[CONTRIBUTION FROM THE BIOLOGICAL LABORATORIES OF HARVARD UNIVERSITY]

A Dielectric Constant Study of ω-Hydroxydecanoic Acid Polymers

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In a recent communication[1] Bridgman and Williams have reported measurements of the electric moments of hydroxydecanoic acid polymers of six different size classes of average molecular weights varying from 905 to 13,900. Agreement between measurements at 79 and 180 meters indicates that there is no anomalous dispersion in this range, such as might have been expected, at least for the larger polymers. At the same time the observed moments are not very different from those calculated on the assumption that each polar group in the molecules orients independently of the rest, although in the case of the larger polymers the observed moments are substantially greater, the two values for the largest polymer studied being 19.0 and 16.4 Debye units, which correspond to a difference of 16% of the calculated value, or, in terms of polarizations, to a difference of 34%. As pointed out by Bridgman and Williams, these facts may be explained readily on the basis of free rotation about the nine C–C bonds between each of the polar groups in the molecules.

It is satisfactory that these results are in general agreement with unpublished experiments of our own made last December and January on polymers kindly sent us by Dr. W. H. Carothers. Since our results were obtained on material from a different source and cover a wider range of average molecular weight (1715–28,650) and frequency (4.8×10^7 to 10^3 cycles per second) and since they differ somewhat in detail from those of Bridgman and Williams, it seems desirable to set them down at this time.

The polymers, whose average molecular weights previously had been "calculated from neutral equivalents" in Dr. Carothers' laboratory, were studied in benzene. Values of the apparent specific volume were calculated from density measurements made with a pycnometer at a single concentration, and values of the optical polarization per gram were calculated on the basis of measurements of the index of refraction of the same solutions for sodium light, done with a Pulfrich refractometer. The dielectric constant was measured at three frequencies. At $\nu = 4.8 \times 10^7$ ($\lambda = 6.4$ meters) measurements were made with a resonance method, previously described,[2] which yields absolute values. Measurements at $\nu = 2.547 \times 10^5$ ($\lambda = 1178$ meters) were made with a General Radio Co. radio frequency bridge. The capacity balance was obtained entirely with a precision condenser placed in parallel with the built-in condensers of the bridge, and the values of the dielectric constant were obtained from the measured capacity of the cell for the unknown on the basis of a calibration in which the cell was filled with various dilute solutions (less than 1 per cent.) of ethanol in benzene, the absolute values of the dielectric constant of which were determined for the occasion by the resonance method at a wave length of 6.4 meters. Measurements at 1000 cycles were made with an audio frequency bridge in exactly the same way.

The results of the study are summarized in Table I. The values of n enclosed in parentheses in the first column give the nearest whole number of decanoic acid units corresponding to the average molecular weight of each polymer sample. The second column gives the weight per cent. of polymer in the various solutions studied. v and p_0 are the apparent specific volumes and optical polarizations, respectively. The three columns headed p_μ give the dipole polarization per gram (total—optical polarization) calculated from the dielectric constant measurements at the three frequencies. In the more dilute solutions these are quite sensitive to small errors in the dielectric constant. In no case did values of the dielectric constant of the same solution measured at $\nu = 4.8 \times 10^7$ and $\nu = 2.55 \times 10^5$ differ by more than 0.023%. The worst measurement at 1000 cycles, the frequency where the results were least accurate, differed from that at $\nu = 2.547 \times 10^5$ by 0.12%. The final column gives the power factors for $\nu = 2.547 \times 10^5$ of the cell filled with solutions. The average value of the power factor of the cell filled with benzene was 1.71×10^{-3} at the same frequency.

These results show clearly that over this wider range of frequency there is no appreciable dispersion. At the same time the correspondence

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[1] Bridgman and Williams, THIS JOURNAL, **59**, 1579 (1937).

[2] J. Wyman, Jr., *Phys. Rev.*, **35**, 6, 623–634 (1930).

TABLE I

Mol. wt.	Wt. %	v	p_0	$p\mu$ ($\nu = 4.8 \times 10^7$)	$p\mu$ ($\nu = 2.55 \times 10^5$)	$p\mu$ ($\nu = 10^3$)	Power factor $\times 10^3$ ($\nu = 2.55 \times 10^5$)
1,715 $(n = 10)$	2.284	0.998	0.281		0.415		1.70
	1.017			0.380	.374		1.77
	0.945				.443	0.390	1.82
3,190 $(n = 19)$	1.995	.994	.279		.441		1.79
	1.034			.378	.379		1.81
4,170 $(n = 24)$	2.069	.996	.279		.418		1.79
	1.068			.410	.415		1.82
5,670) $(n = 33$	2.129	.994	.279		.415		1.79
	1.134				.404		1.80
	1.023			.371	.364		1.77
	0.780				.401		1.77
	.452				.345		1.76
	.297				.371		1.67
9,330 $(n = 55)$	1.968	.993	.280		.416		1.77
	0.875			.404	.414		1.80
28,650 $(n = 168)$	2.319				.410		1.89
	1.433				.419	0.439	1.83
	1.309	.999	.280	.429	.415		1.83

between the observed dipole polarizations per gram and those calculated on the assumption of completely unrestricted orientation of each polar group in the molecules is very close. Such calculated values[3] are very nearly independent of polymer size, as is shown by the following figures, and approach as a limit 39.6 cc. as n, the number of units in the polymer, increases to infinity

n	1	3	10	20	50
p_μ, cc.	0.536	0.447	0.411	0.404	0.400

The observed values of p_μ not only do not vary with polymer size within the accuracy of the measurements, but the average of all the values, 0.402 cc., differs by only about 1% from the calculated values. It seems, therefore, that there must be practically complete freedom of orientation of the polar groups in these molecules. It might be asked whether at the lower frequencies the molecules themselves do not orient as units. Since, however, in this case the measured polarization is that due to the mean square moment of the molecules, and since the mean square sum of any number of vectors arranged at random is the sum of the squares[4] of the vectors, the case is indistinguishable from that in which each polar group orients independently of the rest, and the question is meaningless in terms of dielectric constant measurements. It would be of interest to make a study similar to the present one of polymers with a smaller number of intervening bonds allowing free rotation between the polar groups, and in which consequently the independent orientation of these groups was reduced.

Summary

Measurements of the polarizations of ω-hydroxydecanoic acid polymers of average molecular weights from 1715 to 28,650 show that there is no anomalous dispersion up to frequencies of 4.8 × 10^7 cycles per second. The polarization per gram is independent of polymer size, and is the same as that calculated on the assumption that the polarizations of each molecule is the sum of the polarizations of the various polar groups which it contains. This indicates that owing to free rotation about the intervening C–C linkages each polar group orients in the field without restriction from the rest of the molecule.

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(3) Calculated on the basis of the following values for the three polar groups involved: OH, $\mu = 1.7$ Debye units, $p_\mu = 60$ cc.; COOH, $\mu = 1.4$, $p_\mu = 40.8$ cc.; COOC, $\mu = 1.8$, $p_\mu = 67.4$ cc.

(4) This of course refers to the scalar product.