### Dielectric Properties of Polypeptide Solutions. Measurement of the Dielectric Properties of the $\alpha$ -Helix by the Low Frequency Bridge Method

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The exhaustive research on the polypeptide solution by Doty, Blout and their co-workers<sup>1)</sup> revealed the important fact that the  $\alpha$ -helix can exist not only in the solid state but even in solution. One significant implication of their work is that the  $\alpha$ -helix, one of the stable configurations of polypeptide molecules described by Pauling, Corey and Branson<sup>2)</sup>, can be studied in solution where each  $\alpha$ -helix exists as a free molecule, that is, almost free from soluteinteraction. These results then suggest the possibility and necessity of another type of research, the measurement of the electric dipole moment and the critical frequency of such a molecule with a highly ordered arrangement of residues.

The measurement of the electric dipole moment of the molecule has been considered a useful method of finding the charge distribution and the orientation of the polar groups in a molecule. The method has often been used to determine the molecular structure of a simple molecule in the field of physical chemistry. However, in the usual chain polymer molecule, because of the flexibility of the chain the observed electric dipole moment becomes a complicated function of the internal coordinates and the internal energy of the molecule, and this method does not appear to be as useful as in the case of the simple molecule. For the  $\alpha$ -helix, however, if the Pauling-Corey model is given as the proper configuration and if the molecule is rigid as Doty et al. concluded1), the resultant molecular dipole moment would be proportional to the degree polymerization, unlike the usual chain polymer, and would have a tremendous value in a highly polymerized molecule.

As the measurement of the dipole moment, which is a vectoral value, is essentially different from investigations on non-directional values such as molecular dimension, the observation

will approach the  $\alpha$ -helix and related problems from an entirely different angle.

#### Description of the Low-Frequency **Bridge Circuit**

Though the heterodyne beat method or the resonance method has often been used for the measurement of the dielectric constant of solution, they could yield reliable data only in the highfrequency range and would not be adequate for the purpose of the present investigation. Because the solute, the  $\alpha$ -helix, is a rigid and highly assymmetric rod-shaped molecule and the relaxation time of over-all molecular rotation in the solvent must be fairly great, the apparatus must be designed to cover the low-frequency range where sufficient time can be allowed for very slow orientation polarization. The bridge method seems to be appropriate for the present purpose and the apparatus by which the dielectric constant and loss factor can be measured from 30 cycle to 20 kilocycle was constructed as described below.

1) Low-Frequency Bridge.—The bridge method has been known as the best device for the measurement of the dielectric constant in the low-frequency range.3) For instance, Cole and Gross4) developed a transformer bridge, and Hippel et al. employed the Schering bridge method in their comprehensive research on dielectric materials.5)

The Cole and Gross bridge was designed to fit the guard without the use of the Wagner ground. The measurement of capacitance was obtained by balancing the bridge by changing the capacity of the precision condenser which was set in the conjugated arm of the unknown capacitance. The conductance measurement is performed by a device called the conductance shifter.

The latter, designed by Hippel and his co-workers, has a sample holder in the arm of the precision condenser, and is generally known as a substitution method. In such an apparatus the cell constant used is calibrated by the standard substance. The conductance is given, in this apparatus, by the reading of the dissipation balancing condenser.

For the present purpose the apparatus was designed to combine the substitution method and the conductance shifter. The block diagram of the bridge circuit is shown in Fig. 1.

The low frequency oscillator which continuously

<sup>1)</sup> P. Doty, A. M. Holtzer, J. H. Bradbury and E. R. Blout, J. Am. Chem. Soc., 76, 4493 (1954); P. Doty, J. H. Bradbury and A. M. Holtzer, ibid., 78, 947 (1956).

L. Pauling, R. B. Corey and H. R. Branson, Proc. Natl. Acad. Sci. 37, 205 (1951).
 C. P. Smyth "Dielectric Behavior" and Structure",

McGraw-Hill Book Co., Inc., New York, N. Y. (1955).

<sup>4)</sup> R. H. Cole and P. M. Gross, Jr., Rev. Sci. Instr. 20, 252 (1949).

<sup>5)</sup> Progress Rept. No. 1, Lab. Insulation Res., M. I. T., p. 7 (1947).

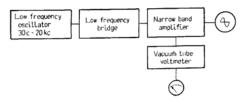


Fig. 1. Block diagram of low frequency bridge.

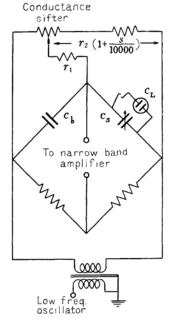


Fig. 2. Low frequency bridge circuit.

generates sine waves in the range of 30 to 20,000 cycles and output voltage from 0 to 20 volts has the same circuit as the Heathkit Model AO-1.

The circuit of the bridge section is shown in Fig. 2. C<sub>s</sub> is the liquid cell whose capacitance is compared with that of a portion of the calibrated The precision condenser precision condenser. (Yokogawa Elect. Co. CDS-500 Variable Air Condenser), in which the use of the worm drive makes possible a scale which can be read to one part in 50,000 of full scale, has a maximum capacitance of 500  $\mu\mu$ F. By using low resistance for the balancing arm the undesirable effects of stray capacitance and induction from the external field can be suppressed at the sacrifice of sensitivity. In the reading of the conductance shifter, the conductance, G, can be given as a three-digit number, s, by the following equation

$$G = \frac{(s/10000)/r_1}{1 + (r_2/2r_1)\{1 - (s/10000)^2\}}$$
 (1)

when  $s \ll 10000$ 

$$G = \frac{(s/10000)/r_1}{1 + r_2/2r_1} \tag{2}$$

where  $r_1$  and  $r_2$  are the resistances which are shown in Fig. 2. The present apparatus was designed so that  $r_1$  can be set at four different values by the use of a rotary switch, which made the measurement of the conductance from 10-5 to 10-9 mho possible. The null detector consists of a narrowband amplifier and vacuum tube voltmeter. The narrow-band amplifier, in which the Wien bridge and the negative feedback system are combined, has a sharp frequency response, an example of which is shown in Fig. 3, and amplifies only the given frequency, cutting out the hamper noise and The wave pattern was harmonic frequency. checked by the cathode-ray oscillograph. The null point can be obtained from the minimum reading of the vacuum tube voltmeter. The relation between the reading of the precision condenser and the vacuum tube voltmeter is plotted for different.

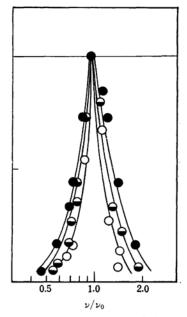


Fig. 3. Frequency response of the narrowband amplifier. Filled circle 90 cycle, half filled circle 1000 cycle, open circle, 10000 cycle.

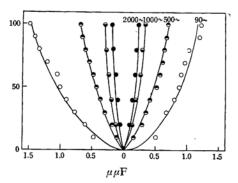


Fig. 4. Reading of vacuum tube voltmeternear null point.

TABLE I. ACCURACY IN CAPACITANCE MEASURE-MENT BY BRIDGE METHOD

Frequency	100	500	1000	2000	
Accuracy	$\pm 0.5$	$\pm 0.2$	$\pm 0.1$	$\pm 0.1 \mu \mu F$	1

frequencies in Fig. 4, and the accuracy of the measurement is given below.\*

- 2) Liquid Cell.—The liquid cell consists of a concentric double cylinder of glass as shown in Fig. 5; the inside of the outer cylinder and the outside of the inner cylinder are silver gilt or spattered with gold. The latter was found to be more satisfactory in chemical and mechanical durability.
- 3) Calibration.—Because the substitution method was used here, the cell constant had to be determined by a pure liquid of known dielectric constant. Benzene, the dielectric constant of which has been given as 2.274 at 25°C with a probable accuracy of 0.1%, was used as a standard substance for the calibration.<sup>6)</sup>

The dielectric constant of ethylene dichloride and dioxane measured by the calibrated liquid cell are plotted against frequency in Fig. 6. The apparent increase in the dielectric constant at low-frequency range may be due to the polarization capacitance

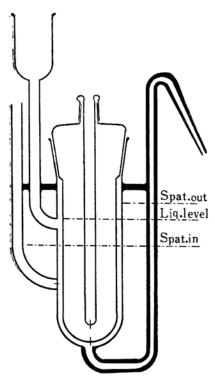


Fig. 5. Liquid cell for the measurement of dielectric constant of solution.

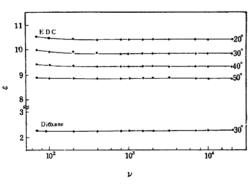


Fig. 6. Dielectric constant of ethylene dichloride and dioxane at various temperatures and frequencies.

on the electrode surface. The polarization effect increases and must be corrected for a liquid of high conductivity but it was negligible for one of small conductivity. The dielectric constants of liquids mentioned above at 1000 cycles where the polarization effect satisfactorily diminished are listed in Table II and were consistent with the values observed by other workers.

TABLE II. DIELECTRIC CONSTANT OF ETHYLENE DICHLORIDE AND DIOXANE

]	Ethylene dichlor	ride				
Temp., °C	ε (Wada)	ε (Smyth*)				
20	10.42	10.42**				
30	9.85	9.87				
40	9.35	9.36**				
50	8.87	8.87				
Dioxane						
Temp., °C	ε (Wada)	ε (Smyth***)				
30	2.295	2.306**				
50	2.245	2.251				
* C. P. Smy		n. Chem. Soc., 53,				

<sup>4242 (1931).</sup> 

# Characterization of Poly-7-benzyl-L-glutamate (PBLG)

1) Polymerization.—The sample used here was prepared by the Blout-Karlson method<sup>73</sup>. The procedure adopted consisted of polymerizing  $\gamma$ -benzyl-N-carboxy-L-glutamate anhydride, usually 3—5% in dioxane solution, by a sodium methoxide initiater at room temperature. After polymerization was completed the reaction mixture was poured into cold ethanol with vigorous stirring. The precipitate was redissolved in dioxane and precipitated by cold ethanol again. No difference in intrinsic viscosity was found between the reprecipitated

<sup>\*</sup> The bridge was found to be stable enough that the reading of the vacuum-tube voltmeter did not fluctuate more than 3/100 full scale after a 20-min. warm-up of the apparatus.

<sup>6)</sup> A.A. Maryott and E.A. Smith, "Table of Dielectric Constant of Pure Liquids", Natl. Bur. Standard (Circ. 514 4951); A. S. Brown et al., J. Chem. Phys. 19, 1226 (1951).

<sup>\*\*</sup> Interpolated in Smyth's data.

<sup>\*\*\*</sup> C. P. Smyth et al., J. Am. Chem. Soc., 53, 2115 (1931).

<sup>7)</sup> E. R. Blout and R. H. Karlson, J. Am. Chem. Soc., 78, 941 (1956).

PBLG and that liopholyzed from the first dioxane solution.

- 2) Solvent. Dimethyl formamide (DMF) was used as the solvent for the light scattering measurement because the PBLG was found to exist as a non-associated molecule in this solvent. DMF was dried by dry sodium bicarbonate and fractionally distilled at 47°C (14 mmHg). For the dielectric constant and light scattering measurement dioxane was purified according to the method of Fieser8) and fractionally distilled after 24 hr. refluxing with sodium. For the polymerization reaction, dioxane was purified by refluxing with sodium for 24 hr. and fractionally distilled just before use. The ethylene dichloride (EDC) for the measurement of the dielectric constant was dried by P<sub>2</sub>O<sub>5</sub> and fractionally distilled at 84°C.
- 3) Light Scattering. The Brice Phoenix type light scattering photometer made by the Shimadzu Co. was used to obtain the molecular weight of PBLG. The apparatus was calibrated according to the Rayleigh ratio of pure benzene  $(R_{90}=48.4\times10^{-6} \text{ at } 436 \text{ m}\mu.^{9})$ . The spectrophotometric calibration was independently done by Ludox solution and the result was quite consistent with the calibration by benzene. Scattering from DMF solution of PBLG was measured by the Erlenmeyer cell and the circular uniformity of which was checked with clean fluorescein by measuring the angular envelope. The cell used had good circular uniformity as the light intensity from the unit volume of the solution was constant to  $\pm 1\%$ from  $\theta = 30^{\circ}$  to 135°. The angle made by the side of the Erlenmeyer cell was sufficient to exclude the effects of back reflection, so that no correction for the data was necessary. Centrifuge by a Hitachi Preparative Ultracentrifuge using a polyethylene tube with a specially constructed tefron cap, at about 60,000 g for 1 hr. and filtration by ultra-fine sintered glass filter were performed to make a dust-free solution and solvent respectively. Measurements were made on the solutions obtained by adding a weighed amount of 1% PBLG dustfree solution to a known volume of clean solvent in an Erlenmeyer cell, on which the scattering was already measured. The concentration after each addition was determined gravimetrically relative to the stock solution.\*

The refractive index increment dn/dc for the evaluation  $K=2\pi^2n_0^2(dn/dc)^2/N\lambda^4$  where  $n_0$  is the refractive index of the solvent,  $\lambda$  is

the wave length of the incident light in vacuo, N is the Avogadro number, was determined by the Debye-type defferential refractometer made by Shimadzu Co. The instrument was usually calibrated before each measurement with a standard KCl solution,  $c = \frac{10.8691 \, \text{g}}{\text{H}_2 \text{O (kg.)}}$ , for which the increment was taken as 0.0015204 on the basis of an extrapolation of data by Kruis. 10)

According to the well known equation established by Zimm, 112

$$Kc/R_{\theta} = \{M_{w}P(\theta)\}^{-1} + 2A_{2}c \tag{3}$$

the weight average molecular weight  $M_w$  can

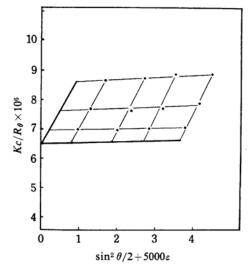


Fig. 7a. Light scattering data for PBLG sample No. 105 in DMF at 23°C.

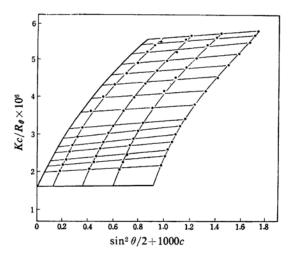


Fig. 7b. Reciprocal angular envelope of solutions PBLG No. 105 in dioxane at 23°C.

<sup>8)</sup> L. F. Fieser, "Experiments in Organic Chemistry" 2nd ed., D. H. Heath & Co., Boston, Mass., (1941).
9) B. A. Brice and M. Halwer, J. Opt. Soc. Am., 40, 765

<sup>\*</sup> The light scattering measurement was performed following a process established by Professor P. Doty and his coworkers at Harvard University.

<sup>10)</sup> A. Kruis, Z. physik. Chem., 34B, 13 (1936).

<sup>11)</sup> B. H. Zimm, J. Chem. Phys., 16, 1093, 1099 (1948).

TABLE III.	MOLECULAR WEIG	HT, MOLECULAR	LENGTH, SPECIA	IC POLARIZATION	DIPOLE
	MOMENT AND	CRITICAL FREO	JENCY OF PBLG	IN EDC	

PBLG	$M_w$	$L_{z,z+1}$	$P_2^{00}(cc)$	$\mu(\mathbf{D})$	$\mu_0(\mathbf{D})$	$\nu_0$
202	180,000	1350	963	2910	3.54	3000
105	154,000	1100	805	2450	3.48	7000
102	102,000	750	494	1570	3.36	16000
201	86,000	690	470	1404	3.58	20000
103	70,000	600	314	1040	3.25	40000

be obtained after extrapolating to c=0 and  $\theta=0$ , where the particle scattering factor  $P(\theta)$  is known to be unity. A typical double plot, that is, the so-called Zimm plot, for one of the PBLG samples in DMF is shown in Fig. 7a. Measurements were also conducted for the dioxane solution as one of the Zimm plot and are shown in Fig. 7b. The molecular length, assuming a rigid rod-shaped molecule at present, can be calculated from the initial slope of the angular envelope in the Zimm plot;

$$L^{2}_{z,z+1} = \frac{9\lambda^{12}}{8\pi^{2}} \frac{(\text{slope})_{c=0}, \theta=0}{(\text{intercept})_{c=0}, \theta=0}$$
 (4)

where  $\lambda'$  refers to the wave length in solution. The final results of the measurement of molecular weight and molecular length are listed with the polymerization condition in Table III. The remarkable increase in molecular weight and molecular length in dioxane solution might result from molecular association which will be discussed in detail later.

## Dielectric Properties of PBLG in Ethylene Dichloride and Dioxane

For a long, rigid rod-shaped molecule, the cavity field in the direction of the rod axis can be assumed to be the same as the external field, and in the  $\alpha$ -helix having point dipoles parallel with the rod axis, only the field of this direction has to be taken into consideration. So the relation between the static dielectric constant of the solution  $\varepsilon_{12}^0$  and the specific polarization of the solute  $P_2$  is given in terms of the weight fraction of the solute  $w_2$ , the specific polarization of the solvent  $P_1$ , and the density of the solution  $d_{12}$  as follows<sup>12)</sup>

$$P_2^0 = \left[ \left( \varepsilon_{12} - 1 \right) / 3d_{12} - P_1 \right] / w_2 + P_1 \tag{5}$$

The specific polarization extrapolated to zero concentration  $P_2^{00}$  and the dipole moment of the  $\alpha$ -helix in the solvent are related

$$\mu^* = (9k/4\pi N)^{1/2} (P_2^{00} \overline{M}_w T)^{1/2}$$
  
= 0.0128 (P\_2^{00} \overline{M}\_w T)^{1/2} (6)

In the dipole moment  $\mu^*$ , the moment induced in the polarizability  $\alpha$  by the reaction field

 $\mu^*R(\varepsilon)$  is taken into consideration and it is given by the moment in vacuo  $\mu$ .<sup>13)</sup>

$$\mu^* = \frac{\mu}{1 - \alpha R(\varepsilon)} \tag{7}$$

To obtain the static dielectric constant  $\varepsilon^0_{12}$  or specific polarization, those values measured by the bridge method at various frequencies must be extrapolated to zero frequency. In this procedure the following problems must be considered:

- 1) The relation between  $\varepsilon_{12}$  and  $\nu$  is not linear.
- 2) The dispersion curve does not agree, in general, with Debye's theoretical one in which a single relaxation time is assumed.
- 3) In the low-frequency range, the polarization effect on the electrode surface of the liquid cell can not be negligible. To cope with these problems, three methods for extrapolation are proposed as follows.
- I) Assuming an empirical functional relation which gives a linear relation especially at the low-frequency range, we extrapolate it to zero frequency.
- II) Extrapolation is made to zero frequency on the Cole-Cole's arc plot. <sup>12</sup> This method, however, does not seem appropriate because of the increase in experimental error of the loss factor at low-frequency.
- III) Extrapolation of the flat part at the low-frequency range in  $\varepsilon_{12} \sim \nu^{-1}$  plotting to  $\nu^{-1} \rightarrow 0.14$ ) This extrapolation will be useful to exclude electrode polarization because it becomes zero at infinite frequency. An underestimate of the dielectric constant will result when the polydispersity in the  $\alpha$ -helix is present.<sup>13)</sup>
- 1) Ethylene Dichloride Solution. The dispersion curve of each PBLG sample in EDC is shown in Fig. 8. It can be seen that the critical frequency becomes lower as the specific polarization and the molecular weight become larger.

In Figs. 9a, 9b and 9c three plottings of these samples are shown and the extrapolated values of  $P_2$  are compared in Table IV. For

<sup>12)</sup> A. Wada, J. Chem. Phys., 29, 674 (1958).

<sup>13)</sup> A. Wada, ibid., 31, 495 (1959).

<sup>14)</sup> J. L. Oncley, Chem. Revs., 30, 433 (1942).

TABLE IV. SPECIFIC POLARIZATION OF PBLG IN EDC EXTRAPOLATED TO ZERO FREQUENCY

Method of extrapolation

PBLG	Í		I	I	III
	$P_{2}^{00}(cc)$	$\nu_0$	$P_{2}^{00}(cc)$	$\nu_0$	$P_{2}^{00}(cc)$
202	950	3000	920	3000	900
105	800	6300	770	7000	780
103	330	33000	314	40000	320

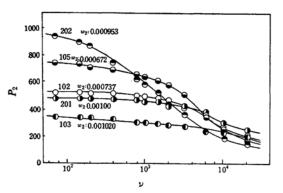


Fig. 8. Dependence of dielectric constant of the EDC solutions of PBLG samples upon frequency at 25°C.

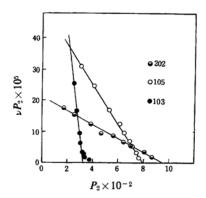


Fig. 9a. Plotting of  $\nu P_2$  as a function of  $P_2$ .

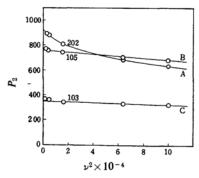


Fig. 9b. Specific polarization of PBLG as a function of  $\nu^2$ . A  $M_w$ : 180,000, B  $M_w$ : 154,000,

C  $M_w$ : 70,000.

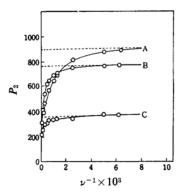


Fig. 9c. Specific polarization of PBLG as a function of  $\nu^{-1}$ . A  $M_w$ : 180,000, B  $M_w$ : 154,000, C  $M_w$ : 70,000.

the first extrapolation method it was incidentally given a linear relation in  $P_2\nu\sim P_2$  plot. This means that the relation  $P_2=P_2{}^0\!\left(1+\frac{\nu}{\nu_0}\right)^{-1}$  can be maintained in this system and  $P_2{}^0$  and the critical frequency  $\nu_0$  are given from the intercept and the slope of this plot respectively. The deviation from the linearity at the low-frequency range may be due to electrode polarization. Though the extrapolated values by these three methods differ slightly, they do not seriously affect the result, as can be seen in Table IV.

For the calculation of the molecular dipole moment, the  $P_2^0$  measured in several concentrations were extrapolated to zero concentration. A typical plot is shown in Fig. 10 and

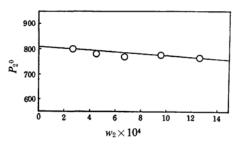


Fig. 10. Concentration dependence of specific polarization of PBLG sample No. 105 in EDC at 25°C.

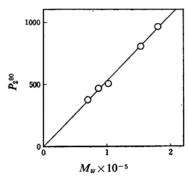


Fig. 11. Dependence of specific polarization of PBLG samples in EDC upon molecular weight.

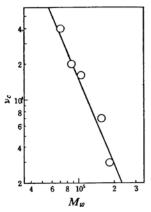


Fig. 12. Double logarithmic plot of critical frequency of PBLG samples in EDC against molecular weight.

the final results are listed with the dipole moment calculated in Table III.

The measured  $P_2$  and dipole moments increase proportionately to the molecular weight as shown in Fig. 11. The dipole moment of the amino acid residue in the  $\alpha$ -helix then can be calculated as 3.5 D. This value is quite consistent with the parallel orientation of the

dipole moment of polar groups 
$$N-C < 0$$

in the  $\alpha$ -helix. Further, the critical frequency, on the other hand, is known to have a linear relation in double logarithmic plot as shown Fig. 12. This behavior is well explained using Perrin's equation with the hydrodynamically equivalent ellipsoid of revolution which has the same volume and length as the  $\alpha$ -helix. That is

$$\tau_{0} = (2\pi\tau)^{-1}$$

$$\tau = \frac{2\tau_{0}}{3} \frac{1}{2\rho^{2} \ln(2/\rho) - \rho^{2}}$$

$$\rho = b/a, \quad \tau_{0} = 4\pi\eta ab^{2}/kT$$
(8)

The solid line in Fig. 13 is the theoretical plot corresponding to  $18.3\,\text{Å}$  of the minor axis, that is  $15\,\text{Å}$  for the diameter of the  $\alpha$ -helix. All of the above results are consistent with and tend to support the belief that in this solvent the PBLG exists as a rigid rod-shaped molecule, the  $\alpha$ -helix given by Pauling and Corey.

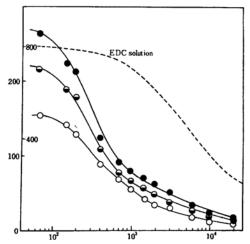


Fig. 13. Dependence of specific polarization of PBLG samples in dioxane solution upon frequency at 30°C.

Filled circle No. 105  $w_2$ =0.000824. Half filled circle No. 103  $w_2$ =0.001282. Open circle No. 102  $w_2$ =0.001112.

2) Dioxane Solution. — In dioxane the  $\alpha$ -helix of PBLG may be in an associated state as Doty et al. concluded.<sup>13</sup> They emphasized that the association is of the end-to-end type but that the rod-like form is not preserved. The increase in the molecular weight and molecular length of PBLG in this solvent, which has been given by the light scattering measurement as shown in Table III, seems to endorse this idea. Moreover, the non-linear relation between the molecular weight and the molecular length suggests that the associated molecule is no longer linear and/or rigid.

For further study on the mechanism of molecular association the information from the electric dipole moment, as a vectoral quantity along the direction of the helical axis, will be useful. Leaving quantitative considerations of this interesting problem to another report<sup>15</sup>), we may conclude, however, that the  $\alpha$ -helix still has a large electric dipole moment in dioxane which is the only non-polar solvent in which PBLG can dissolve.

Examining the dispersion curve of this system in Fig. 13 the critical frequency reveals

<sup>15)</sup> A. Wada, J. Polymer Sci., (1960), in press.

a remarkable shift to lower frequencies compared with that of the same sample in EDC for which the dispersion curve is plotted in the same figure in a dotted line. Therefore, the third extrapolation method could not be used because the left part of the dispersion curve goes out of the range of measurement. Only the second method, the extrapolation in Cole-Cole's arc plot, is effective, as shown in Fig. 14. A linear relation in the plot which was given in the case of EDC solution no longer holds in dioxane. This discrepancy between dioxane and EDC suggests that the molecular association will change the molecular weight distribution. The molecular weight distribution seems to be more polydisperse

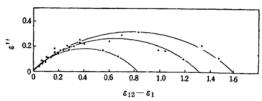


Fig. 14. Cole-Cole's arc plot for the dioxane solution of PBLG No. 105.  $w_2=0.003058$ , 0.001794, 0.000824.

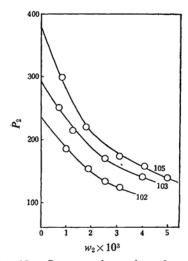


Fig. 15. Concentration dependence of specific polarization of PBLG samples in dioxane at 30°C.

than that of the most probable distribution as in the case of EDC solution. The broader distribution may also be suggested from the flat shape of Cole-Cole's arc in this solvent (Fig. 14). This fact means that the molecules preferably aggregate in certain ranges of molecular weight more than in others as Doty et al. mentioned.<sup>10</sup>

The  $P_2^0$  depends strongly upon the concentration in dioxane as shown in Fig. 15. This strong dependence may originate from the molecular association and/or dipole-dipole interaction which becomes stronger in a nonpolar solvent such as dioxane than in a polar one such as EDC. The absence of concentration dependence in light scattering measurement will support the latter possibility. It is empirically found that the  $P_2^{0-1}\sim c$  plot gives a straight line as shown in Fig. 16. From these extrapolated values the electric dipole moment is computed. In Table V the electric dipole moment, calculated from the original molecular weight and from that of the associated molecule, are listed. Though the result is no longer proportional to the molecular weight, the dipole moment 1~3 D per amino acid residue still suggests that the molecule has an ordered form which has a partial  $\alpha$ -helical configuration.

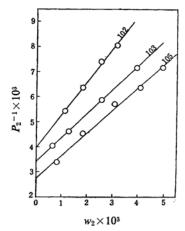


Fig. 16. Reciprocal plot of specific polarization of PBLG samples in dioxane against concentration.

TABLE V. MOLECULAR WEIGHT, SPECIFIC POLARIZATION, CRITICAL FREQUENCY AND DIPOLE MOMENT OF PBLG IN DIOXANE

Dipole moment calcd. from

PBLG	$\overline{M}_w$	$P_2^{00}$ (cc.)	$\nu_0$	Original $M_w$		Associ	ated Mw
						_	^
				$\mu(\mathbf{D})$	$\mu_0(\mathbf{D})$	$\mu(\mathbf{D})$	$\mu_0(\mathbf{D})$
105	660,000	360	400	1650	2.35	3407	1.13
102	1610,000	250	600	1115	2.39	4435	0.60
103	_	300	1100	1010	3.16	-	_

### Summary

The work described above has produced the following conclusions.

- (1) A large electric dipole moment corresponding to the  $\alpha$ -helix described by Pauling, Corey and Branson is found in EDC and dioxane.
- (2) A linear relation between the electric dipole moment and the molecular weight in EDC suggests that the molecule is linear and not flexible.
  - (3) The critical frequency of the orientation

polarization was elucidated by using an equivalent ellipsoid model and the equation for the rotatory diffusion constant derived from Perrin's equation. This fact will support the conclusion of Doty, Bradbury and Holtzer that the  $\alpha$ -helix is fairly rigid in the solution.

(4) In dioxane the  $\alpha$ -helix can be found to be associated and to have a different distribution in molecular weight.

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