(*sym.* $D_{3h}$)[18] was confirmed and the B–N distance found to be 1.44 ± 0.02 Å. The best values for the parameters of dimethylamine are: C–N = 1.46 ± 0.03 Å., C–H = 1.08 ± 0.03 Å.; and the C–N–C angle = 108 ± 4°. The arrangement of the heavy atoms in $B_2NH_7$ was determined to be B–N–B, but the electron diffraction investigation could not eliminate definitely the configuration $H_3B–NH_2–BH_2$ in preference to $H_3B–NH–BH_3$. The mean B–N separation is 1.56 ± 0.03 Å. and the B–N–B angle is tetrahedral to within four degrees.

PASADENA, CALIF. RECEIVED SEPTEMBER 24, 1937

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[18] Professor Zachariasen called my attention to the structure determination of boron nitride made by V. M. Goldschmidt [*Norsk. geol. Tidskrift,* **9**, 258 (1926)] and O. Hassel (*ibid.*, p. 266). The compound was found to have a graphite-like structure with a B–N separation equal to 1.45 Å., somewhat lower than would be expected, but still within the experimental error, in agreement with the electron diffraction investigation of triborine triamine.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

# Polar Group Orientation in Linear Polymeric Molecules. The Omega-Hydroxydecanoic Acids[1]

BY W. B. BRIDGMAN

Recent investigations of dielectric constant-frequency relationships in dilute solutions have shown that the observed times of relaxation of such substances as zein, gliadin, lignin, hemoglobin, etc., are in agreement with the values calculated from the molecular weights of these substances as obtained by classical diffusion, sedimentation, and osmotic pressure methods. In these cases the identity of the electrical and molecular kinetic units is established.

However, equality of the electrical and molecular kinetic units is not to be expected in all cases. It has been shown by workers in this Laboratory that there is a class of molecules, to which certain linear polymers belong, which shows a different but characteristic behavior in dilute solution. As typical of the polymeric substances of this class we have chosen the molecules produced by inter-esterification of ω-hydroxydecanoic acid. These polymers may be represented by the formula

$$HO[(CH_2)_9COO]_{n-1}(CH_2)_9COOH$$

The behavior of these molecules can best be explained by considering that the electrical unit orienting in the applied field is but a small portion of the molecular kinetic unit. This type of molecule shows a definite contribution to the polarization due to orientation of dipoles, but shows no variation of dielectric constant with frequency in the region where dispersion should occur if the entire molecule were being oriented by the field. Further, the specific polarization is found to be independent of the molecular weight and the dipole moment is proportional to the square root of the molecular weight.

## Apparatus

The apparatus used for the greater part of the experimental work was a modified resonance type of dielectric constant apparatus. It was composed of three units; a crystal controlled oscillator, a variable oscillating detector, and a resonating circuit containing the cell. The crystal controlled oscillator used a '37 tube with a crystal having a fundamental of 954.7 kilocycles (314 meters). This oscillator was rich in harmonics, it being readily possible to detect harmonics as high as the twentieth. The variable oscillating detector utilized a 6-A-7 tube and by means of plug-in coils could be operated at frequencies varying from 20,000 to 850 kilocycles (15 to 360 meters). This detector was inductively coupled to the crystal oscillator. In use it was tuned to zero beat with the desired harmonic of the crystal oscillator. The resonator consisted of a special General Radio Company Precision Condenser, Type 222-L, with total capacity of about 100 $\mu\mu$ fd., connected in parallel with the cell and across an inductance coil. The resonator was capacitatively coupled to the oscillating detector and the point of resonance could be determined quite sharply by listening to the heterodyne beat note generated between the two oscillators. The cell used for this work consisted of a small variable condenser, the plates of which were immersed in the dielectric medium. In making a dielectric constant determination, the position of the rotor was varied between two reproducible positions. The difference in capacity between these positions when the plates of the condenser were covered with solution divided by the difference in capacity between the same positions when the cell was filled with solvent, gave the relative dielectric constant of the solution.[2] These relative dielectric constants

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[1] A preliminary account of the results of this research appeared in the Communications to the Editor section of THIS JOURNAL, **59**, 1579 (1937). More complete details are to be found in a thesis submitted to the faculty of the University of Wisconsin in partial fulfilment of the requirements for the Ph.D. degree in August, 1937.

[2] Daniels, Mathews and Williams, "Experimental Physical Chemistry," 2d ed., McGraw-Hill Book Co., New York, 1934, p. 247.

were measured with an accuracy of ±3 parts in 1000. Supplementary measurements at lower frequencies were made by using a radio frequency bridge. All measurements were made at 25 ± 0.05°, with water from a thermostat being circulated through a jacket about the cell. The precision condenser was calibrated for variations due to irregularities of the worm gear by the method of Binns and Kisner.[3]

Density determinations were made with an Ostwald pycnometer of about 8-cc. capacity, fitted with ground glass caps to retard evaporation. The determinations of refractive index were made with a precision immersion refractometer.

### Preparation of Materials

**ω-Hydroxydecanoic Acid.**—The preparation of the monomeric acid and the formation of the polymers was carried out in collaboration with Dr. Oscar Quimby, formerly of this Laboratory. The method of preparation followed that of Lycan and Adams.[4] Methyl undecylenate ($CH_2{=}CH(CH_2)_8COOCH_3$) (Eastman Kodak Company) was ozonized in glacial acetic acid solution. The resulting ozonide was converted to an aldehyde by hydrolysis in the presence of zinc dust.[5] The aldehyde ester was purified by distillation under reduced pressure and the aldehyde group reduced to an alcohol by hydrogenation in a bomb using Raney nickel as a catalyst.[6] After further distillation the ester group was saponified with alcoholic potassium hydroxide. The potassium salt was acidified to give the desired ω-hydroxydecanoic acid. Titration of this material with alcoholic sodium hydroxide solution, using phenolphthalein as an indicator, gave molecular weights of 192 and 190 as compared to the theoretical value of 188. The high value of the observed molecular weights was probably due to a small amount of interesterification because, after a solution of the acid was refluxed with alcoholic sodium ethoxide, back titration with acid gave a molecular weight of 185.

**Polyesters of ω-Hydroxydecanoic Acid.**—In the interesterification of the monomeric acid we were guided by the experiences of Lycan and Adams[7] and of Carothers and Van Natta.[8] In general the polymers were prepared by heating the monomer at temperatures between 200–250° under reduced pressure. The reactions were carried out in a suction flask fitted with a large test-tube through which water was circulated to serve as a condenser. The polymer was dissolved in hot chloroform and crystallized by cooling and dilution with acetone. The polymers were recrystallized repeatedly from the mixed chloroform–acetone solvent until the molecular weight values as obtained by titration after successive crystallizations, did not differ by more than 5 to 10%.

For the molecular weight determination, samples of the polymers were dissolved in alcohol–chloroform solvent and titrated with 0.0848 *N* alcoholic potassium hydroxide, using phenolphthalein as indicator. Because of the small amounts of polymer available, it was not practical to use more than 1 g. of polymer for any one determination. For the final titrations a 10-cc. buret graduated to 0.05 cc. was used. The average molecular weights determined in this way are believed to be accurate to within 2.5%. Titrations for following the course of the crystallizations were made with smaller samples of polymer and an ordinary 50-cc. buret.

The polymers were finally dried in a vacuum oven and kept in a desiccator over sulfuric acid. The polymers prepared in this research varied in molecular weight from 905 to 13,900.

Solvents: **s-Tetrachloroethane.**—This compound was obtained from the Eastman Kodak Company. It was washed with distilled water, dried over anhydrous sodium sulfate, and distilled from phosphorus pentoxide at 145.5–146.5° (uncorr.). The index of refraction as measured with a Pulfrich refractometer was 1.49188.

**Chloroform.**—The liquid was purified by washing twice with 10% sodium hydroxide, twice with 10% sulfuric acid, and twice with water. It was dried with calcium chloride and distilled from phosphorus pentoxide at 59.5° (uncorr.).

**Benzene.**—It was necessary to purify amounts of this chemical on two occasions. The first amount, used in the benzene solutions numbered up to twenty in the tables to follow, was shaken twice with concentrated sulfuric acid, washed with water, dried over phosphorus pentoxide, decanted, and distilled in an all Pyrex still at 78.3–78.5°

TABLE I

DIELECTRIC CONSTANT–WAVE LENGTH DATA FOR SOLUTIONS OF ω-HYDROXYDECANOIC ACID POLYMERS

| Wave length | Soln. 1[a] | Soln. 1A[a] | Soln. 2[a] | Soln. 3[a,b] | Soln. 30[a] |
|---|---|---|---|---|---|
| 16.5 | ... | 0.986 | ... | ... | 1.066 |
| 17.5 | 0.985 | .987 | 1.034 | 1.024 | ... |
| 21.0 | ... | .985 | 1.036 | 1.021 | 1.067 |
| 26.2 | ... | ... | 1.039 | 1.022 | 1.068 |
| 28.6 | .985. | ... | ... | ... | ... |
| 34.9 | ... | .988 | 1.037 | 1.020 | 1.068 |
| 52.4 | ... | .989 | 1.035 | 1.020 | 1.069 |
| 62.9 | .991 | ... | ... | ... | ... |
| 78.6 | ... | .987 | 1.037 | 1.022 | 1.065 |
| 89.8 | .990 | ... | ... | ... | ... |
| 180 | .991 | .988 | 1.032 | 1.021 | 1.070 |
| 210 | ... | .988 | 1.033 | 1.020 | ... |
| 350 | .993 | ... | ... | ... | 1.072 |
| 360 | ... | ... | 1.035 | 1.023 | ... |
| Radio Frequency Bridge | | | | | |
| 585 | 0.992 | ... | 1.038 | ... | ... |
| 1072 | .993 | ... | 1.037 | ... | ... |
| 1802 | ... | ... | 1.031 | ... | ... |
| 3604 | .993 | ... | 1.034 | ... | ... |
| 7208 | ... | ... | 1.040 | ... | ... |

[a] Compositions of solutions: Soln. 1, 2.92% of 13,500, mol. wt. polymer in *s*-tetrachloroethane; Soln. 1A, Soln. 1 after standing for eight days; Soln. 2, 3.19% of 13,500, mol. wt. polymer in benzene; Soln. 3, 3.33% of 13,500, mol. wt. polymer in chloroform; Soln. 30, 7.60% of 11,400, mol. wt. polymer in benzene. [b] The data for this solution have not been corrected for errors due to stray reactances in the leads.

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[3] Binns and Kisner, *Rev. Sci. Instruments*, **5**, 377 (1934).

[4] Lycan and Adams, THIS JOURNAL, **51**, 625 (1929).

[5] Noller and Adams, *ibid.*, **48**, 1074 (1926).

[6] We are indebted to Prof. Homer Adkins of this Department, who performed this hydrogenation.

[7] Lycan and Adams, THIS JOURNAL, **51**, 3450 (1929).

[8] Carothers and Van Natta, *ibid.*, **55**, 4714 (1933).

(uncorr.). This fraction had a density of 0.8722 and index of refraction of 1.49732, both measured at 25°.

The second sample of benzene received the same treatment, except that it was crystallized twice by cooling in an ice-bath before drying. The density in this case was 0.8728 and the index of refraction, 1.49780, again at 25°. This difference in the constants for the two samples is not considered a serious matter, since in all of the observations made in this research the behavior of the solution is compared with that of the solvent from which it was prepared.

## Data

Solutions were made up by weight. In the case of the dipole moment determinations where measurements were made with the same polymer at several concentrations, the most concentrated solution was prepared first and the less concentrated solutions prepared from it by dilution. The solutions were kept in glass-stoppered Erlenmeyer flasks in a calcium chloride desiccator.

The experimental work may be divided into two sections: an attempt to observe anomalous dispersion of the dielectric constant by varying the frequency of the applied field; and the measurement of the polarization and dipole moment for a series of these polymer molecules. The results of the first part of the work are shown in Table I. The ratio of the dielectric constant of the solution to that of the solvent is given in each case.

The molecular polarization data are summarized in Table II. The first four columns of figures give the experimental data. They give, respectively, the mole fraction of solute, $f_2$; the refractive index, $n$; the dielectric constant, $e$ (average of measurements at 180 and 79 meters); and the density, $\rho$. The columns headed $R_{12}$ and $P_{12}$ contain the molar refraction and molar polarization, respectively, of the solutions calculated from the figures given in the first four columns. The quantities $R_2$ and $P_2$ are the molar refraction and molar polarization, respectively, of the pure solute. It is assumed that the total polarization is

TABLE II

REFRACTION AND POLARIZATION DATA FOR ω-HYDROXYDECANOIC ACID POLYMERS IN BENZENE SOLUTIONS

| | $f_2$ | $n$ | $e$ | $\rho$ | $R_{12}$ | $P_{12}$ | $R_2$ | $P_2$ | $\delta/M \times 10^3$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Mol. wt., 13,900 | | | | | |
| Benzene | ..... | 1.49732 | 2.273 | 0.87224 | 26.20 | 26.66 | .. | ... | .. |
| Soln. 13 | 0.00003 | 1.49721 | 2.289 | .87313 | 26.31 | 27.01 | 3670 | 11670 | 3.62 |
| Soln. 12 | .00005 | 1.49712 | 2.295 | .87336 | 26.39 | 27.19 | 3800 | 10600 | 2.85 |
| Soln. 11 | .000085 | 1.49704 | 2.312 | .87416 | 26.48 | 27.54 | 3290 | 10350 | 3.00 |
| Soln. 10 | .00018 | 1.49675 | 2.345 | .87604 | 26.89 | 28.46 | 3830 | 10000 | 2.71 |
| | | | | Mol. wt., 9070 | | | | | |
| Benzene | ..... | 1.49781 | 2.273 | 0.87282 | 26.20 | 26.64 | .. | ... | .. |
| Soln. 29 | 0.00006 | 1.49764 | 2.296 | .87381 | 26.35 | 27.13 | 2480 | 8110 | 3.77 |
| Soln. 28 | .00012 | 1.49748 | 2.310 | .87439 | 26.50 | 27.51 | 2460 | 7130 | 3.03 |
| Soln. 27 | .00025 | 1.49719 | 2.337 | .87622 | 26.82 | 28.24 | 2550 | 6520 | 2.61 |
| | | | | Mol. wt., 7780 | | | | | |
| Benzene | ..... | 1.49732 | 2.273 | 0.87224 | 26.20 | 26.66 | .. | ... | .. |
| Soln. 16 | 0.00011 | 1.49713 | 2.296 | .87363 | 26.43 | 27.25 | 2090 | 5360 | 2.53 |
| Soln. 15 | .00020 | 1.49700 | 2.306 | .87462 | 26.63 | 27.60 | 2200 | 4700 | 1.94 |
| Soln. 14 | .00033 | 1.49673 | 2.331 | .87621 | 26.90 | 28.27 | 2150 | 4910 | 2.04 |
| | | | | Mol. wt., 4110 | | | | | |
| Benzene | ..... | 1.49739 | 2.273 | 0.87224 | 26.20 | 26.66 | .. | ... | .. |
| Soln. 19 | 0.00022 | 1.49712 | 2.302 | .87366 | 26.44 | 27.34 | 1140 | 3140 | 2.94 |
| Soln. 18 | .00038 | 1.49696 | 2.319 | .87448 | 26.63 | 27.79 | 1160 | 3000 | 2.68 |
| Soln. 17 | .00066 | 1.49668 | 2.342 | .87620 | 26.94 | 28.47 | 1150 | 2770 | 2.34 |
| | | | | Mol. wt., 2120 | | | | | |
| Benzene | ..... | 1.49779 | 2.273 | 0.87282 | 26.20 | 26.64 | .. | ... | .. |
| Soln. 22 | 0.00043 | 1.49756 | 2.296 | .87419 | 26.45 | 27.24 | 605 | 1418 | 2.27 |
| Soln. 21 | .00074 | 1.49738 | 2.316 | .87508 | 26.62 | 27.72 | 595 | 1487 | 2.48 |
| Soln. 20 | .00130 | 1.49711 | 2.342 | .87692 | 26.93 | 28.45 | 585 | 1415 | 2.31 |
| | | | | Mol. wt., 905 | | | | | |
| Benzene | ..... | 1.49780 | 2.273 | 0.87282 | 26.20 | 26.64 | .. | ... | .. |
| Soln. 25 | 0.00080 | 1.49756 | 2.301 | .87385 | 26.35 | 27.21 | 213 | 738 | 3.07 |
| Soln. 24 | .00138 | 1.49737 | 2.315 | .87475 | 26.51 | 27.59 | 254 | 717 | 3.07 |
| Soln. 23 | .00267 | 1.49704 | 2.342 | .87625 | 26.80 | 28.31 | 251 | 652 | 2.62 |

the sum of that due to the pure solute and pure solvent. $\delta/M$ is the specific dielectric constant increment.

In Table III are given values of $P_2$ and $R_2$ for each polymer, obtained by extrapolating the data given in Table II to zero concentration. This extrapolation was carried out graphically by use of straight lines, drawn so that the lines representing the various molecular weights all possessed approximately the same slope. The dipole moments, $\mu$, were calculated by making the assumption that the molar refraction represents the deformation polarization, *i. e.*, $P_{\text{orient.}} = P_2 - R_2$. Table III also contains the specific polarization, specific refraction, and the ratio of the dipole moment to the square root of the molecular weight.

TABLE III

DIPOLE MOMENT DATA FOR ω-HYDROXYDECANOIC ACID POLYMERS

| Mol. wt. | $P$ | $R$ | $P/M$ | $R/M$ | $\mu/\sqrt{M}$ | $\mu$ |
|---|---|---|---|---|---|---|
| 13,900 | 11,300 | 3800 | 0.813 | 0.273 | $0.161 \times 10^{-18}$ | $19.0 \times 10^{-18}$ |
| 9,070 | 7,600 | 2500 | .838 | .276 | .166 | 15.7 |
| 7,780 | 5,300 | 2100 | .681 | .270 | .141 | 12.4 |
| 4,110 | 3,300 | 1150 | .803 | .280 | .160 | 10.2 |
| 2,120 | 1,530 | 600 | .722 | .283 | .145 | 6.7 |
| 905 | 780 | 250 | .862 | .276 | .168 | 5.0 |

In Fig. 1 are plotted all the values of the dielectric constants of the benzene solutions against concentration expressed in weight per cent. to show that there is no trend of the dielectric constant with molecular weight when the concentration is expressed in this way.

## Discussion

Calculation of a theoretical dispersion curve according to the Debye equation as modified for dilute solutions by Williams and Oncley[9] for a polymer of molecular weight 13,500, assumed to be spherical in shape, in benzene solution shows that the critical wave length should be approximately 19 meters. Thus more than one-half of the dispersion curve would fall within the range of the apparatus used in this work. Since the dielectric constant is appreciably greater than the square of the refractive index, it appears that there must be a contribution due to dipole orientation. In the case of a 3% solution of polymer, there appears to be an orientation contribution of between 2 and 3% in the dielectric constant. Examination of the data of Table I shows no tendency for the dielectric constant to decrease at the lower wave lengths. Perrin[10] has made calculations for the case of ellipsoids of revolution which show that departure from spherical shape should cause dispersion to take place at even longer wave lengths, and thus be more completely in the range of the apparatus used. As a result of these considerations it is concluded that while there is a contribution to the dielectric constant due to dipole orientation, these polymers do not show dispersion at the frequency expected from consideration of their molecular weight.

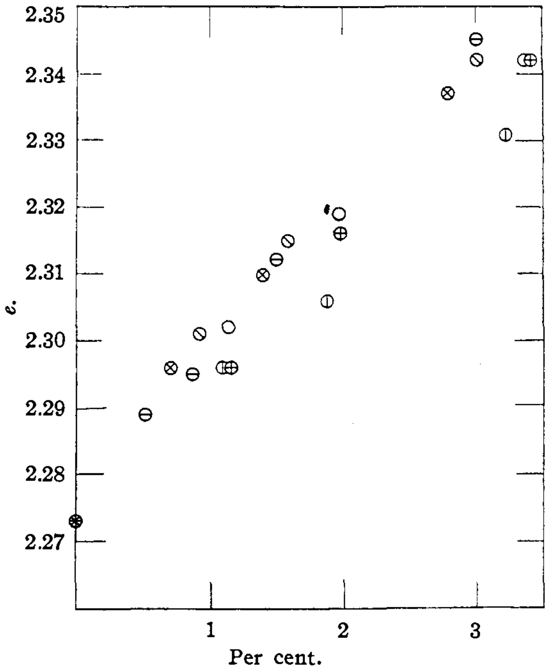

Fig. 1.—Dielectric constants of benzene solutions of polymers: ⊖, 13,900, mol. wt.; ⊗, 9070, mol. wt.; ⦶, 7780, mol. wt.; ○, 4110, mol. wt.; ⊕, 2120, mol. wt.; ⊘, 905, mol. wt.

The dielectric constant and density observations show that while the molecular weight varies over a fifteen fold range, the specific polarization remains essentially constant.[11] From the form of Debye's equation it is a necessary consequence that the molecular dipole moment be proportional to the square root of the molecular weight. This is shown to be the true situation by the data of Table III.

In attempting to explain this dependence of the dipole moment on the molecular weight, four types of molecules must be considered. The first

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[9] Williams and Oncley, *Physics*, **3**, 314 (1932).

[10] Perrin, *J. phys. radium*, **5**, 447 (1934).

[11] Since the appearance of our "Communication to the Editor,"[1] we have learned that Prof. J. Wyman of Harvard University, independently of us, obtained similar data with solutions of these polyesters (THIS JOURNAL, **60**, 328 (1938)).

two types are rigid molecules, one a zwitter-ion and the other a molecule possessing regularly recurring polar linkages. The other two types are molecules of similar chemical structure but characterized by free or partial rotation about the valence bonds.

Both types of rigid molecules lead to a direct proportionality between dipole moment and molecular weight; thus they may be ruled out as inapplicable to these polymers. If we have a dipole ion or zwitter-ion in which the charges are located at opposite ends of the molecule and the molecule is built up in some rigid manner then, excluding small members of this series, the distance between the charges and therefore the dipole moment should vary directly with the molecular weight. For a series of molecules in which polar groups recur at regular intervals, if the structure is rigid so that each additional polar group is added with a definite orientation to the previous group, then neglecting small molecules and small changes in molecular weight, the resultant moment should be proportional to the molecular weight.

However, Kuhn[12] has calculated for long chain molecules in which free rotation takes place about the valence bonds, that the average separation of the ends of the molecule will vary as the square root of the straight chain length of the molecules. Thus for a series of chemically similar molecules, the average separation of the ends of the molecules should vary with the square root of their molecular weight. If this flexible molecule should be a zwitter-ion with the charges at the end of the molecule, then its moment should vary as the square root of the molecular weight.

Wyman has made use of this to explain the dielectric behavior of various amino acids and peptides in aqueous solution. His data are expressed in terms of a dielectric constant increment defined by the equation

$$\delta = \frac{\epsilon_{\text{solution}} - \epsilon_{\text{solvent}}}{C} \qquad (1)$$

in which $C$ is the concentration in moles per liter. It is shown that this increment is proportional to the square of the dipole moment. In the peptides of glycine we have a series of zwitter-ions with the charges at the ends of the molecules. If the above hypotheses are correct, the dielectric increment for these polymers should vary directly with the molecular weight. In Table IV, data of Wyman and McMeekin[13] for the peptides of glycine are presented. It is to be noted that the specific $\delta$ values appear to be approaching a constant value at large molecular weights. In the last column of Table II, specific $\delta$ values for the polymers used in this research are presented. Again $\delta/M$ is essentially constant but its magnitude is only about $^1/_{300}$ as large as the corresponding value for the peptides of glycine. Both the difference in magnitude and the fact that the solvent used in this research was benzene serve to eliminate any possibility of explaining the behavior of these polymers by zwitter-ion formation.

TABLE IV

DIELECTRIC CONSTANT INCREMENT DATA FOR PEPTIDES (WYMAN AND MCMEEKIN)

| | $M$ | $\delta$ | $\delta/M$ |
|---|---|---|---|
| Glycine | 75.05 | 22.6 | 0.301 |
| Diglycine | 132.08 | 70.6 | .535 |
| Triglycine | 189.11 | 113.3 | .599 |
| Tetraglycine | 246.14 | 159.2 | .647 |
| Pentaglycine | 303.18 | 214.5 | .708 |
| Hexaglycine | 360.21 | 234.2 | .650 |
| Heptaglycine | 417.24 | 290.0 | .695 |

The remaining type of molecule to be considered is a chain molecule with recurring polar groups, with sufficient separation between the polar groups and enough freedom of rotation about the intervening valence bonds, so that the polar groups are free to orient independently of one another in an electric field. In such a case the polarization will depend upon the number of dipole moments contained in unit volume and should be independent of the size of the molecules in which they are contained or of their position in the molecule. This picture is consistent with the discovery that the specific polarization for this series of polymers is independent of the molecular weight.

The Debye equation for the molar polarization, $P$, may be written in the form

$$P = \frac{4\pi N\alpha_0}{3} + \frac{4\pi N\mu^2}{9kT} \qquad (2)$$

It is assumed that each molecule possesses a permanent moment, $\mu$, and that each molecule orients independently of the others. It is apparent that at a given temperature the contribution to the molar polarization due to the orientation of dipoles is equal to the product of a constant and the sum of the squares of all of the moments in a mole of substance. In the type of molecule now being considered, the possession of independent dipole moments is assumed, and it follows that the contribution to the polarization from these dipoles should depend on the sum of the squares of these

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(12) Kuhn, *Kolloid Z.*, **68**, 2 (1934).

(13) Wyman and McMeekin, THIS JOURNAL, **55**, 908 (1933).

individual moments. Thus when one calculates a dipole moment for such a molecule by means of the Debye equation, there is obtained an average moment such that its square is the sum of the squares of the individual moments contained in the molecule. Applied specifically to these polymers, the average moment of a molecule containing $n$ meric units is given by

$$\mu^2 = \mu^2_{-\mathrm{COOH}} + (n-1)\mu^2_{-\mathrm{COOC-}} + \mu^2_{-\mathrm{CH_2OH}} \qquad (3)$$

Substituting numerical values of $\mu_{-\mathrm{COOH}} = 1.4\mathrm{D}$, $\mu_{-\mathrm{COOC-}} = 1.8\mathrm{D}$, and $\mu_{-\mathrm{CH_2OH}} = 1.7\mathrm{D}$, we have in Debye units

$$\mu^2 = 4.85 + (n-1)\,3.24 \qquad (4)$$

In Table V values of the dipole moment calculated from equation (4) are compared with the corresponding data obtained by experiment. From their method of preparation, the polymers of ω-hydroxydecanoic acid must consist of long chains made up of polar ester groups separated by nine carbon atoms. By considering that each ester group orients independently of its neighboring groups there is found a suitable explanation for the observed constant specific polarization of these polymers. Further, by applying equation (4) we are able to calculate molecular moments in good agreement with the observed values.

TABLE V

POLARITY OF ω-HYDROXYDECANOIC ACID POLYMERS

| Mol. wt. | $n$ (monomeric units) | $\mu$ (calcd.) $\times 10^{18}$ | $\mu$ (obsd.) $\times 10^{18}$ |
|---|---|---|---|
| 13,900 | 82 | 16.4 | 19.0 |
| 9,070 | 53 | 13.3 | 15.7 |
| 7,780 | 46 | 12.4 | 12.4 |
| 4,140 | 24 | 9.1 | 10.2 |
| 2,120 | 12 | 6.6 | 6.7 |
| 905 | 5 | 4.2 | 5.0 |

It is interesting to remark that equation (3) also may be obtained by applying the theory of Eyring[14] for the calculation of the dipole moments of long chain molecules. However, in Eyring's derivation it is assumed that completely free rotation takes place about all valence bonds in the chain, and this is not necessary to explain the behavior of these polymers. The derivation given above seems more satisfactory for this purpose since it requires only that there be enough flexibility to the chain for each polar group to be free to oscillate independently of its neighbors in a weak electric field.

The author wishes to express his gratitude for the helpful advice of Prof. J. W. Williams throughout the course of this work.

## Summary

1. Polyesters of ω-hydroxydecanoic acid in dilute solution do not show any evidence of anomalous dispersion of the dielectric constant at frequencies where it is to be expected for molecules of such size.

2. For a fifteen-fold range of molecular weight the specific polarization remains essentially constant and the molecular dipole moment varies with the square root of the molecular weight.

3. This behavior can be explained if we consider that the orientation polarization is due principally to the individual oscillations of the recurring polar groups in the molecule, and not to any motion of the molecular kinetic unit as a whole.

4. The polyesters of ω-hydroxydecanoic acid may be thought of as non-rigid linear molecules.

MADISON, WIS. RECEIVED DECEMBER 13, 1937

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[14] Eyring, *Phys. Rev.*, **39**, 746 (1932).