Analysis of Reaction Products in the Ester Preparations.—In order to determine the composition of the esters produced in various conversions of the butenyl chlorides to acetates, runs were made using in each case, unless otherwise specified, 250 ml. of solution approximately 1 N in chloride and acetate. Final analysis of the esters with an accuracy of 2 or 3% was accomplished by distillation through a three-foot Podbielniak type column. The results are summarized in Table VI.

Reaction of Potassium and Diphenylguanidinium Acetates with the Butenyl Chlorides in Acetic Acid.—The reaction mixtures of dry base, dry acetic acid and butenyl chloride were held at 78.6° for the desired interval and then poured into ice-water. The acid was carefully neutralized with concentrated sodium hydroxide and the ester was extracted with ether. After being dried over potassium carbonate, the extracts were distilled. A blank experiment was carried out on methylvinylcarbinyl acetate which showed that the ester remained unchanged under the conditions of the experiment.

Reaction of Crotyl Chloride with Potassium Acetate in Acetic Anhydride.—A mixture of 25 ml. of crotyl chloride and 28 g. of dry potassium acetate and 300 ml. of fractionated acetic anhydride (b. p. 139.0–139.1°) was heated on a water-bath under reflux with efficient stirring. After the heating period, the mixture was quite dark. The volatile material was distilled (25–40°) at reduced pressure, the distillate was poured onto crushed ice and the mixture was allowed to stand for an hour to hydrolyze the anhydride. The resulting solution was neutralized and treated as in the previous case. On distillation of the ester, there was no evidence of secondary acetate.

Reaction of Methylvinylcarbinyl Chloride with Tetraethylammonium Acetate in Acetone.—A mixture of 41 g. of tetraethylammonium acetate prepared from the directions of Steigman and Hammett,[17] 20 ml. of the butenyl chloride and 200 ml. of dried and fractionated Merck C. P. acetone was boiled under reflux. After heating, the volatile material was distilled from salts at reduced pressure, the receiver being cooled with a dry-ice-bath. The distillate was then fractionated. There was no evidence of any crotyl acetate in the product.

Reaction of Silver Acetate with the Butenyl Chlorides in Acetic Acid.—A mixture of 45 g. of silver acetate which had been recrystallized from water and dried over sulfuric acid for three days, 25 ml. of butenyl halide and 250 ml. of dry acetic acid was stirred at room temperature. At the end of the reaction period, excess sodium chloride was added, the mixture was filtered and the filtrate was treated as in the case of the runs with potassium acetate in acetic acid.

Summary

The kinetics of conversion of crotyl and methylvinylcarbinyl chlorides to ethyl ethers and acetates and the compositions of the products of the conversions have been studied. The compositions of the products can be well accounted for on the basis that bimolecular replacement of the chloride group by an ethoxide or acetate ion gives rise only to normal product while solvolytic or S_N1 type reaction gives rise to a mixture of allylic isomers.

By choosing conditions unfavorable for the S_N1 type of reaction, it is possible to convert the butenyl halides to the corresponding pure acetates or ethyl ethers.

The Relation of Dielectric Properties to Structure of Crystalline Polymers. I. Polyesters

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

The interpretation of dielectric properties in terms of molecular structure[1,2] may be attempted for assembles of macromolecules when knowledge of polymer constitution and structure permits recognition of polar groups and of their relative disposition. The following factors have been considered in the succeeding report of the dielectric behavior of linear polyesters.

The most probable source of orientation polarization in solids containing long chain molecules with polar linkages has been attributed to the rotational–vibrational (liberational) motion of atomic groups rather than to the unified displacement of a given molecule.[3,4] Of course, potentials inhibiting rotation around most single bonds, especially the carbon–carbon bond,[5] prevent complete independence of the motion of polar groups from the size and form of their attached chains.

Also, in polymers, the loss component, ϵ'', of the dielectric constant generally deviates from the value it should have at an absorption maximum on the Debye theory for a single relaxation time.[6,7]

(1) P. Debye, "Polar Molecules," Chemical Catalog Co., New York, N. Y., 1929.

(2) C. P. Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, N. Y., 1931.

(3) W. A. Yager, *Trans. Electrochem. Soc.*, **74**, 113 (1938).

(4) W. O. Baker and C. P. Smyth, THIS JOURNAL, **60**, 1229 (1938).

(5) See C. Gorin, J. Walter and H. J. Eyring, *ibid.*, **61**, 1876 (1939), and references therein.

(6) W. A. Yager, *Physics*, **7**, 434 (1936).

(7) R. M. Fuoss and J. G. Kirkwood, THIS JOURNAL, **63**, 385 (1941).

In polymer chains, the dipoles do not exhibit Brownian motion along three axes but rather primarily an intrachain kinking.[8] An internal viscosity related to macroscopic plasticity,[9] brittleness and softening has been postulated to cause the absorption. Specific rate constants from the relaxation times can be employed in an absolute rate analysis of the temperature variation of loss. Such treatment, suggested by Eyring,[10] was developed by Frank,[11] and gave a precise correlation in simple alkyl halides with structure and with viscous flow,[12] from which dipole orientation seems to differ considerably in extent of motion.

The linear supercondensation polyesters[13] and polyamides[14] possess many of the desired qualities of model polymers for dielectric studies. These polymers have simple polar groups (ester or amide linkages) regularly spaced along hydrocarbon chains. This intrachain spacing is readily varied, in forming the polymers, by selecting dibasic acids, glycols and diamines of appropriate chain lengths. Thus the effect of articulation or coupling of the orienting units along a given chain may be detected. This variation likewise alters the number of dipoles per cc. and is thus useful in studying the volume polarization. Further, these polymers are generally highly crystalline, and diffraction studies have revealed the relative arrangement of the polar groups in adjacent chains, and whether the dipoles are surrounded by other dipoles or by hydrocarbon groups.[15] The interchain forces constraining dipole motion may be specifically explored by comparing polyesters and polyamides of the same concentration of polar groups per unit of chain length, since the hydrogen bonding from the amido link causes a twofold increase in attraction as estimated from fusion properties. The average chain lengths of the polymers may be determined accurately.[16] Finally, the polymers are prepared essentially chemically pure and of high stability, and the effect of any

technically important contaminant such as water may be ascertained and interpreted.

Experimental

Materials.—The seven polyesters were prepared by Mr. C. J. Frosch and Mr. W. S. Bishop of these Laboratories. Procedures similar to those of Carothers[13] were employed. The products were unfractionated and therefore contained the distribution of molecular weights calculated for a random reaction of end groups,[17] and found experimentally.[16] The molecular weights lay in general in the "superpolyester" range, above M_w ~6000. The products were free from all oxidation or similar degradation. Their high crystallinity and consequent sharp melting points permitted preparation of test discs of precise and constant geometry. The polyesters were melted in vacuum, thus freed of gas bubbles, and allowed to solidify slowly, between glass plates held apart by shims. The thickness of individual samples was quite uniform, and was determined by numerous micrometer readings. Among the discs, the average thickness varied from 40 to 60 mils. Decamethylene oxalate cracked badly on cooling, so that the dielectric results may be complicated by the presence of voids. All of the samples were annealed to states of maximum crystallinity,[18] and were thoroughly dried.

Dielectric Measurements.—For the frequency range 1 to 100 kc., the dielectric constant and equivalent parallel conductance were measured on a shielded conductance–capacitance bridge.[19] Precise and reproducible contact with the electrodes was obtained in a condenser cell described below in connection with the Q-meter, on which measurements from 100 kc. to 75 megacycles were made.

The type 100A Q-meter,[20] the test cell, measuring technique and corrections described in a previous paper[3] were employed for the measurements on the polyesters. All other measurements were made on the much improved type 160A Q-meter employing a new type test condenser and a special thermostat.

The measuring technique previously described[3] is unsatisfactory for measurements above or below room temperature since it requires removal of the test sample from the test condenser at each frequency. The only alternative is to leave the sample in place, tune the LC circuit with the test condenser connected, disconnect the test condenser and retune the circuit with the internal tuning condenser. This method is less desirable than the former because corrections must be applied at high frequencies for the differences in lead inductance and series resistance of the internal tuning and test condensers in computing the capacity

(8) W. Kuhn, Z. physik. Chem., **A161**, 1, 247 (1932); *Kolloid Z.*, **68**, 2 (1934); **76**, 258 (1936).

(9) J. M. Davies, R. F. Miller and W. F. Busse, THIS JOURNAL, **63**, 361 (1941).

(10) A. E. Stearn and H. Eyring, *J. Chem. Phys.*, **5**, 113 (1937).

(11) F. C. Frank, *Trans. Faraday Soc.*, **32**, 1634 (1936).

(12) W. O. Baker and C. P. Smyth, *J. Chem. Phys.*, **7**, 574 (1939).

(13) W. H. Carothers and J. W. Hill, THIS JOURNAL, **54**, 1559 (1932).

(14) W. H. Carothers and J. W. Hill, *ibid.*, **54**, 1566 (1932); W. H. Carothers, U. S. Patents 2,071,250 (1937) and 2,130,523 (1938).

(15) C. S. Fuller, *Chem. Rev.*, **26**, 143 (1940).

(16) W. O. Baker, C. S. Fuller and J. H. Heiss, Jr., THIS JOURNAL, **63**, 2142 (1941).

(17) P. J. Flory, *ibid.*, **58**, 1877 (1936).

(18) C. S. Fuller, W. O. Baker and N. R. Pape, *ibid.*, **62**, 3275 (1940).

(19) W. J. Shackelton and J. O. Ferguson, *Bell System Tech. J.*, **7**, 70 (1928).

(20) The construction, theory and operation of the Q-meter are described in a manual furnished by the manufacturer, Boonton Radio Corporation, Boonton, New Jersey. The type 100A Q-meter is now superseded by the type 160A, which is a much improved model and covers the frequency range from 50 kc. to 75 mc.

and loss of the test specimen. The capacity of the sample is given by

$$C_x = \frac{C_1 - C_2}{D + B(C_1 - C_2)} - C_f$$

where $D = (1 - \omega^2 L_1 C_1)^2$ and $B = (L_2 + L_1(1 - \omega^2 L_1 C_1))\omega^2$. C_2 and C_1 denote the capacity of the internal tuning condenser at resonance with the test condenser connected and disconnected, respectively. C_f is the fixed capacity of the test condenser. L_1 and L_2 represent the series inductance of the internal tuning condenser and test condenser, respectively. For the arrangement employed L_1 is 0.00148 μH and L_2 is 0.03 μH. The dielectric loss factor, ϵ'', is given by the equation

$$\epsilon'' = \frac{IZ C_{oe} A^2}{C_a} \left[\frac{E_1 - E_2}{E_1 E_2} - F_M \right]$$

IZ, the voltage impressed on the measuring circuit, was determined experimentally at each test frequency, and a calibration employed for subsequent tests. C_{oe}, the effective capacity necessary to resonate a given coil at a given frequency, is obtained from the relation

$$C_{oe} = C_1/1 - \omega^2 L_1 C_1$$

Furthermore, $A = 1 - \omega^2 L_2(C_x + C_f)$. E_2 and E_1 represent the readings of the Q-voltmeter in volts at resonance with the test condenser connected and disconnected, respectively. F_M is a factor to correct for series resistance as noted above. It is negligible at frequencies below 10 mc. but increases rapidly with increasing frequency and magnitude of the test capacity. Calibration curves were prepared for F_M versus frequency and C_x at room temperature employing the test condenser as a variable air condenser. Although F_M

was found to vary somewhat with temperature, this variation was erratic and of a second order so that the room temperature calibration was employed at all temperatures.

A complete description of the new test condenser and thermostat is omitted for brevity. The test condenser of gold-plated brass was designed so that it may be used either as a clamping condenser for a specimen or as a variable air condenser. The electrodes are 2 inches in diameter, with the variable electrode an integral part of the housing which is connected to ground. The high tension electrode is fixed and insulated from the housing by means of clear, fused quartz. Since it is desirable to minimize the lead inductance of the test condenser, the coaxial type of construction was employed. The high tension lead was brought out through a coaxial tube $^3/_8''$ in diameter and $4''$ long. A coaxial jack was mounted directly over the high tension terminal on the Q-meter and was designed so that the test condenser could be connected or disconnected from the measuring circuit simply by screwing it in or out of the coaxial jack.

Thermostating a test condenser in such close proximity to the Q-meter presented some difficulty. The design finally adopted consists essentially of a metal cylindrical jacket fitted at one end with a heating and cooling chamber and constructed so that it will slide over the test condenser. A small ring heater is employed for heating and provision is made for siphoning liquid nitrogen into the cooling chamber. An air thermo-regulator serves for temperature control. This metal thermostat with the test condenser in place fits into a Dewar flask with an opening in the bottom large enough to permit the coaxial tube of the test condenser to pass through. The entire assembly is mounted on top of the Q-meter directly over the coaxial jack and lined up so that the test condenser can be screwed in and out of the jack. The test condenser is screwed out of the jack and kept in a raised position at all times except during a measurement so as to minimize heat exchange between the Q-meter and test condenser.

The d. c. conductivity was negligibly small for all samples.

Results and Discussion

Figure 1 illustrates the planar zigzag chains which comprise most linear polyesters. Only certain types have been shown; for instance, polyethylene azelate represents an odd-membered dibasic acid which results in the two carbonyl dipoles of a chemical repeating unit being parallel, and evidently this same structure could easily be arranged in other polyesters. Chain oscillations continuously distort instantaneously the planarity of the carbon skeleton. Since such motion normal to the chain axis generally requires twisting about valence bonds, the modes contributing the orientational polarization from the models of Fig. 1 will not be uniformly distributed along the chains, for the potentials hindering rotation about bonds

POLYETHYLENE SEBACATE

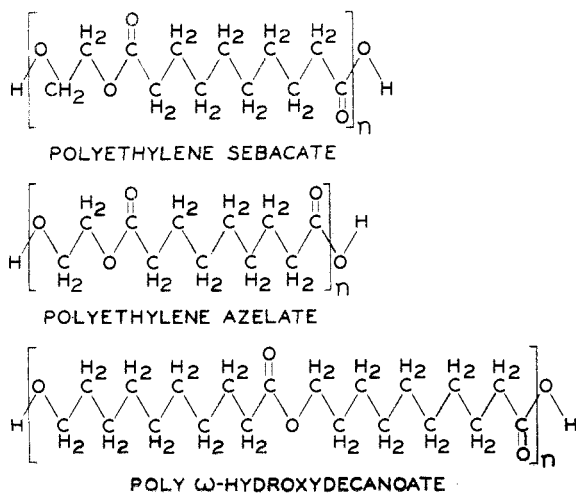POLYETHYLENE AZELATE

POLY ω-HYDROXYDECANOATE

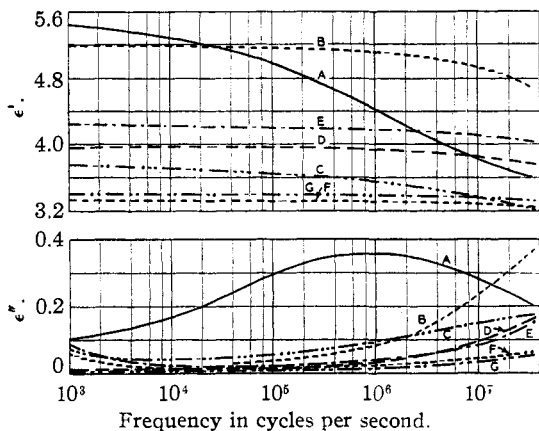Fig. 1.—Structural formulas of typical polyesters.

Fig. 2.—Frequency variation of dielectric constant and loss factor of polyesters at 25°: A, polyethylene succinate; B, polyethylene adipate; C, polydecamethylene oxalate; D, polyethylene azelate; E, polyethylene sebacate; F, polydecamethylene sebacate; G, poly-ω-hydroxydecanoate.

at the polar groups probably are lower than for the CH_2–CH_2 bonds.[21] However, the CH_2–O bond may have a high potential.[22] Small segments of the chains may act as relatively stiff units bounded by more flexible linkages. That such chain flexibility does obtain is clearly indicated by the data of Fig. 2, in which the values of ϵ' for such structures as polyethylene sebacate (see Fig. 1) considerably exceed the square of the refractive index, yet successive dipoles along the chain are oppositely directed and should cancel if the whole molecule is rigid. If only the terminal groups on the chains move in the applied field, the static dielectric constant would be virtually independent of the concentration of polar groups in the compound. This is contrary to experimental results, as will appear below. Pelmore and Simons[23] examined this aspect of five linear polyesters containing both opposite and parallel dipoles, as diagrammed in Fig. 1, and likewise concluded from the relaxation times that polar chain segments must be acting.

Although discussion of the effect of polar group concentration would be preferred in terms of specific polarization, there is yet no local field equation adequate for such anisotropic and highly interacting solids.[24] Hence we use simply the static dielectric constant, ϵ'_0. The concentrations are computed as follows.

(21) S. C. Schumann and J. G. Aston, *J. Chem. Phys.*, **6**, 485 (1938).

(22) B. Crawford and Joyce, *ibid.*, **7**, 307 (1939).

(23) D. R. Pelmore and E. L. Simons, *Proc. Roy. Soc.* (London), **A175**, 468 (1940).

(24) J. H. Van Vleck, "Dielectrics" (Annals N. Y. Academy of Sciences **40**, Art. 5), 289 (1940), and other discussions therein.

Let

n_1 = number of —CH_2— groups of molecular weight M_1. per cc.

n_2 = number of polar (ester) linkages of molecular weight M_2, per cc.

ρ = density of the polymer

b = ratio of number of CH_2 to O—C— groups per chemical repeating unit

$$n_1 = bn_2 \qquad (1)$$

N = Avogadro's number

Then

$$\rho = (n_1 M_1 + n_2 M_2)/N \qquad (2)$$

The experimental values of these quantities appear in Table I. The densities at 25° were from weighing and displacement of a known volume of inert liquid by the solid polymer. Polyethylene is included to represent the limiting case of all —CH_2— and no polar groups.

TABLE I

Compound	ρ, 25°	$n_1 \times 10^{-22}$	$n_2 \times 10^{-22}$	ϵ'_0
Polyethylene	0.924	4.00	0	2.33
ω-Hydroxypolydecanoate	1.064	3.41	0.38	3.40
Polydecamethylene sebacate	1.086	3.48	.39	3.32
Polydecamethylene oxalate	1.130	3.00	.60	3.70
Polyethylene sebacate	1.148	3.05	.61	4.20
Polyethylene azelate	1.172	2.99	.66	3.96
Polyethylene adipate	1.250	2.64	.88	5.16
Polyethylene succinate	1.358	2.29	1.14	5.60

Relations from Table I appear graphically in Fig. 3. The density of the solids increases linearly with the concentration of polar groups. However,

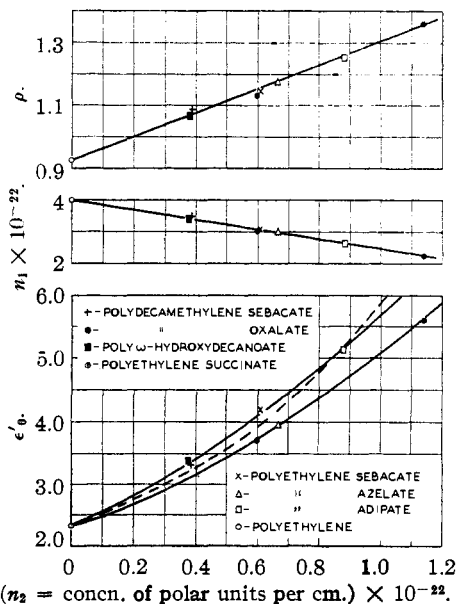(n_2 = concn. of polar units per cm.) $\times 10^{-22}$.

Fig. 3.—Dependence of static dielectric constant and density on concentration of polar groups in polyesters.

this increase in density is actually greater than is caused by the heavier —O—CO— units in the chain. This can be shown by simple calculation, and emphasizes the considerable contribution of the dipole forces to the lattice energy. The proportionality of n_1 to n_2 in agreement with the ratio of the polar to methylene groups *along* the chains agrees with the idea of regular packing in the series. The increase of ϵ'_0, the static dielectric constant, with n_2, shown in the lower curves of Fig. 3, emphasizes the comparative independence along the chain of librating polar groups.

The dashed curve on Fig. 3 is the value ϵ'_0 would have if the orientation polarization calculated from the equation of Debye for non-interacting dipoles agitated by ordinary Brownian movement, with local fields described by the Lorentz equation, were directly proportional to n_2. However, certainly the above conditions are poor approximations for linear macromolecules in the solid. Hence, we shall not at present discuss the specific polarization, despite the advantages of the Onsager field equation.[25] Also, recent treatments[26] of the internal Brownian motion in randomly-kinked chains[8] require modification for partially crystalline systems, in which considerable sections of the chains are extended in the lattice. In dilute solutions of many chain polymers assignment of effective group moments is less uncertain. There is agreement on highly convolved chains, in which the individual dipoles have almost complete freedom. Further, the molecular dipole moment appears to vary with the square root of the molecular weight.[27-31] The studies of Wyman and Bridgman on the self-polyesters of ω-OH-decanoic acid are especially relevant here, since they concluded that there was nearly complete freedom of group orientation in solutions. Evidence of large interaction (rather than intrachain restraint) reducing the freedom of the dipoles in the solid polymers arises from the two-fold higher specific polarizations (0.8) of polydecanoates found by Bridgman compared to the values (0.4) we estimate for the solid from approximate field equations.

Since the orientation polarization is reduced in the solid compared to the dissolved state, the smooth rise of ϵ'_0 with n_2 in Fig. 3 suggests a comparable reduction factor in all of the polyesters. This would agree with the structural evidence[15] of layers of dipole vectors either perpendicular to (odd esters) or inclined at another angle (even esters) with the chain axes. The association of these dipoles may control the solid arrangement. In any case, they occur in layers, and seemingly the interaction is largely in these planes rather than between them, so that the spacing of dipoles *along* the chain is not a predominant factor. However, some interaction along the chain appears in two of the points on the lower solid line on the ϵ'_0 curves of Fig. 3. The points on this line for polyethylene succinate and polydecamethylene oxalate show a reduced ϵ'_0, expected from the proximity of the dipoles, especially the carbonyl groups, along a given chain. Presumably because of this closeness, the polyethylene succinate chain does not conform to the usual sort of planar zig-zag configuration,[15] and polydecamethylene oxalate has an unusual cross-sectional packing.[15] The lower ϵ'_0 value for polyethylene azelate is related to another interesting structural change. As noted, the planes containing the polar groups in polyesters having an odd-numbered acid (C_9 for the azelate) are perpendicular to the chain axes. Thus dipoles in adjacent chains come more directly into interaction than when these planes are tilted. Further, the disposition of these resultant dipoles along the chain may actually cause the vertical rather than tilted planes. For in the azelate model of Fig. 1, it is seen that the vector dipoles of the ester groups do not point in the alternately back and forth directions obtaining in the even esters. In the latter, every other dipole along a chain points in the same direction and at the same angle with the chain axis. Thus, the tilted planes containing the carbonyl groups also may be considered to contain rows of "head-to-tail" dipoles. However, in the odd polyesters the vector dipoles all lie on the same side of a given chain. If the chains shifted so that the carbonyl groups in adjacent molecules formed one tilted plane containing "head-to-tail" dipole vectors, the dipoles attached to the other ends of the acid unit (say the azelaic unit) would be uncompensated between chains and would tend to shift the chains back. The vertical form of the odd polyesters with the dipoles shifted neither one way nor the other in adjacent chains probably represents the minimum energy, as indicated by the X-ray

(25) L. Onsager, THIS JOURNAL, **58**, 1486 (1936).

(26) J. G. Kirkwood and R. M. Fuoss, *J. Chem. Phys.*, **9**, 329 (1941).

(27) J. Wyman, *ibid.*, **60**, 328 (1938).

(28) W. B. Bridgman, *ibid.*, **60**, 530 (1938).

(29) I. Sakurada and S. Lee. *Z. physik. Chem.*, **B48**, 245 (1939).

(30) S. Lee, *J. Soc. Chem. Ind.*, Japan, **43**, 190 (1940).

(31) M. Takei and H. Erbring. *Kolloid-Z.*, **94**, 312 (1941).

studies. The same situation occurs for the polydecanoate, and it likewise has the dipole planes perpendicular to the chain axis, in the crystal.

TABLE II

DIELECTRIC PROPERTIES OF POLYETHYLENE SEBACATE

$f \times 10^{-6}$	ϵ' $t = 64.5°$	ϵ''	ϵ' $t = 26.3°$	ϵ''	ϵ' $t = -98.5°$	ϵ''
75	4.03	0.119	3.69	0.305	2.62	0.009
70	4.03	.112	3.60	.298	2.63	.010
60	4.05	.104	3.70	.264	2.70	.010
50	4.03	.094	3.73	.218	2.65	.011
40	4.08	.077	3.80	.203	2.68	.011
30	4.10	.067	3.81	.183	2.72	.015
20	4.08	.053	3.81	.152	2.65	.012
10	4.08	.036	3.87	.115	2.72	.017
5	4.12	.026	3.97	.088	2.59	.010
3	4.13	.020	3.98	.073	2.75	.013
1	4.16	.014	4.01	.051	2.75	.019
0.5	4.15	.010	3.99	.039	2.79	.019
.3	4.17	.008	4.06	.035	2.78	.020
.1	4.16	.005	4.06	.028	2.80	.026
.03	4.13		4.06	.017	2.77	.031
.01	4.15		4.07	.014	2.78	.037
.003	4.15		4.08	.011	2.81	.038
.001	4.13		4.09	.009		

Figure 4 illustrates the frequency dependence of ϵ' and ϵ'' for polyethylene sebacate over a temperature range down to $-98.5°$. Representative data are shown in Table II. As suggested on Fig. 2, absorption maxima occur at the lower temperatures. These are shown as a function of temperature for various frequencies up to 75 mc. in Fig. 5. Wide deviations from the ideal Debye behavior are evident, in agreement with most other polymer systems.[3,7] The ϵ'' vs. ln f peaks are much broader, and max. ϵ'' is lower, than expected from the theory for a single relaxation time. However, the concept of group orientation inhibited by interchain potentials is supported by the temperature studies. For it is apparently possible to eliminate absorption and to reduce ϵ' to little more than the square of the refractive index on reducing the kinetic energy of the groups by cooling. The absorption maxima may be readily shifted along the frequency scale by temperature. As the temperature is lowered, the number of groups possessing the energy requisite for surmounting the barriers opposing libration decreases. This

means that the absolute reaction rate[32] is reduced, and the polar units are finally unable to follow an alternating field. Thus, at a given temperature, the frequency of maximum ϵ'' indicates about the rate constant at which most of the orienting units are able to oscillate over the barriers. Of course, for gases, on the Debye theory the frequency of maximum absorption equals $1/\tau'$, where τ' is the relaxation time for the dipoles, but in a liquid or solid a given dipole interacts on the surrounding matter to produce an additional polarization so that the relaxation time of the medium, τ, obtains. The familiar expression

$$\tau = \tau' [(\epsilon_0 + 2)/(\epsilon_\infty + 2)] \qquad (3)$$

relates these two relaxation times, where ϵ_0 is the dielectric constant at zero, and ϵ_∞, at infinite frequency. Since the expression above for relating τ to τ' really involves an accurate formula for the local field, which is not yet known for these solids, we shall regard τ for the dielectric as a rough measurement of the rate process for the movement of the atomic groups. It is hoped that subsequently this approximation may be improved. Also, the problem of the distribution of relaxation times about an apparent average value will be omitted from this preliminary discussion.
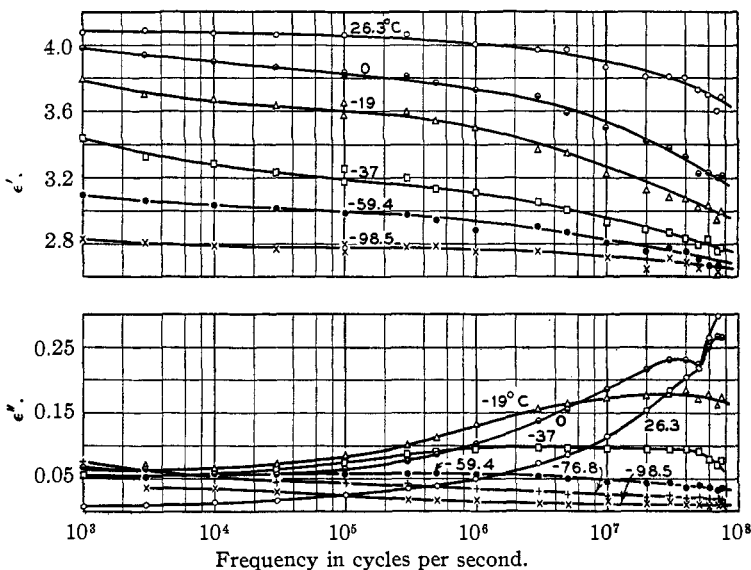

Fig. 4.—Frequency variation of ϵ' and ϵ'' of polyethylene sebacate, $-100°$ to $25°$.

The hindered orientation of groups in polyethylene sebacate may then be regarded as analogous to a unimolecular reaction[10,11] whose

(32) S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes." McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

absolute rate constant, k', is in general given by

$$1/\tau = k' = Ce^{-E/RT} \qquad (4)$$

where C is the "steric" factor, E the activation energy in cal. per mole, T the absolute temperature and R the gas constant.

We assume that E is virtually temperature independent; actually, since E represents a difference between energy levels which does depend on temperature, the corrections of Rushbrooke[33] should properly be applied.

From the loss maximum of Fig. 4, τ is obtained from the frequency producing ϵ'' max. at a given temperature. Although Fig. 5 shows several maxima, the ϵ'' curves here overlap, and do not provide a reliable estimate of the mean τ for a given temperature. A plot of $1/\tau$ against $1/T$ gives a straight line, the slope of which is E/R, and $E = 12,100$ cal. per mole of orienting groups, for polyethylene sebacate. This value is most significant
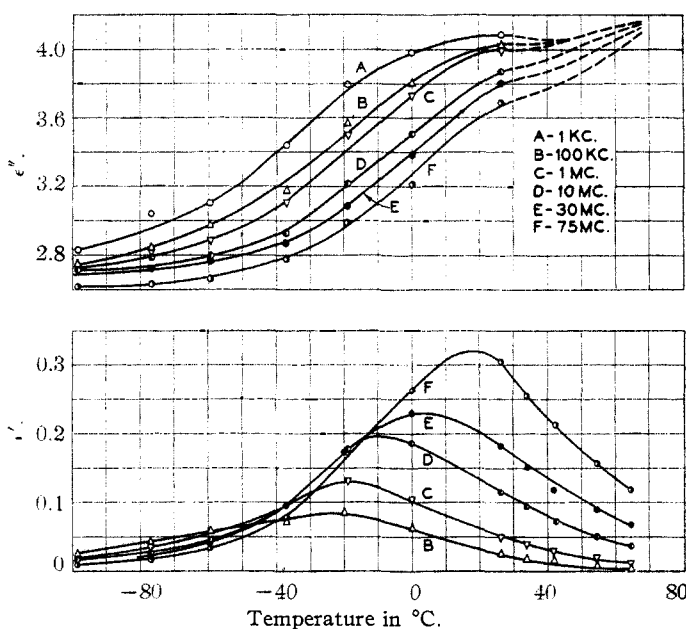

Fig. 5.—Temperature variation of ϵ' and ϵ'' of polyethylene sebacate, 1 kc. to 75 mc.

when compared to the larger value for a polyamide.[34] Further, the entropy term is large; in equation (4), $C = 4.3 \times 10^{18}$. This indicates that the neighbors of an orienting group must coöperate in its motion, such as by momentary displacements to reduce steric hindrance or by concentration of energy in the vicinity, as interpreted previously.[12]

The entropy term in the above expression should be significantly related to the distribution of relaxation times found for a given system. A distribution of relaxation times implies a variety of motions and configurations surrounding the orienting groups and causing different rates of surmounting the restraining barriers. This is just what the entropy of activation, or "activation in many degrees of freedom,"[11] means. Studies connecting explicitly the distribution function with the entropy or "steric" term in the rate equation are in progress.

Reduction in intermolecular coupling appears to give a sharper experimental distribution. Thus, consistent with the above concept, absorption peaks at high temperatures, with high plasticizer contents, or from "soft," weakly interacting polymers at ordinary temperatures are comparatively sharp.

Figure 5 bears interestingly on the phase changes in linear condensation polymers. Their high crystallinity[15,18] precludes a wide softening range, and the rise in ϵ' (accompanied by dispersion) over the broad temperature interval in Figure 5 corresponds to little physical change in the solid. However, the polymer melts (in thermodynamic equilibrium)[35] at $\sim70°$. This is, however, just above the temperature at which the dipoles are able quite freely to follow at least frequencies of 10^8. The ester linkages, or the carbonyl units, are thus undergoing increasingly violent thermal oscillations and are able to surmount the barriers imposed by the lattice array. Figure 5 may thus be regarded as indicating the prelude to fusion. Similar studies on other crystalline polymers including cellulose derivatives give evidence on the role of polar groups in melting. These are also further corroboration of the segment theory of polymer melting.[18]

The occurrence of absorption maxima far below the melting point, as for polyethylene succinate in Fig. 2, simply marks the onset of a particular oscillation—not necessarily that required for breakdown of the lattice.

Summary

The dielectric constant and loss of typical linear polyesters have been determined (over a

(33) G. S. Rushbrooke, Trans. Faraday Soc., 36, 1055 (1940).
(34) Baker and Yager, This Journal, 64, 2171 (1942)
(35) Baker. unpublished studies.

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

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 δ_m, of this two-layer arrangement were determined on the Q-meter and the true capacity, C_x, and loss, tan δ_x, calculated from the equations

(1) Yager and Baker, THIS JOURNAL, **64**, 2164 (1942).
(2) Carothers, U. S. Patents 2,071,250 (1937) and 2,130,523 (1938).
(3) Carothers, U. S. Patent 2,191,367 (1940).
(4) Fuller, Baker and Pape, THIS JOURNAL, **62**, 3275 (1940); see also Baker and Fuller, *ibid.*, **64**, October (1942).
(5) Yager, *Trans. Electrochem. Soc.*, **74**, 113 (1938).