement. Consequently the formation of still longer chains was studied by lowering the temperature as far as -195°C (liquid nitrogen). Since it was desired to have sufficient water present at all temperatures the following procedure was adopted. A glass absorption cell about 3 mm thick was filled with a dilute solution of dye in water (about 10<sup>-4</sup> *M* which is too dilute for the *P* band to appear at room temperature). As the tem-

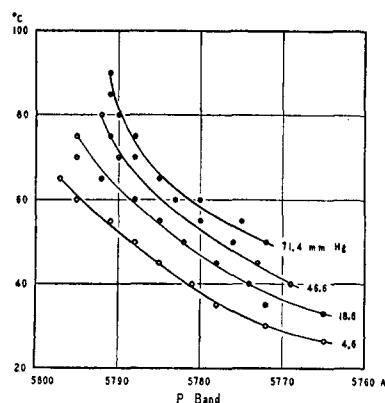


FIG. 3. The position of the maximum absorption of the *P* band depends upon both the temperature of the film and the water vapor pressure indicated for each curve. The *P* band disappeared just above the highest temperature shown for each curve.

perature is lowered to about -10°C pure ice crystals (free of dye) form; between them there is a concentrated dye solution. As soon as the ice starts to form the *P* band appears. If the temperature is lowered further the chains lengthen, since the heat motion does not break them as frequently. Table I gives an example of the continuous change of the *P* band with lower temperatures.

Even a 10<sup>-5</sup> *M* solution of dye in water, which has only a faint pink color, shows the *P* band when frozen. At low temperatures polymerized dye films on glass show spectroscopic behavior of the *P* band similar to that of frozen water solutions (Table I).

Increasing the temperature of dye films causes the *P* band to shift continuously to *longer* wavelengths and finally to disappear; increasing the water vapor pressure of the environment of the films causes the *P* band to shift continuously to *shorter* wave-lengths and to become more intense. The simultaneous application of these two opposing effects was studied. The water vapor pressure was kept constant while the temperature of the film was increased until the *P* band disappeared. Then the film was restored to its original condition, a different water vapor pressure was established, the experiment was repeated, and so forth. The results are shown in Fig. 3. The spectroscopic behavior is in accord with the concept that a thermodynamic equilibrium exists between formation and destruction of chains so that the chain length increases with increase of water concentration relative to the dye (in this region), and decreases with increasing temperature.

### 4. POLARIZED ABSORPTION AND FLUORESCENCE OF THE *P* BAND

With films of dye prepared in the manner described in Section 2, as the solvent evaporates one can follow the development of the polymerized state by the fluorescence excited with the near ultraviolet light of a mercury arc passing through a Wood filter. If evaporation occurs in relatively dry air, the yellow fluorescence appears as the concentration becomes high enough to initiate gel formation and reaches its maximum intensity when the gel state is attained. The fluorescence of the film then becomes weaker

corresponding to the less polymerized state which occurs in equilibrium with the relatively dry air. Placing the film in moist air, or breathing on it, causes the  $P$ -band fluorescence to flash up again. These observations are in accord with the data published by F. Katheder.<sup>26</sup> When the film is dried out entirely and irreversibly, the weak red fluorescence of crystals appears. This is a broad band with its maximum at about 6200Å.

The experiments of Scheibe<sup>12</sup> in which the electric polarization of the  $P$  band was determined by aligning the polymer chains with streaming orientation were repeated. The gel was squeezed between two glass plates, one of which was moved linearly with respect to the other one. Polaroids were used as polarizer and analyzer. It was confirmed that the electric polarization of the  $P$  band both in absorption and in fluorescence is along the polymer axis, that is, parallel to the direction of relative motion of the two glass plates.

##### 5. INFLUENCE OF POLYMERIZATION ON THE MOLECULAR BANDS

The molecular bands shift their positions but slightly as the concentration of the dye becomes great enough to form the gel, for which the  $P$  band is most highly developed, but the absorption coefficient of the 5230 Å molecular band decreases until it becomes roughly half as great when the  $P$  band shows its greatest strength.<sup>5, 23</sup> The 4900Å molecular band is affected to a smaller extent. However, if the concentration of the dye becomes so great that the polymer band already starts to fade from lack of water, according to Scheibe and Kandler<sup>13</sup> the 5230 molecular band shifts to 5430 (described as 5300 to 5425 by them) and the 4900 molecular band shifts to 5100Å, due to "neighborhood action of adjoining polymer chains." In the present investigation during the depletion of water a continuous shift of the 5230 molecular band to 5430 was not visually observed. The 5430 band appeared just when the  $P$  band started to fade, broaden, and shift continuously to longer wave-lengths. Meanwhile the two molecular bands became less distinct without appreciably changing their positions and finally blurred out to a general broad absorption band without distinct maxima

<sup>26</sup> F. Katheder, *Kolloid Zeits.* **92**, 299 (1940); **93**, 28 (1940).

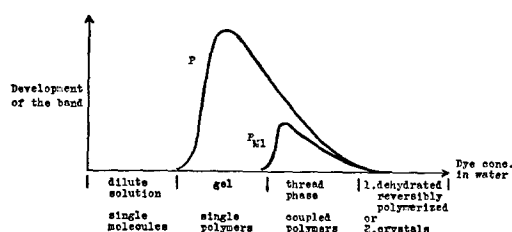


FIG. 4. A qualitative representation of the dependence of the  $P$ - and  $P_{M1}$ -band relationship on dye concentration in water. By a higher development of the band is meant more absorption at the maximum, a narrower band, and the maximum shifted to shorter wave-lengths.

when the water was entirely removed. After the 5430 band had appeared, it also faded, broadened, and shifted continuously to longer wave-lengths simultaneously with the  $P$  band. It seemed obvious to interpret the neighborhood action as a secondary polymerization of many chains all parallel to each other forming threads and coupled together in the  $x$ - $y$  plane of Fig. 1. The hypothesis which is introduced to explain the spectroscopic behavior gains support from the fact that Sheppard had to assume (for other reasons) that there exist not only molecular chains called "nematoids" but also aggregates of sideways coupled chains termed "smectoids".<sup>11</sup>

To study this behavior, films slightly thicker than those described in Section 2 were used. Figure 4 qualitatively describes the development of this second polymer band in relation to the

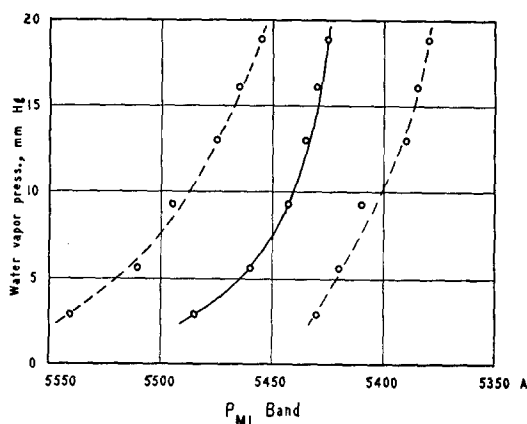


FIG. 5. — position of maximum absorption. --- position of the edges at estimated half-maximum absorption. The above data were taken simultaneously with those shown in Fig. 2 where the conditions and behavior are described. The  $P_{M1}$  band behaves very similarly to the  $P$  band. The  $P_{M1}$  band is only about 1.5 times the  $P$ -band width. The displacement between the bands remains nearly constant at 300Å, for various water vapor pressures. The  $P_{M1}$  band is always weaker and broader than the  $P$  band under the same conditions.

$P$  band as the dye concentration in water changes. This second polymer band at 5430A will be called the  $P_{M1}$  band (polymer band due to modified molecular band). The  $P_{M1}$  band needs higher dye concentration to appear than does

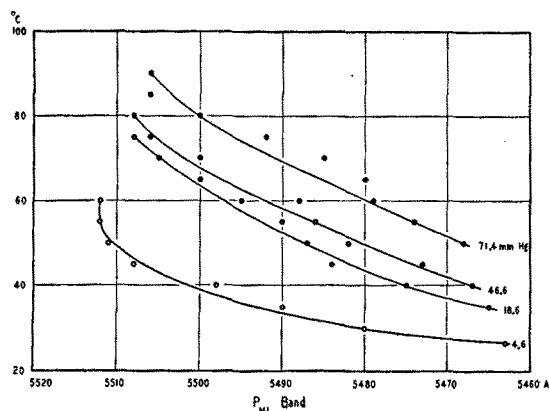


FIG. 6. The position of the maximum absorption of the  $P_{M1}$  band depends upon both the temperature of the film and the water vapor pressure indicated for each curve, analogous to the behavior of the  $P$  band shown in Fig. 3. The above data were taken simultaneously with those shown in Fig. 3. The curves for both bands run nearly parallel and both bands disappear at nearly the same high temperature. The distortion of the lowest curve may be due to the beginning of crystal formation, for which the conditions are favorable.

the  $P$  band, but from there on both bands respond in much the same way to water depletion.

Figure 5 shows the measurements of position and breadth of the  $P_{M1}$  band as a function of the water vapor pressure. Figure 6 gives the position of the  $P_{M1}$  band as a function of temperature and water vapor pressure combined. Figure 7 is a spectrogram of all three bands—the  $P$  band and both modified molecular bands.

The polarization of the  $P_{M1}$  band in absorption is not in the same direction as that of the  $P$  band. Oriented dye films on glass in moist air were obtained by sliding one glass plate off the other one and quickly drying the remaining oriented gel (which was between the plates). The electric polarization of the  $P_{M1}$  band in absorption is perpendicular to the single polymer chains, that is, in the plane of the molecules, in accordance with the hypothesis that it is the 5230A molecular band modified by the coupling between polymer chains. The fact that the  $P_{M1}$  band appears at a higher dye concentration than that necessary for the  $P$  band and the fact that the  $P_{M1}$  band

absorption is weaker than that of the  $P$  band indicate that the coupling between polymer chains is weaker than the coupling between the molecules of a single polymer chain.

## 6. EVIDENCE FOR DYE THREAD FORMATION

If NaCl (or, for instance, KCl,  $\text{HgCl}_2$ ,  $\text{SrCl}_2$ ) is added in excess to a dilute solution of the dye in water ( $10^{-4} M$ ), the common negative ion ( $\text{Cl}^-$ ) salting-out effect causes the dye molecules to coagulate into visible threads, which eventually coalesce to form a thick suspension (showing  $P$ -band fluorescence), leaving the supernatant liquid colorless.

The dye was spread on a clean mercury surface in air, using 95 percent ethyl alcohol as the solvent for a dilute spreading solution. If now the dye film is compressed to a small area by a mica barrier, visible threads of dye are formed. When the barrier is moved back, making more area available, the film does not re-expand and the threads remain.

Films of dye obtained in the manner described at the beginning of Section 2 show, in air, under a binocular microscope, threads of dye from about 10 to 100 microns long, confirming Jelley's observation.<sup>9</sup> Furthermore, these threads do not change their appearance (length) when the film is put in a water-saturated atmosphere (breathed onto), in spite of the fact that the  $P$  band shifts according to Fig. 2. This is further evidence that the dye molecules, when deposited on a surface in a polymerized configuration, do not move their anchor points with respect to that surface as the water vapor pressure is changed.

## 7. WATER:DYE MOLECULAR RATIO FOR POLYMERS

Sheppard<sup>10, 11, 22</sup> has proposed a special model with two water molecules linking each dye molecule to each neighbor along the polymer

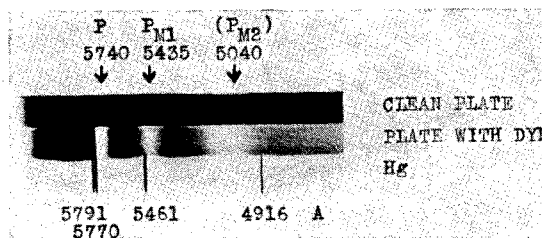


FIG. 7. Spectrogram of the dye on glass in ordinary air made in the manner described at the beginning of Section 2, using a Zeiss constant deviation prism spectrograph and Eastman 103 D plate.

chain. Attempts were made in the present investigation to measure the amount of water taken up by the dye to attain a certain stage of polymerization. The following figures indicate the orders of magnitude of the effects to be expected.



One may cover, for instance, 100 cm<sup>2</sup> of glass (or metal) surface with 8.3 (10)<sup>17</sup> dye molecules [5(10)<sup>-6</sup> g/cm<sup>2</sup>] with a film in which the dye is dehydrated but polymerizable by water vapor. If now as many water molecules are taken up to achieve the polymerization as there are dye molecules present, the hygroscopicity of the dye should be great enough to reduce the water content of 20 cc of saturated air at 20°C from 100 percent to 92.7 percent relative humidity. It is not possible to weigh this mass of water [25 (10)<sup>-6</sup> g] with a normal balance, but it is possible to measure the change of the humidity in the gaseous state by using the position of the *P*-absorption band (Fig. 2) of dye films on small glass test plates as indicating hygrometers.

Many different experimental arrangements were used, but in principle they were all based on the idea that a certain amount of water-saturated air was admitted to a vessel containing the glass plates clean and then the glass plates covered with the dye; the differences in relative humidity were measured. The amount of water taken up by the walls of the vessel and the clean glass plates was always greater than the amount taken up by the dye itself. To minimize the amount of water adsorbed on the vessel walls many different surfaces were tried. The best results were obtained with glass covered with silver or with polystyrene. But it was only possible to determine that a vessel containing several plates covered with the dye films always took up 5 or 10 percent more water to attain a certain high relative humidity than when the plates were without the dye.

These results were not very reproducible and one may conclude only that for films polymerized to the maximum extent the amount of water taken up by originally dehydrated dye is of the order of magnitude of  $\frac{1}{2}$  to 10 water molecules per dye molecule.\*

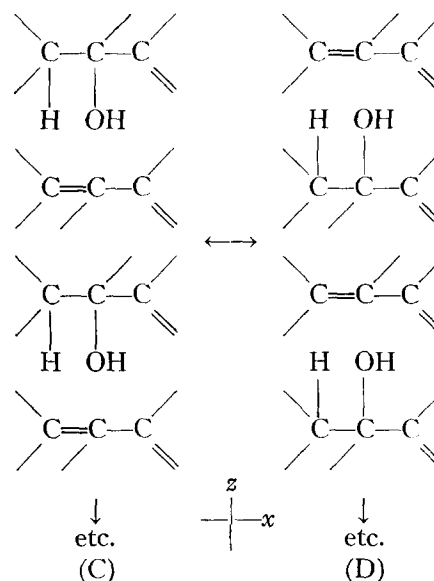
## 8. DISCUSSION

All authors agree that the 5730A polymer band (the *P* band) belongs to a polymer chain of 1,1'-diethyl-2,2'-cyanine chloride molecules lined up in a direction perpendicular to the planes of the molecules which are coupled together by

\* In the gel (10<sup>-2</sup> M) there are about 5500 water molecules per dye molecule.

water molecules. The question is an open one of how the water accomplishes the coupling and whether an intercoupled system of conjugated double bonds or a system of coupled optical resonators furnishes a more adequate description. The first picture is analogous to an electron migration along the polymer chains; the second to an exciton migration. The optical properties of the *P* band (width, transition probability, resonance fluorescence) fit both pictures equally well, but it seems difficult if not impossible to write a valence structure for the conjugated system along the whole polymer chain.

One conceivable structure supporting the hypothesis of exciton migration, but different from that proposed by Sheppard,<sup>10, 11, 22</sup> is suggested here. This structure is offered *only* as an example of other similar configurations, all of which may actually contribute to the resonance coupling.



In this picture the plane of the paper is the *x-z* plane of Fig. 1; in other words, the planes of the dye molecules are perpendicular to the paper and the polymer axis is in the *z* direction. The groups of three C atoms represent the three central C atoms of the dye molecule (Fig. 1). A water molecule, placed midway between a pair of dye molecules and probably coplanar with them, is attached first to one of the pair (configuration C) and then to the other of the pair (configuration D) by opening the double bond

between two C atoms. The positions of the H and OH nuclei do not change during this "resonance." In this polymer the ratio of water molecules to dye molecules would be 1:2. The introduction of a water molecule between two dye molecules modifies the resonance along the  $x$  direction and may be the reason why the absorption coefficient of the 5230Å molecular band decreases with polymerization.<sup>5,23</sup> The second molecular band at 4900Å (polarized along  $y$  of Fig. 1) may not be influenced in the same way, since cases are known in which the transition from a dye to the leukodye influences only one of the absorption bands. The new "resonance" along the polymer axis ( $z$ ) could account for the polarization of the absorption and fluorescence of the new main polymer band at 5730Å and the coupling of the electronic transition in the molecular bands with this  $P$  band (as indicated by the fluorescence excitation). The fact that the polymerization is *ad libitum* reversible by admission or removal of water vapor, once part of the molecules are anchored to the surface with the right spacing,\* is independent of the special assumption introduced for the coupling by water molecules. The same is true for the irreversibility of polymerization by water vapor once the dye molecules are permitted to form the crystalline state.

The  $P_{M1}$  band, which appears when secondary polymerization joins polymer chains to form threads, depends upon the presence of water in a manner very similar to that of the  $P$  band. The question arises, therefore, whether a second hydration occurs coupling the ends of the dye molecules together. Such an hypothesis seems improbable, however, since the special steric conditions necessary for such interaction are hardly fulfilled at two different places of the dye molecules. The following assumption is much more plausible. The water molecules are necessary for lining up the dye molecules to form polymer chains, but by this process all planes of the dye

molecules are forced into parallel positions. If now polymer chains join together to form threads, the molecules in all adjacent chains also become coplanar. This coplanarity corresponds to a lining up of the optical resonators in the molecules and is therefore favorable for an exciton migration. If the water is partially or entirely removed, the coplanarity will be correspondingly partially or entirely destroyed; this in turn de-couples the adjacent dye molecules. As mentioned in Section 5, the removal of the water does not restore the structure of the normal molecular bands, but produces only a visibly structureless general absorption in the spectral region of the molecular bands, and causes the disappearance of the  $P$  and  $P_{M1}$  bands. This is understandable since dye molecules adsorbed on glass in such an array are supposed to give an absorption spectrum broadened and blurred by the adsorption forces and by the non-coplanarity of the dye molecules.

Irradiation with light of wave-length in the  $P_{M1}$  band (electrically polarized perpendicular to the axis of the polymer chains) causes no fluorescence in the  $P_{M1}$  band but produces fluorescence in the  $P$  band only (electrically polarized parallel to the axis of the chains).<sup>27</sup> This indicates an interaction between the two different excited states such that the energy absorbed in the resonator system of the coupled molecules is transferred to the excitation along the polymer chains. The transition probability of the  $P$  band is so much higher than that of the  $P_{M1}$  band that the energy once transferred will be emitted before it has a chance to flow back into the molecular resonators.

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\* This fraction of the dye molecules will not readily form the crystalline state when dehydrated. To transform them into the crystalline state the adsorption forces must be overcome (heat of desorption). It is possible to get such a transformation at room temperature after a sufficiently long waiting period (perhaps months).

<sup>27</sup> G. Scheibe, *Zeits. f. Electrochemie u. angew. physik. Chemie* **47**, 73 (1941).