

120° temperature range for one) for the frequency interval 1 kc. to 75 mc. These macromolecular chain polymers are of known structure and composition, so that the observed polarization and dispersion were related to the orientation and concentration of polar groups in the chains and to their relative positions in adjacent chains. The dielectric constants, ϵ' , of all of the polymers exceed the refraction value even at room temperature. The oscillation of individual dipole groups (ester linkages) contributes the orientation polarization. These dipoles interact somewhat along a given chain, but chiefly between chains, to cause the observed broad dispersion. The polyesters exhibit principally high frequency absorption,

with maxima at low temperatures. This supports the concept of small oscillating units in the chains, in agreement with the observed activation energy of orientation.

The packing of the chains is strongly influenced by the dipoles and the formation of dipole layers makes the interaction, which contributes to dielectric absorption, largely independent of polar group concentration.

The dielectric results reveal thermal motion in the polymers. These chain oscillations are supposed to account for mechanical properties such as thermal retraction associated with chain kinking in long chain molecules.

MURRAY HILL, N. J. RECEIVED NOVEMBER 13, 1941

[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, INC.]

The Relation of Dielectric Properties to Structure of Crystalline Polymers. II. Linear Polyamides

BY W. O. BAKER AND W. A. YAGER

Linear condensation polymers have been selected as appropriate for study of the effects of molecular structure and molecular order on the dielectric properties of solids.¹ They represent an important class of structural and insulating plastics. Polyesters have been treated previously and the general implications of such an investigation have been reviewed. The present report includes preliminary results on the polyamides, in which the —O— of the ester linkage has been replaced by the —NH— group. Conditions for extensive hydrogen bonding have thus been introduced, and the whole structure resembles that of polypeptides and proteins. The dielectric measurements indicate great mobility in the alternating field of some atomic group, possibly a charged hydrogen. The close analogy of the polyamides to the polyesters allows assignment of the observed differences to the NH group. Certain of the results may be examined for direct evidence of isomerism in the amido linkage. Thus, the linear polyamides may assist, as models, in elucidating the structure of proteins.

Experimental

Materials.—The polyamides were obtained commercially (du Pont Company) or from the procedures of Carothers.² They were pure, white

polymers with weight average molecular weights greater than 10,000. All were carefully protected from degradation during preparation of the test discs.¹ The co-polyamide was of the 50-50 composition noted in the patent describing it.³ All samples were annealed to states of maximum crystallinity,⁴ unless otherwise noted. The sample discs were molded and machined to a two-inch diameter and 50-mil thickness, were thoroughly dried over phosphorus pentoxide, or conditioned as noted, and equipped with electrodes as previously described.⁵

Dielectric Measurements.—The bridge and Q-meter apparatus and technique used for the polyesters were again employed.

The dielectric loss of polyhexamethylene sebacamide at and above 100°, and of polyhexamethylene adipamide at 100% relative humidity was too high for direct measurement on the Q-meter. Consequently, the top electrode of the test cell was raised above the test specimen, thus introducing a series air gap. The effective capacity, C_m and loss, $\tan \delta_m$, of this two-layer arrangement were determined on the Q-meter and the true capacity, C_x , and loss, $\tan \delta_x$, calculated from the equations

(3) Carothers, U. S. Patent 2,191,367 (1940).

(4) Fuller, Baker and Page, *THIS JOURNAL*, **62**, 3275 (1940); see also Baker and Fuller, *ibid.*, **64**, October (1942).

(5) Yager, *Trans. Electrochem. Soc.*, **74**, 118 (1938).

(1) Yager and Baker, *THIS JOURNAL*, **64**, 2164 (1942).

(2) Carothers, U. S. Patents 2,071,250 (1937) and 2,180,323 (1938).

$$\tan \delta_x = \frac{C_a}{C_a - C_m} \tan \delta_m$$

$$C_x = \frac{C_a C_m}{C_a - C_m} \cdot \frac{1}{1 + \tan^2 \delta_x}$$

where C_a represents the series air capacity. C_a was calculated from the above equations by measuring C_m and $\tan \delta_m$ and then the corresponding C_x and $\tan \delta_x$ directly on the capacitance and conductance bridge.

The direct current conductivity of the polyamides was determined after the application of 100 volts for one minute, by use of a Leeds and Northrup H.S. type galvanometer.

Results and Discussion

The structural formulas of two typical polyamides appear in Fig. 1. Evidently, the concentration of polar groups may readily be varied with methylene "spacers," as in the polyesters.¹

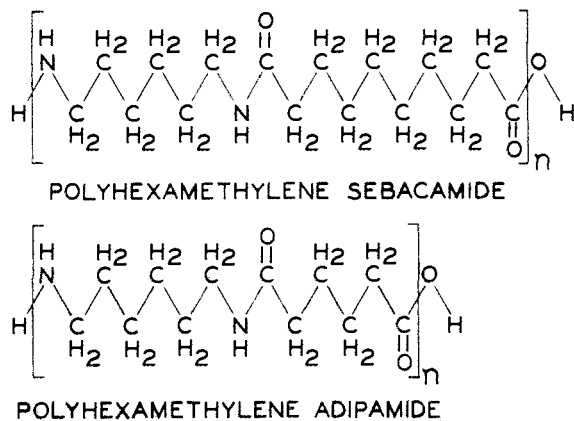


Fig. 1.—Structural formulas of typical linear polyamides.

Likewise, the polar groups in adjacent chains occur in layers,⁴ and their interaction includes hydrogen bonding⁶ as well as dipole and dispersion forces. The presence of a bonding hydrogen profoundly alters the properties of the polymers. The primary valence chains wander in kinked paths through the crystalline and intercrystalline matter,⁴ but in addition a network of secondary forces (hydrogen bonds) obtains. Thus, the interchain forces, and hence the restraints on dipole orientation, should exceed those for the polyesters, as confirmed below. Such predictions of polymer properties from structural formulas have been possible only recently.

Figure 2 shows the dielectric behavior of several polyamides at 25°, with the curves A for polydecamethylene sebacate included for direct com-

parison. Apparently an appreciable orientation polarization contributed by the motion of the polar groups is present in all of the solids. The polyester has the same concentration of polar links in the chain as the polydecamethylene sebacamide of curve C (9 methylene groups per linkage). The polyamide exhibits significant dispersion at room temperature. The restraint of orientation found in the polyesters¹ appears much increased in the polyamides, in accord with their higher melting points and mole cohesion. The sequence of ϵ' values in Fig. 2 also shows expected increased polarization in the polyamides with increasing concentration of polar groups in the chain. Curve C, for polydecamethylene sebacamide, with 9 CH₂ groups per polar linkage is followed by curve B (polyhexamethylene sebacamide) with 7 and Curve E, for polyhexamethylene adipamide, with 5.

Evidently polyhexamethylene adipamide possesses a broad maximum in ϵ'' at room temperature. This breadth and height of maximum indicate a distribution of relaxation times, generally found in solids. The ϵ'' values for the polyamides have been corrected for d. c. conductivity, which, as noted later, is appreciable for these pure compounds.

The ϵ'' curves in Fig. 2 do not follow the order of the ϵ' for increasing values of the ordinates. This is related to an important aspect of the dielectric behavior of linear polymers. The concentration and resultant moments of the polar groups in the chain determine the essential polarity of the polymer, but it has been emphasized that the interaction with neighboring chains chiefly governs the observed loss. The following discussion indicates some factors causing a variation in interaction and hence in loss. In the melts of these polymers, strong dipole association facilitates the formation of the dipole layers observed in the solid. This layering is distorted, however, in the portions of the polymer which are imperfectly or hardly crystalline, and hence the dipole interaction would be expected to vary with the degree of molecular organization present in the solid studied. This degree of order controls considerably many physical properties of the plastics, such as elastic modulus.⁴ Hence, some correlation between physical and mechanical properties and dielectric behavior is a necessary, and observed, consequence of solid structure. The variety of ordered states which may be produced in natural products like

(6) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, Chap. IX.

cellulose derivatives⁷ should likewise be reflected in their dielectric values; the effect is general. Clearly, the dipoles may be disposed differently in adjacent chains either by shifting along the chain, or rotation about its axis. Both of these conditions are present in the non-crystalline regions of linear polymers, as diffraction studies show.^{4,7} If the argument above that the longer relaxation time of the polyamides compared to the polyesters is caused by strong intergroup action, principally hydrogen bonding, is correct, then altered relative positions of the groups should alter the dielectric loss. This is shown by Curves C and D of Fig. 2. Curve C is for annealed polydecamethylene sebacamide, in which the polar groups are as efficiently packed and as extensively hydrogen bonded as the lattice-forming deficiencies of long chains permit.⁷ The sample of curve D, however, was the same polyamide rapidly quenched from the melt. It contains relatively few crystallites, and the chain segments are rotated so that the hydrogen bonds are, on the average, less efficiently directed and formed than in the annealed compound. They resemble the hydrogen bonding in a liquid rather than in a well-ordered solid. Still, they are strong enough to stabilize the chains in their disordered configurations of higher free energy (compared to the crystal) for long periods, as shown by the rate of crystallization of polyamides in the solid state.⁴ However, the reduced forces in the quenched material permit augmented though still hindered dipole freedom, and hence curve D lies clearly above curve C, for ϵ' and ϵ'' . These differences were caused not by a change in the composition of the chains, but only in their *relative positions*.

The structural variations possible in condensation polymers allow another test of the hypothesis that interaction is modified by relative positions and hydrogen bonding of amido links. If a polyamide is prepared by the intercondensation of two different dibasic acids and two different diamines, say in equimolar ratios, some of the polar groups will associate as usual, but, along a chain, the "repeating units" are quite random in composition, so that many of the dipole groups in

(7) W. O. Baker, C. S. Fuller and N. R. Pape, *THIS JOURNAL*, **64**, 776 (1942).

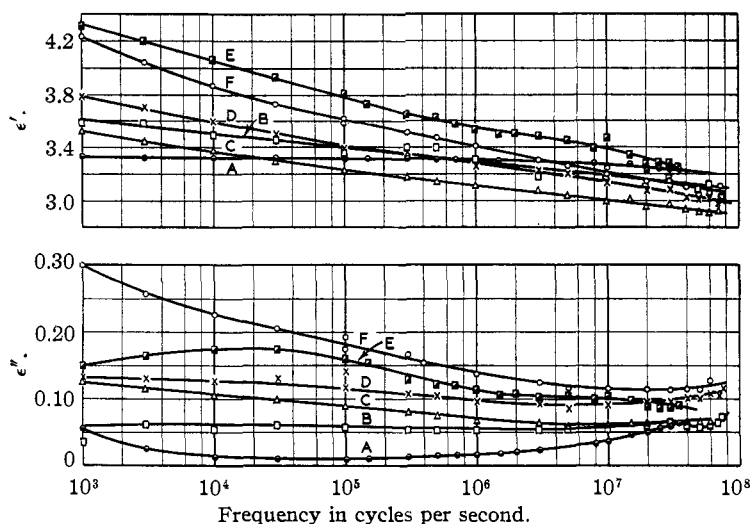


Fig. 2.—Frequency variation of dielectric constant, ϵ' , and loss, ϵ'' , of polyamides at 25°C: A, polydecamethylene sebacate; B, polyhexamethylene sebacamide; C, polydecamethylene sebacamide, annealed; D, polydecamethylene sebacamide, quenched; E, polyhexamethylene adipamide; F, polyhexamethylene-decamethylene adipamide-sebacamide.

adjacent chains will be unable to coincide to form a layer, and will be found surrounded by the hydrocarbon portions of the molecules.^{7a} The compound of curve F was thus obtained from hexamethylenediamine, decamethylenediamine, adipic acid and sebacic acid.⁸ Its average polar group concentration is one per 7 methylene groups, so that it should compare with curve B, yet it shows markedly increased dielectric constant and loss. The average composition of the copolyamide chains is the same as that of polyhexamethylene sebacamide, but the irregular spacing between linkages in the molecule reduces the hydrogen bonding and other interaction in the solid so that ϵ' and ϵ'' are much enhanced. This is further emphatic indication that the chains do not act as units, but that each individual dipole is sensitive to its own environment. Also, the intrachain coupling would be little different in the copolyamides than in the normal polyamides, so seemingly the interchain action alters the dielectric properties. The effect of these changes in interaction in the quenched and co-polyamides on the distribution of relaxation times in the polymer alone forms an extensive study.

The orientation of polar groups is probably not the sole source of high polarization in polyamides, especially at elevated temperatures. A new mechanism which we associate with the isomerism of the amido linkage seems necessary to explain the

(7a) W. O. Baker and C. S. Fuller, "Conference on Physics of the Solid State," N. Y. Academy of Sciences, February, 1942.

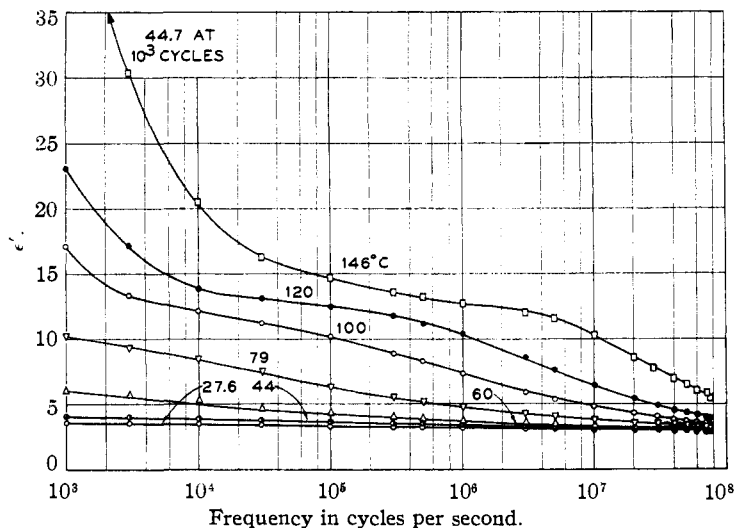
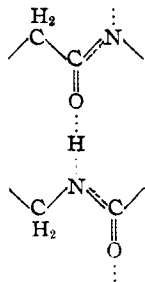


Fig. 3.—Frequency variation of ϵ' of polyhexamethylene sebacamide, 27.6 to 146°.

succeeding results, as in Figs. 3 and 4, for polyhexamethylene sebacamide, which are typical of the series. Some representative values are also given in Table I. At 1 kc. ϵ' has a value at 146° (70° below the melting or softening point of the polymer) of about 48, and ϵ'' is about 27. In addition, as is seen from its temperature variation in Fig. 7, there is a relatively high d. c. conductivity in the compound. The galvanometer behavior indicated that this was not from a space charge. These compounds are likewise free from ionic impurities, as determined by ashing, extraction and quantitative analysis.

The isomerism of the amido linkage has been chiefly considered in the structure of polypeptides and proteins. Hydrogen bonding is important in the molecular configuration of these compounds.⁸ A group of the type shown here probably occurs



(8) For a review and discussion see W. T. Astbury, *Trans. Faraday Soc.*, **36**, 871 (1940).

within and between folded polypeptide molecules,^{8a} and between the polyamide molecules here treated. Huggins⁹ has proposed that the hydrogen in the bridge is virtually ionic. At least one may regard it as in one of two potential minima, one provided by the oxygen and the other by its "own" nitrogen. These two minima are separated by a hump, over which charged hydrogens with requisite energy may oscillate.¹⁰ The dielectric results are consistent with a concept embodying mobile, charged atoms which can contribute an atomic polarization and anomalous dispersion by moving translationally (vibrationally) from one potential minimum to another in the dipole layers. This motion should be strongly temperature-depend-

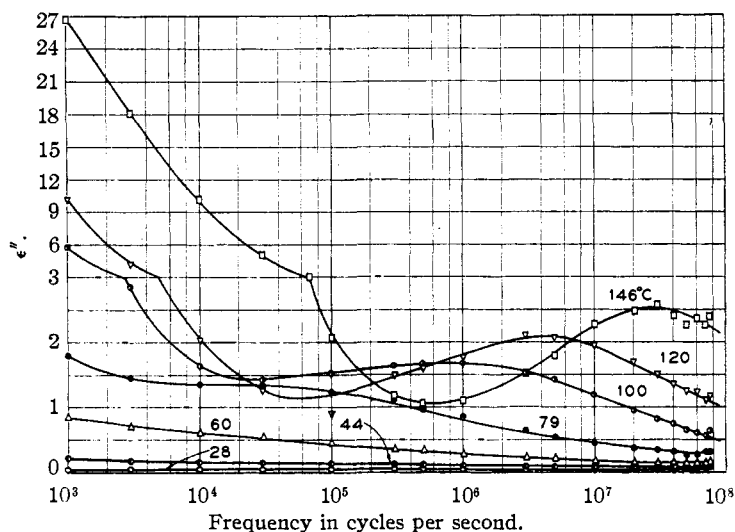


Fig. 4.—Frequency variation of ϵ'' of polyhexamethylene sebacamide 27.6 to 146°.

ent, which is supported by the data of Figs. 3, 4 and 5. The high frequency ϵ'' maxima of Fig. 4 represent a second mechanism and seemingly correspond to the maxima observed at lower temperatures for the polyesters. They occur at elevated temperatures presumably because the oscillations of, say, the carbonyl groups are inhibited by hydrogen bridges of the sort shown in the diagram above. From curve A of Fig. 6, obtained as noted before for the polyester¹ (curve B), $E =$

(8a) Frank, *Nature*, **138**, 242 (1936).

(9) M. L. Huggins, *J. Org. Chem.*, **1**, 407 (1937).

(10) This idea was forwarded by M. L. Huggins in a discussion in April, 1939.

TABLE I
DIELECTRIC PROPERTIES OF POLYHEXAMETHYLENE SEBAC-AMIDE

$\times 10^{-6}$	$\epsilon' = 27.6^\circ$		$\epsilon' = 79.0^\circ$		$\epsilon' = 146.0^\circ$	
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
75	3.0	0.072	3.49	0.324	5.45	2.39
70	2.93	.065	3.38	.313	5.78	2.26
60	3.12	.060	3.46	.283	6.06	2.35
50	3.09	.058	3.47	.270	6.54	2.27
40	3.12	.061	3.55	.312	6.96	2.40
30	3.17	.063	3.62	.328	7.61	2.56
20	3.13	.061	3.68	.380	8.65	2.47
10	3.19	.057	3.80	.442	10.31	2.27
5	3.28	.055	4.11	.541	11.55	1.79
3	3.19	.053	4.37	.649	12.03	1.51
1	3.31	.052	4.76	.866	12.74	1.10
0.5	3.40	.054	5.18	.964	13.12	1.07
.3	3.40	.054	5.55	1.11	13.52	1.18
.1	3.42	.060	6.32	1.24	14.80	2.07
.03	3.46	.062	7.74	1.33	16.26	5.14
.01	3.50	.056	8.46	1.35	20.44	10.23
.003	3.58	.062	9.35	1.46	30.40	18.12
.001	3.59	...	10.24	1.80	47.66	26.6

23,300 cal. per mole of polyamide polar unit, nearly twice the polyester value of 12,100.

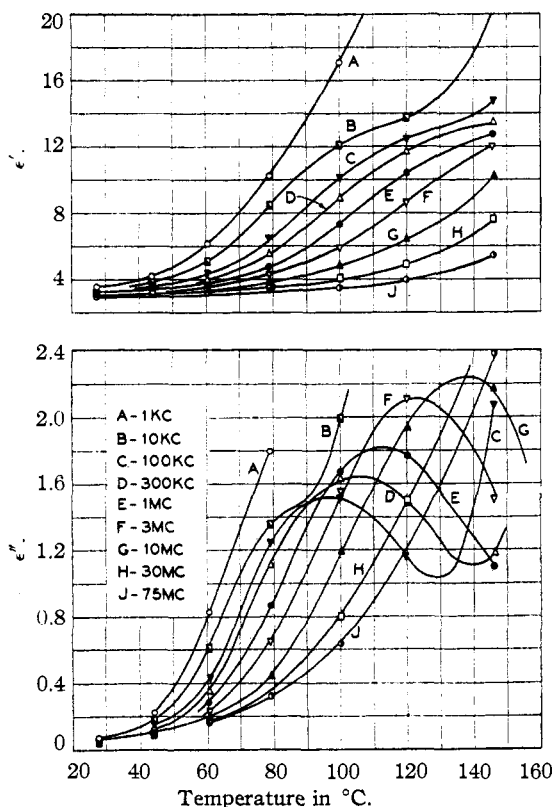


Fig. 5.—Temperature variation of ϵ' and ϵ'' of polyhexamethylene sebacamide, 1 kc. to 75 mc.

Further, the activation process apparently produces another sort of enhanced freedom for the

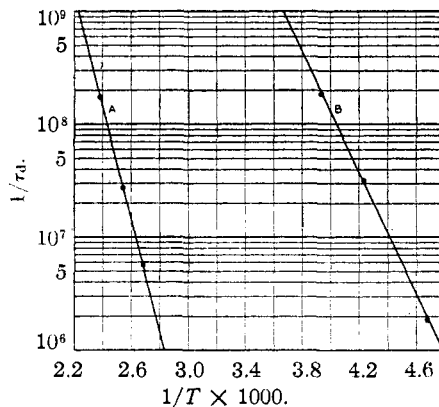


Fig. 6.—Temperature dependence of the relaxation time of the dielectric, τ_d , for polyhexamethylene sebacamide (curve A) and polyethylene sebacate (curve B).

bridge hydrogen. It may pass over to one or the other of the positions near the O or N but possibly it can also acquire even more freedom and act like a migrant ion over very short distances, thus causing the high d. c. conductance. The temperature coefficient of this conductance appears in Fig. 7,

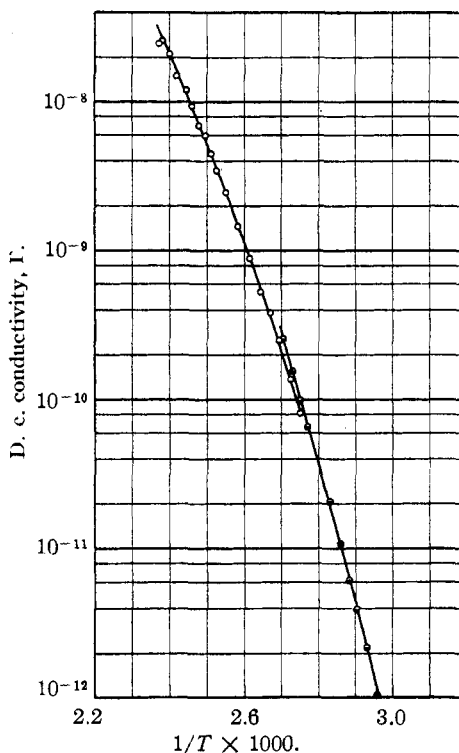


Fig. 7.—Temperature dependence of the d. c. conductivity, Γ , of polyhexamethylene sebacamide.

and corresponds to an activation energy of 29,700 cal. per mole of conducting particle. This value is several fold the dissociation energy for a hydro-

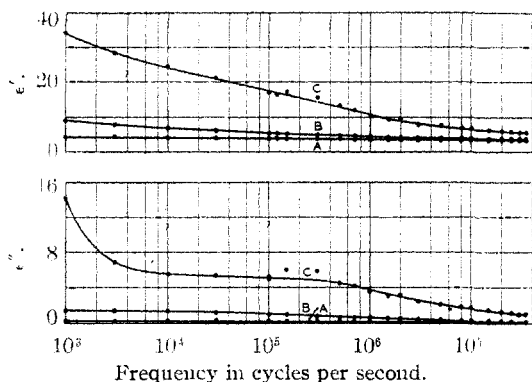


Fig. 8.—Effect of sorbed water on frequency dependence of ϵ' and ϵ'' of polyhexamethylene adipamide at 25°: dry (curves A), 60% R. H. (curves B) and 100% R. H. (curves C).

gen bond,¹¹ and may well reflect the energy necessary to liberate charged hydrogens from restraining negative force fields around a given N or O atom. It is less than half the energy of the N—H bond, but one would expect this link to be perturbed and weakened by the hydrogen bridges in the solid polyamides and by its adjacent carbonyl. (It should be emphasized that the atomic or nuclei motion cannot contribute, however, to the resonance in the amide linkage.) The d. c. conductance and low frequency loss may thus represent different degrees of the same sort of hydrogen motion. They are not to be regarded as measuring very different phenomena. The low frequency loss may not exhibit a maximum. Molten polyamides and the solids at higher temperatures thus are apparently semi-conducting materials.

It is a striking contrast that the relaxation time of the dielectric is 5×10^{-9} sec. for polyethylene sebacate at -19° and for polyhexamethylene sebacamide at 146° . This large difference may be regarded chiefly as a consequence of the effect of molecular structure on the solid state. The isolated molecules would show no such different kinetic characteristics, nor would they be expected to show diverse intrachain coupling. On the other hand, the polyester melts at 74° , the polyamide at 215° ; a 141° interval emphasizes the different forces. The relaxation times reflect thermal motion present in the polymers irrespective of the applied field, and hence are related to the elastic and plastic properties of the solids.

The explanation of hydrogen bridging and charged hydrogen motion in these bridges as the source of the extraordinary dielectric properties of

typical linear polyamides suggests that strong hydrogen bonding agents added to the polymers at ordinary temperatures should produce the same effect as elevated temperatures alone. This is confirmed in Fig. 8 for water, whose sorption is of technical importance. Curves A were obtained from polyhexamethylene adipamide dried two weeks over calcium chloride, curves B, for the substance equilibrated (fifty-six days) at 60% relative humidity, and curves C, after immersion in distilled water, all at 25°. Evidently the combination of bound water (about 10% for saturation at room temperature) and the amido groups causes a high dielectric constant and appreciable dispersion. ϵ'' is again corrected for d. c. conductance. Water may be here considered as a loosening (plasticizing) or pseudo-ionizing medium, which substitutes for intermolecular polyamide bonds, and facilitates motion of the whole system.¹ Thus, if the dielectric results are admitted to show enhanced interchain motion directly, the mechanism discussed above could apply to the dependence on pH and degree of swelling of the physical properties of polypeptides and proteins. For example, the molecular motion in muscular contraction would be controlled by the degree of interchain force reduction, and hydrogen bonding suppression, as indicated by many other researches. The present results also cause inquiry of how much wandering of hydrogen atoms among peptide linkages, and hence energy exchange, occurs in proteins swollen or thermally agitated. This latter is related to the hypothesis of energy transfer recently proposed by Szent-Györgyi.¹²

We are grateful to Dr. B. S. Biggs and Mr. W. S. Bishop for providing certain of the polyamides studied.

Summary

The dielectric constant and loss have been determined over a 120° temperature interval and over the frequency range 1 kc. to 75 mc. for typical linear polyamides. All of the polymers evidenced dipole orientation accompanied by anomalous dispersion, even at room temperature. The magnitudes of ϵ' and ϵ'' rise with the polar group concentration in the long molecules, but are sharply modified by the interaction between groups in adjacent molecules. The interaction was varied by reducing the crystallinity by quenching, and by forming co-polymers in which the polar groups

(11) See review in J. J. Fox and A. E. Martin, *Trans. Faraday Soc.*, **36**, 897 (1940).

(12) Szent-Györgyi, *Nature*, **148**, 157 (1941); see also London, *J. Phys. Chem.*, **46**, 305 (1942).

were displaced from their usual layer structure. Reduced interaction always caused enhanced polarization.

The dielectric properties of the polyamides show steep temperature coefficients; at 146°, 70° below its melting point, polyhexamethylene sebacamide has $\epsilon' \sim 48$, $\epsilon'' \sim 27$, at 1 kc. This compound also has a high frequency absorption as-

sociated with a relaxation process of activation energy 23.3 kcal. per mole, about twice the value for the analogous polyesters. Further, the polyamides show a high d. c. conductivity at elevated temperatures, which may be caused by mobile, charged atoms, such as hydrogen, resulting from isomerism in the amido linkage.

MURRAY HILL, NEW JERSEY RECEIVED JANUARY 6, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Dropping Mercury Electrode in Acetic Acid. II. Electrocapillary Curves and the Theory of Maxima^{1,2}

BY G. BRYANT BACHMAN AND MELVIN J. ASTLE³

In a preceding paper⁴ it was shown that ions and molecules with low polarographic reduction potentials give discontinuous current-voltage curves in acetic acid solutions. In the present investigation this phenomenon has been related to the adsorption processes occurring on the drop through a study of electrocapillary curves.

Discontinuities in anhydrous acetic acid are fundamentally the same phenomena as maxima in water systems. They differ in that they seem to be limited to substances of rather low reduction potential. Since the occurrences of maxima in aqueous solutions have been associated with the adsorption of ions and molecules on the mercury drop, it is reasonable to assume that a similar association exists in acetic acid solutions. A convenient method of studying adsorption on charged mercury surfaces is through the medium of electrocapillary curves.

The electrocapillary curve for ammonium acetate in anhydrous acetic acid shows a marked difference from the same curve in water in that the top of the curve is broad and rather flat and two maxima instead of one are present. Double maxima are very uncommon in water although Kemula and Beer⁵ observed them in some cases using the dynamic drop weight method. Addition of water causes the two maxima in acetic acid to approach each other and to blend into one

well-defined maximum at 50 mole per cent. water (Fig. 1).

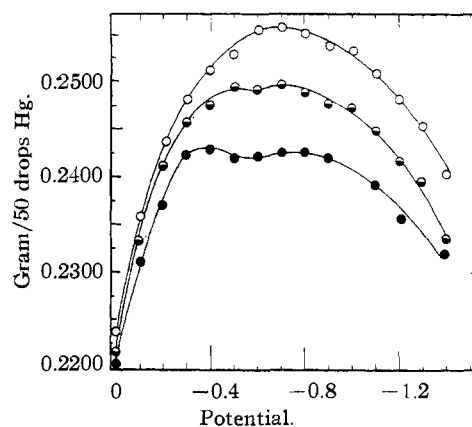


Fig. 1.—The effect of solvent composition on the electrocapillary curve for mercury in ammonium acetate solutions: ●, 0.25 *M* NH₄OAc in acetic acid; ◐, 0.25 *M* NH₄OAc in acetic acid and water (35 mole %); ○, 0.25 *M* NH₄OAc in acetic acid and water (50 mole %).

When salts are added to a solution of ammonium acetate in acetic acid, the effect on the electrocapillary curve depends on the reduction potential of the cation of the salt. If the cation has a half-wave reduction potential more negative than the *first* electrocapillary maximum for solutions of ammonium acetate in acetic acid (about -0.3 volt) then the resulting curves have the same general shape as the electrocapillary curve for ammonium acetate alone. Such cations are designated as Class I cations and include Zn⁺⁺, Pb⁺⁺, Cd⁺⁺, Co⁺⁺, Sb⁺⁺⁺, Ni⁺⁺, Cr⁺⁺⁺ and Bi⁺⁺⁺. Figure 2 shows typical curves of this sort for Zn⁺⁺ together with the corresponding current-

(1) Presented before the Physical and Inorganic Section at the Atlantic City meeting of the American Chemical Society, September 8-12, 1941.

(2) From the Ph.D. thesis of Melvin J. Astle.

(3) Present address: University of Kentucky, Lexington, Kentucky.

(4) Bachman and Astle, *THIS JOURNAL*, **64**, 1303 (1942).

(5) W. Kemula and E. Beer, *Roczniki Chem.*, **16**, 259 (1936).