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## The Infrared Streaming Dichroism of Some Synthetic Polypeptides<sup>1</sup>

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The first results of observing the infrared dichroism of flowing polymer solutions are reported. With poly- $\gamma$ -benzyl-L-glutamate, quantitative correlations have been made between the data obtained by this method and viscosity data on solutions, as well as infrared data on films. The helical configuration in solution has been confirmed for poly- $\gamma$ -benzyl-L-glutamate and poly-L-glutamic acid, and demonstrated for poly- $\epsilon$ -carbobenzyloxy-L-lysine and a 7:3 copoly L-glutamic acid:L-lysine hydrobromide. The absence of observable dichroism indicates that sodium poly-L-glutamate and poly-L-lysine hydrochloride have random configurations in aqueous solutions.

### Introduction

Observations have been made on the infrared dichroism of crystals and oriented films, and from these data information may be obtained concerning the orientation of chemical groups within the crystal or film. However, many interesting polymers normally exist in solution, fail to crystallize, and are greatly altered (reversibly or otherwise) on deposition as a film. Furthermore, it is often extremely difficult to prepare a film of known, uniform thickness and orientation. We have developed techniques for making quantitative observations on the dichroism of dilute polymer solutions subjected to known conditions of flow, using polarized infrared radiation. Positive results have been obtained with the synthetic polypeptides poly- $\gamma$ -benzyl-L-glutamate, poly-L-glutamic acid, poly- $\epsilon$ -carbobenzyloxy-L-lysine, and a copolymer, 70 mole per cent. L-glutamic acid:30 L-lysine hydrobromide. Significant negative results have been obtained for sodium poly-L-glutamate and poly-L-lysine hydrochloride. Poly- $\gamma$ -benzyl-L-glutamate (PBLG) was selected as a trial compound to test the potentialities of this method, and a series of experiments has been run covering a wide range of molecular weights, concentrations and flow gradients. At high molecular weights and concentrations, direct determination of the rotary diffusion constant becomes possible, and our results pose some interesting rheological questions.

The molecular orientation necessary for the observation of dichroism was produced by flowing the polymer solutions through a modified infrared liquid cell. This method is analogous to the methods for producing visible streaming birefringence in capillary tubes or rotating coaxial cylinders. In the optical cell used, there exists a range of velocity gradients from zero at the center of the cell to a maximum value at either cell wall. The maximum gradient  $G_{\max}$ , or the dimensionless ratio of  $G_{\max}$  to the rotary diffusion constant  $\theta$  of the polymer  $\alpha_{\max} = G_{\max}/\theta$ , is the best parameter for characterizing the fluid flow. A calculation of observed optical density change as a function of reduced gradient has been published elsewhere,<sup>2</sup> and need only be mentioned here. A separate discussion of the apparatus has also appeared.<sup>3</sup>

**Poly- $\gamma$ -benzyl-L-glutamate: A Test of the Method.**—A series of experiments was run on poly- $\gamma$ -benzyl-L-glutamate (PBLG) samples with weight average molecular weights ( $MW_w$ ) ranging from 84,000 to 740,000 (degree of polymerization from 400 to 3,400).<sup>4</sup> Chloroform plus 0.5% by volume of formamide was used as the solvent in all cases, and solution concentrations ranged from 0.30 g. polymer/100 ml. of solution to 10.0 g./100 ml. Most of the data were taken with the radiation electric vector aligned parallel to the flow direction, since this is the direction in which the greatest changes in optical density are observed. Furthermore, data taken in this direction alone usually permit a calculation of density changes in other directions.<sup>2</sup> A few observations were made with the radiation electric vector perpendicular to the flow direction, thus permitting direct calculations of dichroic ratios.

**Results.**—Figure 1 shows a typical spectrum with and without flow. In this case the concentration is 0.30 g./100 ml. of solution, the weight average molecular weight ( $MW_w$ ) is 740,000, and the maximum gradient  $G_{\max} = 10,500 \text{ sec.}^{-1}$ . Figure 2 shows the final result of a complete experiment, with optical density with solution flowing relative to density with solution at rest plotted as a function of  $G_{\max}$ . The solid curve is obtained from the calculation of orientation,<sup>2</sup> taking the rotary diffusion constant from equation 1 and using the solution viscosity. Note that the observed density change is slightly less than the change calculated for a perfectly-oriented absorber. Other data taken at lower values of  $\alpha_{\max}$  give observed changes greater than calculated for a single molecular weight, since the polymer preparations are not monodisperse.

At high concentrations it was found that the time-decay of orientation (after cessation of flow) occurred over a time of seconds to minutes and could be observed directly. The results of such an experiment are shown in Fig. 3. The rotary diffusion constant thus obtained for a polymer with  $MW_w$  195,000 and concentration of 10 g./100 ml. of solution is  $\theta = 0.079 \text{ sec.}^{-1}$ . With higher molecular weight polymers and the same concentration the decay of orientation occurred in a very peculiar oscillatory manner with a period of several minutes, as shown in Fig. 4.

**Interpretation of Results on PBLG.**—The initial set of experiments on PBLG was run with a double purpose: to obtain information on the polymer, and to test the apparatus, experimental methods and

(1) This paper is Polypeptides. XXV. For the previous paper in this series see E. R. Blout and M. E. DesRoches, *THIS JOURNAL*, **81**, 370 (1959).

(2) G. R. Bird, *J. Chem. Phys.*, **28**, 1155 (1958).

(3) G. R. Bird, M. Parrish, Jr., and E. R. Blout, *Rev. Sci. Instr.*, **29**, 305 (1958).

(4) E. R. Blout and R. H. Karlson, *THIS JOURNAL*, **78**, 941 (1956).

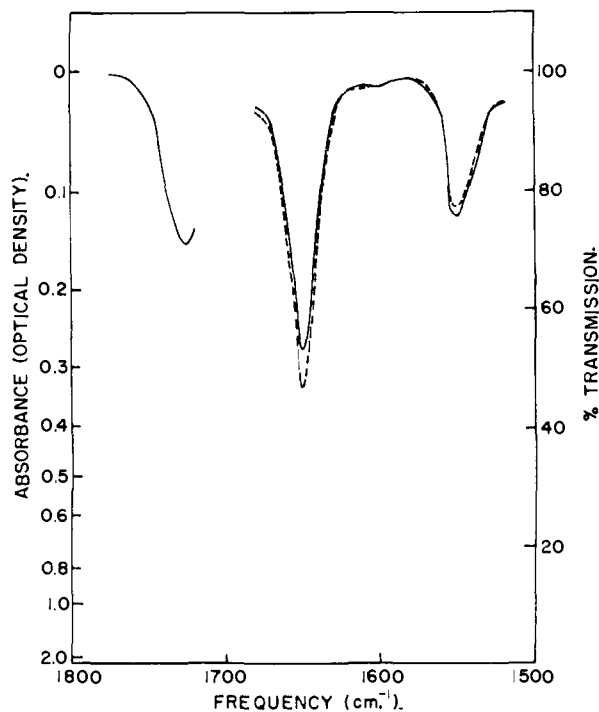


Fig. 1.—Absorption spectrum of poly- $\gamma$ -benzyl-L-glutamate (PBLG) solution at rest and flowing: solvent, chloroform plus 0.5% formamide by volume; concentration, 0.30 g. of polymer/100 ml. of solution; molecular weight,  $MW_w = 740,000$ ; cell thickness, 0.0268 cm.; solid curve, solution at rest; broken curve, solution flowing with maximum gradient  $G_{max} = 10,500 \text{ sec.}^{-1}$ ; 100% reference, a matched cell containing solvent only. The region from 1720 to 1680  $\text{cm.}^{-1}$  is obscured by a strong solvent band (formamide), but no strong PBLG band falls in this region. The radiation electric vector is parallel to direction of flow. The band at 1730  $\text{cm.}^{-1}$  (benzyl ester carbonyl) shows no appreciable dichroism, and the two curves coincide. The 1650  $\text{cm.}^{-1}$  band (polypeptide amide I) shows parallel dichroism, while the band at 1550  $\text{cm.}^{-1}$  (polypeptide amide II) shows perpendicular dichroism.

calculations developed for streaming dichroism studies. The molecular weight-viscosity relationship for this  $\alpha$ -helical polymer has been determined in a number of solvents including chloroform-formamide<sup>5</sup> and some experimental information is available on the polydispersity of PBLG preparations. It has been shown that PBLG preparations have a low polydispersity in the range of molecular weights near 100,000, and, in fact, the actual distribution approaches a Poisson distribution. The highest molecular weight preparations are known to be more polydisperse.<sup>6</sup> From the known weight-average molecular weights and the viscosity data, the rotary diffusion constants in chloroform were calculated from the various PBLG preparations making use of equation (1) as shown. The rotary constants obtained experimentally ranged from  $\Theta = 1.46 \times 10^6 \text{ sec.}^{-1}$  for  $MW_w$  of 84,000 in  $\text{CHCl}_3$  at 27° to  $\Theta = 2.44 \times 10^2 \text{ sec.}^{-1}$  for  $MW_w$  of 740,000.

(5) P. Doty, A. M. Holtzer, J. H. Bradbury and E. R. Blout, *THIS JOURNAL*, **76**, 4493 (1954). P. Doty, J. H. Bradbury and A. M. Holtzer, *ibid.*, **78**, 947 (1956).

(6) J. T. Yang and P. Doty, personal communication.

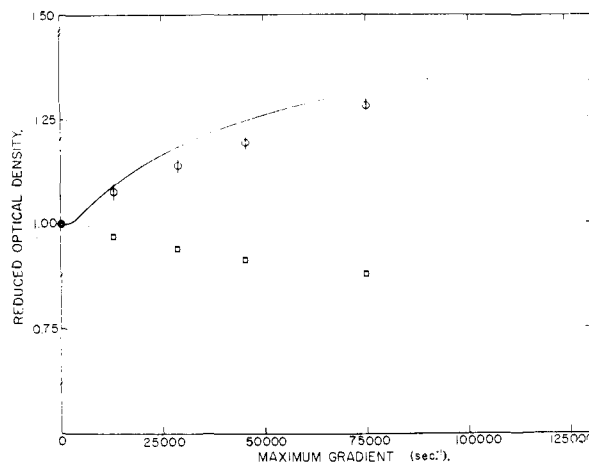


Fig. 2.—The optical densities of two absorption bands of poly- $\gamma$ -benzyl-L-glutamate in solution as a function of streaming velocity gradient: solvent, chloroform plus 0.5% formamide by volume; concentration, 1.00 g. of polymer/100 ml. of solution; molecular weight,  $MW_w = 195,000$ ; cell thickness, 0.00837 cm. The radiation electric vector is parallel to flow direction. Densities are relative to the density of solution at rest in each case. Circles: densities of the 3300  $\text{cm.}^{-1}$  band (amide N-H stretch, parallel dichroism) at various values of  $G_{max}$ , the maximum gradient in the cell. Vertical lines indicate the estimated experimental uncertainty in density measurement. Density of solution at rest is 0.0896, and the plotted densities refer to this value as unity. Squares: densities of the 1550  $\text{cm.}^{-1}$  band (amide II, perpendicular dichroism); density at rest is 0.126. Solid line: a plot based on the calculation of ref. 2. The rotary diffusion constant of this polymer is calculated to be  $1.43 \times 10^4 \text{ sec.}^{-1}$  at infinite dilution in  $\text{CHCl}_3$  at 27°. The viscosity of this solution is 9.7 times the viscosity of  $\text{CHCl}_3$ , and the rotary diffusion constant is decreased by this factor. Thus  $\alpha_{max} = 6.78 \times 10^{-4} G_{max}$ . This plot assumes perfect orientation of the absorber parallel to the unique axis of the polymer molecule. For perpendicular dichroism this plot is to be reflected across unit density, and the ordinate distance from  $D = 1$  reduced by 0.5.

$$\Theta = \frac{3kT}{16\pi\eta a_1^3} [2\ln 2p - 1] \quad (1)$$

- $\Theta$  = rotary diffusion constant
- $k$  = Boltzmann's constant
- $T$  = absolute temperature
- $\eta$  = solvent viscosity
- $a_1$  = semi-major axis (0.5 of polymer length)
- $p$  = axial ratio of hydrodynamically equivalent ellipsoid: an ellipsoid having the same length and volume as the cylindrical molecule here encountered

Knowing the rotary diffusion constant of a PBLG solution, one might hope to calculate the degree of molecular orientation at a known rate of flow, and, from this, the change in optical density relative to the density without flow. The observed change in optical density of a given band should always be proportional to the calculated change. If any absorbing dipole is perfectly oriented along the unique molecular axis, the density change observed for this band should equal the calculated change. Unfortunately, the agreement between observation and simple theory is not complete for PBLG, and some

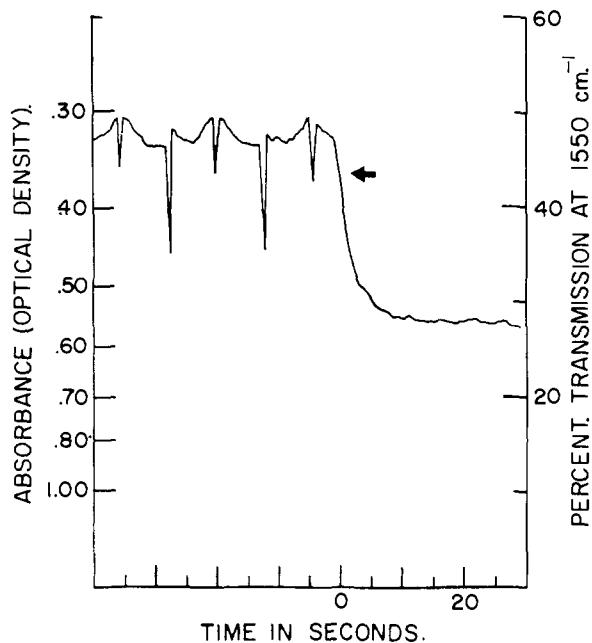


Fig. 3.—Decay of dichroism after cessation of flow: poly- $\gamma$ -benzyl-L-glutamate of molecular weight  $MW_w = 195,000$  in a solvent, chloroform plus 0.5% by volume formamide; concentration 10.0 g. of polymer/100 ml. of solution; 100% reference, a matched cell containing the solvent; cell thickness, 0.00382 cm. This trace shows transmission at the  $1550\text{ cm}^{-1}$  amide II band (perpendicular dichroism) as a function of time. On the left, the solution is flowing, with  $G_{max} = 4630\text{ sec}^{-1}$ . The downward spikes are pumping reversal transients, exaggerated by a deliberate setting of the servo-system of the Perkin-Elmer model 21 spectrometer to respond rapidly and to overshoot an abrupt transient. The arrow marks the point at which the pump came to a full stop and all mechanical motion ceased. A number of these traces were observed, the results were converted to optical density units, and an exponential decay constant of 6.4 sec. was obtained for decay to  $1/e$  of the initial density change. This corresponds to a rotary diffusion constant of  $7.9 \times 10^{-2}\text{ sec}^{-1}$ , to be contrasted with  $1.43 \times 10^4\text{ sec}^{-1}$  for the polymer infinitely diluted in the same solvent.

detailed consideration must be given to the shortcomings of both the simple theory and the PBLG chloroform-formamide system.

PBLG in pure chloroform is associated end-to-end as demonstrated by Doty, *et al.*<sup>5</sup> This association is greatly decreased, but not completely removed, by the addition of formamide. Such an association has the effect of increasing the average molecular weight and the polydispersity of a sample. The drastic effect of polydispersity on streaming dichroic observations has been discussed.<sup>2</sup> The discrepancy between the observed and calculated results in some of our data, particularly that taken at very low degrees of orientation, is attributed to this association and to the polydispersity of the unassociated polymer.

The simple theory of streaming orientation has been developed for highly dilute solutions in which interactions between macromolecules are negligible. Even at the lowest concentrations compatible with reasonably large solute optical absorption and small

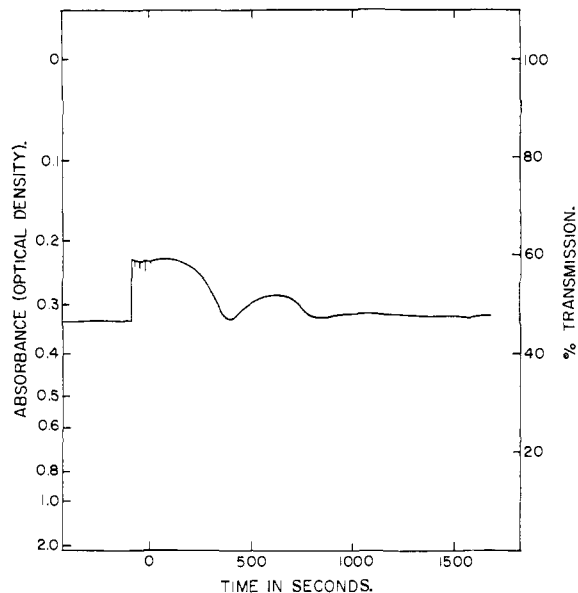


Fig. 4.—Decay of dichroism after cessation of flow with a higher molecular weight polymer. Conditions for this tracing are identical with those for Fig. 3, except that the polymer here observed has  $MW_w = 390,000$ , cell thickness 0.00378 cm. Note the contraction of the time-scale from Fig. 3 to 4. At the far left, the solution is observed at rest. The large vertical rise marks the onset of pumping, and the small downward spikes are reversal transients. Pumping was stopped at  $t = 0$ . The phenomena underlying the oscillatory decay of dichroism are complex, involving the formation of liquid crystals. Visual observations of the movement of the crystals with a  $40\times$  microscope and crossed polarizers have not clarified the oscillatory decay. The form and period of the decay curves are identical for the  $3300\text{ cm}^{-1}$  band except for reversal of the sense of dichroism.

solvent absorption this is no longer true. To extend the theory into the range of moderate concentrations, the solvent viscosity in equation 1 may be replaced by the viscosity of the solution. The validity of this change is limited to small degrees of orientation, for at high concentrations and high degrees of orientation the rotary diffusion parameter  $\Theta$  becomes a function of angular orientation rather than a constant, and the theory of Peterlin and Stuart fails altogether.<sup>2,7</sup>

**Conclusions from PBLG.**—While the combined effects of end-to-end association, polydispersity and finite concentration make it impossible to calculate directly the intrinsic orientation of an absorbing dipole, relative to the helix axis, we can at least compare the relative orientations of various absorption bands. As may be seen from the circled points of Fig. 2, the  $3300\text{ cm}^{-1}$  band (N-H stretch) follows rather closely the theoretical density changes calculated for an ideal polymer-solvent system with a perfectly-oriented parallel absorber. Therefore we shall consider the dipole responsible for the  $3300\text{ cm}^{-1}$  absorption as being perfectly oriented along the polymer helix for present purposes of discussion.

(7) A. Peterlin and H. A. Stuart, *Z. Physik*, **112**, 129 (1939). A. Peterlin, *ibid.*, **111**, 232 (1938).

The relative density changes  $\Delta D/D_0$  observed for the 1550  $\text{cm}^{-1}$  amide II absorption band are opposite in sign to those for the 3300  $\text{cm}^{-1}$  band. Amide II is a band of composite character, mostly N-H deformation, but partially C=N stretch.<sup>8</sup> The calculations on streaming orientation<sup>2</sup> indicate that a perfectly oriented perpendicular absorber will exhibit relative density changes  $\Delta D/D_0$  opposite in sign and one-half as large in magnitude as the changes observed for a perfectly oriented parallel absorber. When the 3300 and 1550  $\text{cm}^{-1}$  bands are compared this is observed to be the case, so we conclude that the dipole responsible for the 1550  $\text{cm}^{-1}$  absorption has perfect perpendicular orientation relative to the axis of the helix.

The relative density changes observed for the 1650  $\text{cm}^{-1}$  band (amide I, C=O stretch) are of the same sign as those for the 3300  $\text{cm}^{-1}$  band. If this dipole were perfectly oriented parallel to the axis of the helix, it would exhibit relative density changes identical to those observed for the 3300  $\text{cm}^{-1}$  band. The changes observed for the 1650  $\text{cm}^{-1}$  band are smaller by a factor 0.65, so the amide I band is an imperfectly oriented parallel absorber. "Orientation" here refers to the direction of the oscillating dipole associated with the absorption, rather than the direction of mechanical oscillation of a chemical group, since the two need not always coincide.

It must also be remembered that one strong absorption band may mask other, weaker bands of quite different origin. Thus the strong 1650  $\text{cm}^{-1}$  C=O band probably masks a weaker phenyl ring band (1600–1650  $\text{cm}^{-1}$  in many aromatic compounds). Since the benzyl ester C=O stretching band at 1730  $\text{cm}^{-1}$  arises from a group on a flexible side chain and shows no dichroism, the phenyl ring absorption is also presumably non-dichroic, and degrades the orientation observed at 1650  $\text{cm}^{-1}$ .

These observations on solutions have been compared with observations on cast, oriented films. The film data are complicated by the non-uniformity in sample thickness and degree of orientation. Even so, it is clear that the 1650  $\text{cm}^{-1}$  band is less oriented than the 3300  $\text{cm}^{-1}$  band. For example, the dichroic ratios observed for a typical cast film are 3.93 for 3300  $\text{cm}^{-1}$  and 2.96 for 1650  $\text{cm}^{-1}$ . These are consistent with the solution data, and provide another illustration of the indifference of absorptions associated with the helical configuration to changes of solvent or physical environment.

**Interpretation of the Slow Decay of Orientation in Concentrated Poly- $\gamma$ -benzyl-L-glutamate Solutions.**—While no theory exists for streaming orientation in a concentrated polymer solution, the results of some experiments are easily interpreted, and demonstrate the utility of this method for the study of concentrated solutions. An analysis of several time decay curves of orientation similar to Fig. 3 led to a natural logarithmic time constant of 6.4 sec. describing the decay of dichroism in this solution. This is equivalent to a rotary diffusion constant of  $7.9 \times 10^{-2} \text{ sec}^{-1}$ , which may be compared with a constant of  $1.4 \times 10^{+4} \text{ sec}^{-1}$  for the same polymer in the same solvent at infinite dilution.

The slow decay of orientation observed for 390,000 MW<sub>w</sub> polymer (Fig. 4) is not easily interpreted. An examination of the liquid with a low power polarizing microscope revealed the presence of aggregates, and a series of photomicrographs demonstrated the very slow decay of orientation of the aggregates. These are the liquid crystals observed by Robinson and Ward<sup>9</sup> and others. It is clear that a number of competing processes operate in this liquid. The streaming gradient presumably destroys the liquid-crystal structure, and the decay of dichroism on cessation of pumping may involve the de-orientation of true solution phase, the formation of liquid crystals, and finally the de-orientation of the liquid crystals. The observations of Robinson and Ward indicate that the liquid crystals will be oriented parallel to the cell walls even after the various de-orientation processes are complete. Even with the array of mechanisms available, it is difficult to account for the three and possibly four changes in sign of the rate of change of optical density with time. The possibility that this oscillatory pattern results from the form-optical rotatory power of the liquid crystals reported by Robinson and Ward may be excluded on very simple grounds. The decay curves for the 1550 and 3300  $\text{cm}^{-1}$  bands are generally identical in form and period, while one would predict quite different optical rotatory powers at such different frequencies. Because of the  $\lambda^{-2}$  dependence of this form-optical rotatory power and the thinness of the sample, one would expect such optical rotatory effects in the infrared to be small.

**Conclusions on the Method for Streaming Dichroic Observations.**—With solution viscosity employed in the calculation of rotatory diffusion constants, and with allowance made for the known end-to-end association of poly- $\gamma$ -benzyl-L-glutamate in chloroform-formamide, the agreement between observed and calculated orientations is quite satisfactory. If a more exact test is to be made of the method, a monodisperse polymer will be necessary, along with a solvent system which eliminates all associations between polymer molecules. It seems clear that streaming dichroic observations will not compete with the established visible birefringence methods for determining molecular shapes, but that observations of dichroism may be useful in revealing association and polydispersity. The principal use of this method is that it extends the available region for optical investigation of polymers in solution through the infrared (and ultraviolet, for that matter), and that it offers much information on the detailed molecular configuration of polymers.

**Results on Other Synthetic Polypeptides.**—Poly-L-glutamic acid samples derived from PBLG by debenzilation<sup>10</sup> have been examined by this same technique. Some chain cleavage occurs during the debenzilation reaction, so the poly-L-glutamic acid (PGA) obtained is more polydisperse in molecular weight and no quantitative correlation between dichroism and molecular weight has been attempted. The free acid is soluble in

(9) C. Robinson and J. C. Ward, *ibid.*, **180**, 1183 (1957).

(10) E. R. Blout and M. Idelson, *THIS JOURNAL*, **78**, 497 (1956); M. Idelson and E. R. Blout, *ibid.*, **80**, 4631 (1958).

(8) R. D. B. Fraser and W. C. Price, *Nature*, **170**, 490 (1952).

dioxane-water, and was run in a solvent of 90 parts dioxane-10 parts  $D_2O$  by volume. The results were essentially identical to those on PBLG: parallel dichroism for the 3300 (N-H stretch) and 1650  $cm^{-1}$  (amide I) bands, and perpendicular dichroism for the 1550  $cm^{-1}$  (amide II) band. Indeed, the spectrum (with and without flow) of PGA in the region 2000-1500  $cm^{-1}$  is very similar to the PBLG spectrum. A typical trace has been shown in the paper on dichroism instrumentation,<sup>3</sup> and will not be reproduced here.

A second portion of the sample of poly-L-glutamic acid which gave dichroism as the free acid in solution was converted to the sodium salt and dissolved in  $D_2O$ . No significant dichroism was observed with gradients of the same magnitude as those used in the free acid experiment.

Poly- $\epsilon$ -carbobenzyloxy-L-lysine of  $MW_w$  575,000 was run in chloroform solution, and dichroism was observed. The bands similar to those in PBLG (3300, 1650 and 1550  $cm^{-1}$ ) gave dichroism identical in direction to the PBLG bands. The bands associated with the carbobenzyloxy residue, 1705 and 1520  $cm^{-1}$  gave little or no significant dichroism. A trace with and without flow is shown in Fig. 5.

Samples of poly-L-lysine-HCl derived from preparations of the carbobenzyloxy derivative were dissolved in  $D_2O$  and a flowing experiment was run. No significant dichroism was observed for these solutions.

A copolymer of 7:3 L-glutamic acid-L-lysine hydrobromide<sup>11</sup> was dissolved in  $D_2O$ . The result of the flowing experiment showed parallel dichroism for the amide I band, which is lowered in frequency to 1642  $cm^{-1}$  by deuteration. The amide II band was completely removed in the deuteration process, and the N-D vibration of 1450  $cm^{-1}$  was masked by a strong solvent absorption, so no observations could be made for these bands.

### Conclusions

The observation of parallel streaming dichroism of the infrared bands at 3300 and 1650  $cm^{-1}$  and of perpendicular dichroism at 1550  $cm^{-1}$  is proof of a rigid rod-shaped structure, and indicates the structural similarity of these polymers. For most of the polypeptides giving significant dichroism, the observations confirm earlier conclusions that the structure is in fact helical. No prior information existed regarding the structure of poly- $\epsilon$ -carbobenzyloxy-L-lysine in  $CHCl_3$ , and the results obtained here are to be taken as a reliable indication that this, too, has a helical structure. Indeed, we regard this apparatus and method as a "helix-indicator."

The failure to observe significant dichroism with sodium poly-L-glutamate and poly-L-lysine hydrochloride is consistent with the view that electrostatic repulsion must destroy the helical configuration and force these molecules into random configurations.<sup>10</sup> The results are particularly conclusive in the case of sodium poly-L-glutamate, since the

(11) E. R. Blout and M. Idelson, *THIS JOURNAL*, **80**, 4909 (1958).

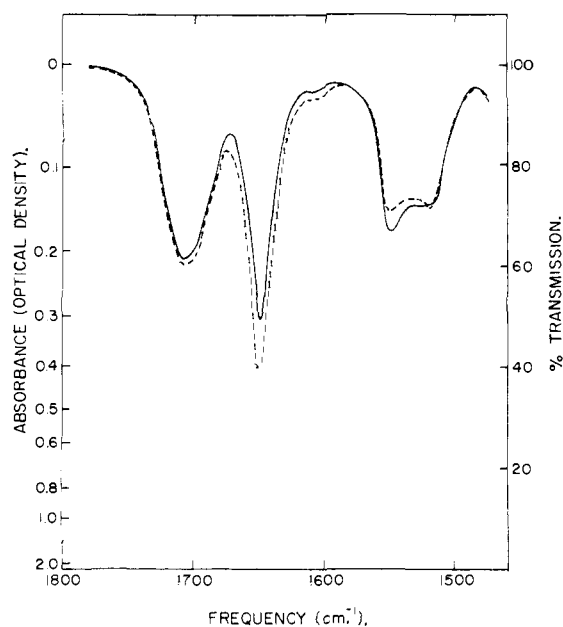


Fig. 5.—Streaming dichroism of poly- $\epsilon$ -carbobenzyloxy-L-lysine; 3.0 g. of poly- $\epsilon$ -carbobenzyloxy-L-lysine, MI-2-358-200, having  $MW_w = 575,000$  in 100 ml. of solution: solvent, analytical reagent chloroform; cell thickness, 0.00428 cm.; 100% reference, a matched cell containing solvent; solid curve, solution at rest; broken curve, solution flowing,  $G_{max} = 52,500$  sec.<sup>-1</sup>; radiation electric vector parallel to flow direction. Two of the bands, 1650 and 1550  $cm^{-1}$ , are polypeptide amide bands, showing the magnitude and direction of dichroism associated with the  $\alpha$ -helix in other polypeptides. The band centered at 1520  $cm^{-1}$  is associated with the epsilon N-H group of the lysine residue, and shows no significant dichroism. The band centered at 1705  $cm^{-1}$  is associated with the C=O stretching vibration of the carbobenzyloxy group, and shows very slight dichroism. This may be due to a slight increase in cell thickness resulting from the pumping pressure.

sample used was known to be appreciably oriented in acid solutions of dioxane- $D_2O$ . Thus conversion to the sodium salt must produce some drastic change in configuration, and the streaming dichroism results point to a random configuration.

The observation of infrared dichroism of flowing polymer solutions has given qualitative and quantitative confirmation of many of the known properties of some helical polypeptides in solution, and has provided new information on other polypeptides. The method may be extended to a variety of natural and synthetic polymers having elongated shapes in solution. Results of investigation on some natural high polymers will appear in a forthcoming publication.

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