along the fiber axis, but in random orientation about it, and either parallel or antiparallel to it. Each chain has a zigzag carbon planar configuration, with glycol units in the 1,3-positions.

Thanks are due to Dr. Cutler West, who drew attention to the fact that this particular fiber, because of the short fiber periodicity, might be sufficiently simple for an attempt at complete structure analysis; and who very kindly supplied the samples from which the X-ray data were obtained.

Summary

The structure of polyvinyl alcohol has been determined from a study of its X-ray fiber diagram. The experimental data consist of photographs taken with copper radiation filtered through nickel. The reflections, about thirty in number, were indexed with reference to a pseudo-orthorhombic cell of the following dimensions: $a = 7.82$, $b = 2.52$, $c = 5.60$ Å. The periodicity along the fiber axis, namely, 2.52 Å., points to a planar zigzag configuration for the carbon chain, with glycols in the 1,3 positions. There are two chain segments, $—CH_2CHOH—$, in the unit cell, giving a calculated density of 1.31. The reported value is 1.293. The symmetry is $C_{2h}^2—P2_1m$ with the carbons and oxygens lying in planes of symmetry. Positions for these atoms have been found such that the calculated intensities give satisfactory agreement with the limited number of observed intensities. The structure consists of long chain molecules so oriented that pairs of chains are linked through hydroxyl bonds.

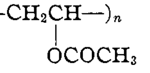
NEW ORLEANS, LOUISIANA RECEIVED JULY 26, 1941

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

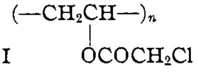
Electrical Properties of Solids. XI. Polyvinyl Acetate and Polyvinyl Chloroacetate*

BY DARWIN J. MEAD AND RAYMOND M. FUOSS

I. **Introduction.**—A number of the papers of this series have dealt with a polar polymer of very simple structure, polyvinyl chloride, in which the dipoles are attached directly to the carbon atoms which make up the chain. In this paper we shall present the results of an experimental study of two polymers, polyvinyl acetate (I) and polyvinyl chloroacetate (II), in which the polar groups are attached to the chain carbons by flexible ester-oxygen hinges.

I 

$(—CH_2CH(OCOCH_3)—)_n$

II 

$(—CH_2CH(OCOCH_2Cl)—)_n$

Qualitatively, one can make several predictions concerning their electrical properties. First, granting that the extremely broad absorption of polyvinyl chloride is caused by a distribution of relaxation times characteristic of the polymeric chain, we expect that the absorption peak for the acetates will be much sharper than for the chloride, because the flexibility of the oxygen bond places a rotational degree of freedom between the chain and the dipole. Consequently the orientation of the acetate dipoles is much less influenced by the convolutions of the chain than that of the chloride dipoles. Second, the off-chain dipoles in I and II are restricted to the chain by the bond as far as relative translational motion is concerned and therefore we expect less association and hence a higher static dielectric constant in the polymers than in the corresponding monomers. Third, since the resultant $—COCH_2Cl$ dipole is stronger than the $—COCH_3$ dipole, and possesses an additional degree of rotational freedom, the static dielectric constant should be greater for the chloroacetate, and it should give a sharper absorption curve. Data presented here confirm these predictions.

Two samples of polyvinyl acetate were studied; their weight average molecular weights, as determined by their intrinsic viscosities, were in the ratio 2.2:1. The one with the lower degree of polymerization had, at a given temperature, its maximum absorption at a frequency 2.2 times that for the maximum in the sample of higher molecular weight. The distribution of relaxation times,[1] although much sharper than that for the $(—CH_2CHCl—)_n$ polymers, is therefore still about a most probable value which is proportional to the number of monomer units in the polymer.[2] Since the acetates were unfractionated, we conclude further that the reciprocal of the frequency

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* Presented September 10, 1941, at the Atlantic City meeting of the American Chemical Society.

[1] Fuoss and Kirkwood, THIS JOURNAL, **63**, 385 (1941).

[2] Kirkwood and Fuoss, *J. Chem. Phys.*, **9**, 329 (1941).

of maximum absorption is proportional to the average molecular weight, as was found for the case of polyvinyl chloride.[3]

In the high temperature range,[4] the points for these polymers in the $\epsilon'' - \epsilon'$ plane map circular arcs[5] which, on the low frequency end, extrapolate to the correct static dielectric constants. Based on these values, we find moments per monomer unit of 2.3×10^{-18} for the acetate and 4.9×10^{-18} for the chloroacetate. But the high frequency ends of these arcs, however, extrapolate to values considerably larger than the square of the index of refraction. The clue to this puzzling behavior is found in the data at lower temperatures: a second maximum in absorption appears, and in the intermediate temperature range the $\epsilon'' - \epsilon'$ maps are *unsymmetrical* for our working range of frequency (60 cycles to 10 kilocycles). Several empirical descriptions are possible: if the whole curve is to be explained on the basis of a distribution of relaxation times, we must have either an unsymmetrical distribution or else a distribution parameter which is a function of frequency. An alternative description could be based on the simultaneous presence of two mechanisms for absorption: the dipole rotation which controls at higher temperatures or low frequencies, and a second mechanism which is the determining one at low temperatures or high frequencies. There is some evidence for a transition[4] between two physical states of the polymers: a high temperature form in which the time of elastic relaxation is short compared to the time required to establish thermal equilibrium and a low temperature form in which the time of elastic relaxation is very long compared to the time required to change the bulk temperature. Further experimental work, especially on static dielectric constants as a function of temperature, on high frequency electrical properties, and on mechanical properties, will be necessary before a decision can be made between the various possibilities.

II. Materials, Apparatus and Procedure.—The polyvinyl acetates were commercial samples of Gelva 60 and Gelva 15, made by Shawinigan Chemicals, Ltd. The as-received powders were pressed into 10 mil sheets, and stored in a desiccator over phosphorus pentoxide for a week, and then disks for electrical measurements (5-cm. diameter, 2–3 mm. thick) were pressed from the dried sheet. (Gelva 15 pressed six minutes at 120°; Gelva 60 six minutes at 140°.) Aquadag electrodes were then painted on the disks, after which they were again dried in the desiccator before measurement.

The density of the acetate disks was 1.17 as determined from their weight and dimensions, giving 73.6 cc. per monomer unit as the molar volume. The index of refraction was determined by means of a Benford refractometer[6]; the result was $n = 1.47$. Both Gelva 15 and Gelva 60 had the same density and index of refraction within the experimental error of the determinations.

The electrical and mechanical properties of the polyvinyl acetates were very sensitive to humidity; the effects can best be described by saying that the absorbed water acted like a plasticizer. Some typical results at 35° and 60 cycles are given in Table I. Compared to the air-dry weights, the samples in the desiccator lost 1% and the samples in the humidifier gained 4% in weight. The final electrical measurements are based on samples which were carefully dried.

TABLE I

INFLUENCE OF HUMIDITY ON POLYVINYL ACETATE

Gelva	ϵ'	ϵ''
15[a]	3.33	0.098
15[b]	4.15	.467
15[c]	10.45	2.64
60[a]	3.28	0.059
60[b]	3.95	.288
60[c]	9.68	2.76

[a] Sample dried in desiccator. [b] Sample exposed to room atmosphere (July). [c] Sample in 100% humidity chamber at room temperature.

The polyvinyl chloroacetate was obtained from a commercial sample of Mowilith G. The polymer was dissolved in ethylene dichloride and reprecipitated by slowly adding petroleum ether, with constant stirring, in order to separate some monomer and some low molecular weight material which was present. Analysis by combustion in the Parr bomb gave 29.1% chlorine, as compared with 29.5% calculated for $(C_4H_5O_2Cl)_n$. The density of the pressed polymer was 1.45, giving a molar volume of 83.3 cc. per monomole. The index of refraction was 1.54.

Electrical measurements were made in the platinum-faced cell[4] which has already been described. Some improvements have been made in the electrical equipment in the direction of increased sensitivity. These included a cathode ray oscillograph as null-point indicator and a power amplifier for supplying voltage to the parallel bridge. As usual, the Schering bridge[7] was used in the range 60–1000 cycles and the parallel bridge[8] in the range 1–10 kilocycles. A few measurements were made in the radio-frequency range[9]; we gratefully acknowledge the help of Mr. S. I. Reynolds in these determinations, as well as for several determinations in the megacycle range by the method of susceptance variation.[10]

Since it has been shown[2,3] that the electrical properties of large polymers are not very sensitive to the degree of polydispersion, no fractionations were made. The viscosi-

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[3] IX, Fuoss, THIS JOURNAL, **63**, 2401 (1941).

[4] Fuoss, *ibid.*, **63**, 369 (1941).

[5] Cole and Cole, *J. Chem. Phys.*, **9**, 341 (1941).

[6] Benford, *J. Optical Soc. Am.*, **29**, 352 (1939).

[7] Fuoss, THIS JOURNAL, **59**, 1703 (1937).

[8] Mead and Fuoss, *ibid.*, **61**, 2047 (1939).

[9] Reynolds and Race, *Gen. Elec. Rev.*, **41**, 529 (1938).

[10] Hartshorn and Ward, *Jour. Inst. Elec. Eng.*, **79**, 597 (1936).

ties of the different polymers were determined in a Bingham viscometer at several concentrations in cyclohexanone ($\eta_{25} = 0.0200_0$) at 25°. The results are summarized in Table II, where concentrations c are given as monomoles of polymer per kilogram of solution. The viscosities were extrapolated to zero pressure, from measurements made at pressures ranging from 70 to 150 cm. water. From the zero-pressure viscosities, the intrinsic viscosities $[\eta] = (\eta/\eta_0 - 1)/c$ were calculated. The $[\eta]$ values were linear in concentration; the values for $c = 0$ in the table are, of course, extrapolated, and are proportional to the weight-average molecular weight.

TABLE II

VISCOSITY OF DETERMINATIONS

Gelva 15		$(C_4H_5O_2Cl)_n$		Gelva 60	
$c \times 10^2$	$[\eta]$	$c \times 10^2$	$[\eta]$	$c \times 10^2$	$[\eta]$
5.18	5.22	6.10	11.36	4.99	11.25
2.92	4.80	4.95	10.84	2.81	10.40
0.00	4.25	3.87	10.60	0.00	9.25
		2.95	9.95		
		0.00	8.6		

III. Experimental Results.—An abstract of the data is given in Tables III–VI. Data at other frequencies and temperatures are summarized in tabular form, as American Documentation Institute Document No. 1595.[11]

In Table III are given the dielectric constants ϵ' and loss factors ϵ'' for polyvinyl chloroacetate at 60 cycles as a function of temperature. Figure 1 gives the loss factors and dielectric constants at different temperatures as functions of frequency for this polymer. In addition to the high maximum in the 60-cycle loss factor at 58°, there is a minimum at −30°, after which the curve rises with decreasing temperature, indicating the presence of a second maximum in absorption somewhere below −80°. The high temperature maximum in absorption is due to dipole rotation, as subsequent discussion will show. The mechanism underlying the low temperature absorption is still unknown: it is describable in terms of an extremely broad distribution of relaxation times and possibly is due to response of the whole sample as a single giant molecule to the field. In other words, the viscosity is so high in the low temperature range that the segments of the chain molecules are no longer mechanically independent, but, due to the very long time required for molecular motion, we have in effect a three dimensional cross-linked polymer rather than an aggregate of more or less independent chain molecules. It is interesting to note that the dielectric constant–temperature curve must have another inflection region at low temperatures: the curve is nearly linear from −10 to −80°, with $\Delta\epsilon'/\Delta T = -0.0031$, and since $\eta^2 = 2.37$ is the lower limit which must eventually be reached, a more rapid decrement should appear at still lower temperatures.

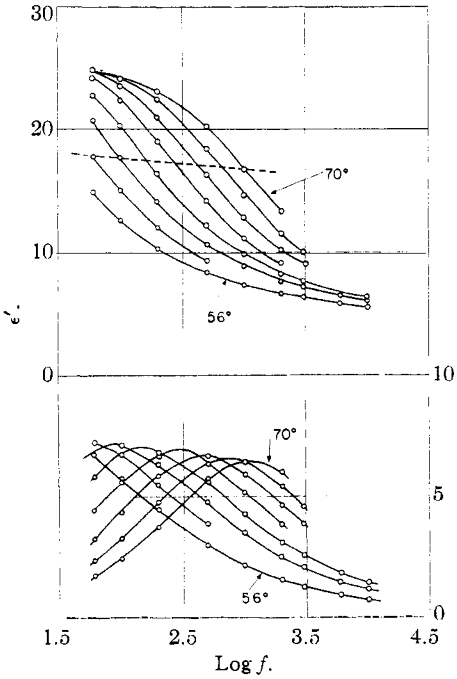

Fig. 1.—Electrical properties of polyvinyl chloroacetate at 2° intervals.

TABLE III

ELECTRICAL PROPERTIES OF POLYVINYL CHLOROACETATE AT 60 CYCLES

t, °C.	ϵ'	ϵ''	t, °C.	ϵ'	ϵ''
−80	4.163	0.0404	44	6.43	1.292
−70	4.192	.0352	46	7.07	1.868
−60	4.226	.0283	47	7.43	2.18
−50	4.256	.0245	49	8.40	3.04
−40	4.283	.0225	50	8.89	3.45
−30	4.312	.0216	52	10.48	4.63
−20	4.343	.0221	54	12.38	5.75
−10	4.380	.0241	56	14.86	6.77
0	4.422	.0287	58	17.80	7.23
10	4.482	.0374	60	20.70	6.85
20	4.515	.045	62	22.81	5.84
25	4.618	.067	64	24.21	4.43
30	4.767	.116	66	24.75	3.21
35	5.08	.265	68	24.91	2.33
40	5.64	.646	70	24.73	1.72
42	5.98	.908			

Data for the frequency dependence of electrical properties in the high temperature range, where dipole rotation is responsible for the response to

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[11] For a copy of the tables, order Document 1595 from the American Documentation Institute, Offices of Science Service, 2101 Constitution Ave., Washington, D. C., remitting 24 cents for microfilm or 60 cents for photocopies readable without optical aid.

the field, are given in Tables IV, V and VI. The temperatures are chosen to give one curve with the maximum loss near the center of the working range of frequency, and one each for increasing and for decreasing loss factors in this range.

TABLE IV

ELECTRICAL PROPERTIES OF POLYVINYL CHLOROACETATE AT VARIABLE FREQUENCY

	$t = 56°$		$t = 66°$		$t = 70°$	
f	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
60	14.86	6.77	24.75	3.21	24.73	1.72
100	12.55	5.79	23.54	4.33	24.24	2.41
200	10.26	4.47	21.02	5.89	23.14	3.71
500	8.27	2.99	16.28	6.68	20.20	5.74
1 k.c.	7.29	2.15	12.89	5.96	16.73	6.49
2	6.58	1.55	10.36	4.66	13.25	6.02
3	6.27	1.27	9.02	3.88	...	..
6	5.82	0.92	...	..	...	..

TABLE V

ELECTRICAL PROPERTIES OF GELVA 15 AT VARIABLE FREQUENCY

	$t = 54°$		$t = 66°$		$t = 80°$	
f	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
60	5.51	1.576	8.38	0.457	7.95	0.043
120	4.85	1.285	8.13	.783	7.93	.066
240	4.35	0.981	7.71	1.219	7.93	.116
500	3.99	.738	6.90	1.614	7.92	.218
1 k.c.	3.87	.522	5.95	1.659	7.84	.372
2	3.61	.415	5.10	1.464	7.59	.658
3	3.53	.335	4.71	1.270	7.43	.875
6	3.35	.247	4.15	0.990	6.72	1.268
10	3.33	.192	3.83	.780	5.94	1.465

TABLE VI

ELECTRICAL PROPERTIES OF GELVA 60 AT VARIABLE FREQUENCY

	$t = 60°$		$t = 69°$		$t = 85°$	
f	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
60	6.73	1.776	8.43	0.444	7.90	0.047
120	5.78	1.664	8.25	.768	7.89	.053
240	5.03	1.358	7.84	1.200	7.88	.091
500	4.45	1.077	7.04	1.619	7.86	.145
1 k.c.	4.11	0.787	6.08	1.683	7.85	.246
2	3.82	.581	5.20	1.498	7.80	.452
3	3.66	.484	4.78	1.324	7.61	.617
6	3.48	.356	4.25	1.011	7.19	.988
10	3.38	.280	3.83	0.794	6.55	1.264

IV. Discussion.—The general behavior of the polyacetates in the high temperature range is shown in Fig. 2, where the loss factors and dielectric constants of Gelva 60 are given as functions of temperature for different frequencies. It will be noted that the dielectric constant rises with increasing temperature at a given frequency, and that the curves for the different frequencies all approach a limiting envelope. This envelope gives the static dielectric constant ϵ_0 as a function of temperature. With increasing frequency, the temperature of maximum absorption increases from 59.5° at 60 cycles to 79.8° at 10 kilocycles. A plot of log f against $1/T_m$ is slightly concave-down; the average slope gives $Q = 59.0$ kcal. The most probable relaxation time ($\tau_m = {}^1/_2\,\pi f_m$) changes exponentially with temperature and can be used as a measure of the internal viscosity if we assume, as is usual in relaxation phenomena, that $\tau_m \sim \eta$.

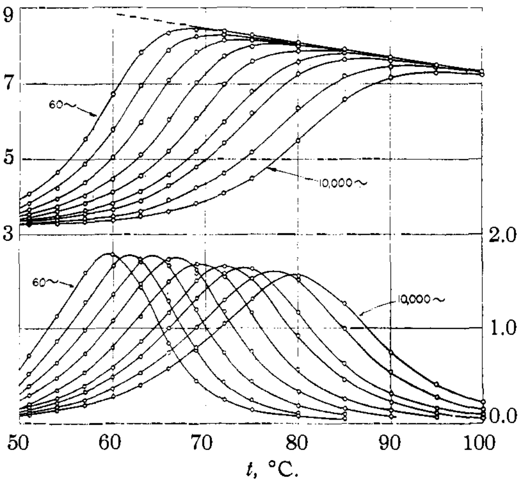

Fig. 2.—Electrical properties of polyvinyl acetate (Gelva 60) at 60, 120, 240, 500, 1000, 2000, 3000, 6000 and 10,000 cycles.

It is interesting to observe that the slope of the ϵ'–T plots decreases with increasing frequency, and that simultaneously, the width of the ϵ''–T maxima increases, while the height of the maximum decreases, corresponding to the decrease of static dielectric constant with increasing temperature. The ϵ''–T curves at fixed frequency for the acetates can be shown[4] to be of the form

$$\epsilon'' = 2\epsilon''_m x/(1 + x^2) \qquad (1)$$

where

$$\log Tx = A + BT \qquad (2)$$

The constant B decreases with increasing frequency. The change of $d\epsilon'/dT$ with frequency, the change of the half-width of the ϵ''–T maxima and the variation of B of Eq. (2) are all indications that a distribution of relaxation times, rather than a single relaxation time, is required to describe the properties of the polymers.

The best test plot for determining distributions is the one proposed by Cole,[5] in which ϵ'' is plotted against ϵ'. In the high temperature range (Fig. 3a, for example), the points fall on the arc of a circle, which extrapolates to the static dielectric

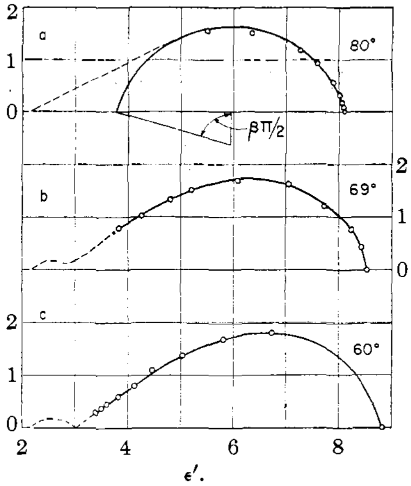

Fig. 3.—Complex loci for polyvinyl acetate (Gelva 60).

constant determined by the envelope of the ϵ'–T curves. The center of the circular arc lies below the ϵ' axis; from the decrement[3] of the ϵ''–log f curves or the locus of the center, the distribution parameter β can be determined. For Gelva 60 at 75°, for example, $\beta = 0.82$ as determined from the low frequency points. Similarly, Gelva 15 and polyvinyl chloroacetate give values of β in the range 0.7–0.9, if the high temperature–low frequency data alone are considered. If β is unity, the system is describable in terms of a single relaxation time. We see that the polyacetates are very much nearer to the case of a single time of relaxation than the polyvinyl chloride systems[3] for which β was of the order of 0.3–0.5. The physical interpretation of this result is that in polyvinyl chloride, the orientation of the dipoles is determined by the polymer chain, and hence we have a broad distribution of relaxation times, while in the case of the acetates, free rotation at the ester-oxygen bond between the dipole and the chain gives the dipoles much more rotational freedom. The values of β increase with increasing temperature, and apparently tend toward unity as the limit, corresponding to independent orientation of the polar groups when the thermal motion is violent enough.

The static dielectric constants of the polymers described here are much larger than those of the corresponding monomers. For the two acetates at 80°, $\epsilon_0 = 8.0$, and for polyvinyl chloroacetate at 70°, $\epsilon_0 = 25.5$. Monovinyl acetate at 25° has a dielectric constant of 5.8 and ethyl chloroacetate, which has approximately the polar structure of vinyl chloroacetate, has a dielectric constant of 12.0 at 25°.[12] The difference between the static constants, especially for the chloroacetate, is striking. On the assumption that association is responsible for the low dielectric constant of liquids, compared to the value of the moments of the corresponding molecules in the gas phase, the high dielectric constants of linear polymers is, however, not surprising. In the liquid, the dipoles are on mechanically independent molecules, so that they can rotate in their mutual fields, while in the polymers, they cannot cancel unless permitted to assume the proper relative orientation by the polymeric chain which carries them. The amount of cancellation possible probably depends on the shape, size and location of the polar groups on the chain; conversely, we may expect some information about the geometry of the polymeric molecules from a comparison of the static constants of a series of polar monomers and polymers. Some progress has been made on this problem.

By a coincidental compensation of effects, polyvinyl acetate gives a value for $H_{\text{max.}}$, the in-phase component of the reduced polarization,[1] which is very nearly equal to the theoretical value[2] of 0.267 for a polydisperse system of the type $(CH_2{\cdot}CHX)_3$. (For Gelva 15, $H_{\text{max.}}$ = 0.262 at 60° and 0.254 at 80°.) Since the polyvinyl acetate is unplasticized, the chains are not free to move independently, as was assumed in the theoretical calculation and, as was shown in the case of polyvinyl chloride, the result of chain interaction is a decrease of $H_{\text{max.}}$ and a broadening of the $H - x$ curve. On the other hand, the extra freedom of rotation provided for the off-chain dipoles of the acetate by the oxygen bond sharpens the distribution function over the theoretical one for the chain dipoles of the chloride, and raises the value of $H_{\text{max.}}$. As has just been mentioned, these two influences give a value of H for polyvinyl acetate which is in fictitious agreement with theory.

The two acetates are quite similar in their electrical properties, except that a given response appears at a higher temperature for the material of higher molecular weight. This is best shown by a plot of log f_m against $1/T$ (Fig. 4), where it is

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[12] These values were obtained by measurements in the platinum cell (Mead and Fuoss, THIS JOURNAL, **61**, 2047 (1939)) using the Schering bridge at 1000 cycles. The conductance of the liquids was rather high (acetate $\kappa_0 = 2 \times 10^{-9}$; chloroacetate 9×10^{-9}), but no special attempts to purify them, beyond distillation and one treatment with activated aluminum oxide (Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935)) was made, because only approximate values of their dielectric constants were needed for our present purposes.

seen that the two polymers give parallel lines (with $Q = 59.8$ kcal., in good agreement with the value obtained by plotting $\log f$ against $1/T_m$). The vertical displacement of the two lines of Fig. 4 is equivalent to a constant ratio of 2.2 between the frequencies for maximum absorption at a given temperature for the two polymers. Since τ_m varies as $1/f_m$, the most probable times of relaxation are in the ratio 2.2:1. This is, however, the same as the ratio of the limiting intrinsic viscosities (Table II), which are in turn measures of the weight-average molecular weight, assuming equal degrees of branching in the two polymers. Consequently we find that the reciprocal of the frequency of maximum absorption is proportional[2] to the degree of polymerization, as has already been shown to be true for the simpler polyvinyl chloride.[3]

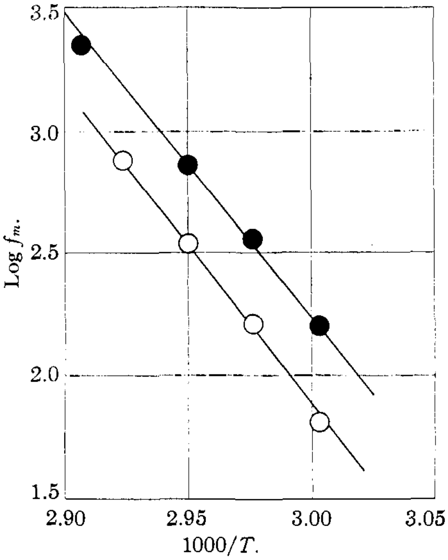

Fig. 4.—Dependence of absorption on temperature and molecular weight: ○, Gelva 60; ●, Gelva 15.

The moments per monomer unit were calculated by methods developed in previous papers of this series.[1,3] It was not necessary to extrapolate for ϵ_0 in the case of the polyvinyl acetates, because the envelope of the $\epsilon' - T$ curves (Fig. 1) determines the static dielectric constant. Using $n = 1.47$, $\varphi(n^2) = 2.85$ and

$$P_2'(0) = [\varphi(\epsilon_0) - \varphi(n^2)]V/9 \qquad (3)$$

where

$$\varphi(x) = (x - 1)(2x + 1)/x \qquad (4)$$

we determine $P_2'(0)$, the static polarization due to permanent dipoles. Then the relation

$$\tilde{\mu} = 0.0127(P_2'T)^{1/2} \qquad (5)$$

determines $\tilde{\mu}$, where

$$\tilde{\mu} = \sqrt{(\mu\bar{\mu})_{\text{av.}}/n} \qquad (6)$$

is the average moment per monomer unit of an n-mer in which μ is the moment of the molecule and $\bar{\mu}$ is the vector sum of μ and the moment induced by μ in the surrounding medium. For the Gelvas, there was a slight systematic dependence of $\tilde{\mu}$ on temperature: Gelva 60 gave $\tilde{\mu}$ (60°) = 2.46, $\tilde{\mu}$ (70°) = 2.42, $\tilde{\mu}$ (80°) = 2.37, $\tilde{\mu}$ (90°) = 2.33 and $\tilde{\mu}$ (100°) = 2.28 and Gelva 15 gave $\tilde{\mu}$ (60°) = 2.42, $\tilde{\mu}$ (70°) = 2.39, $\tilde{\mu}$ (80°) = 2.34 and $\tilde{\mu}$ (90°) = 2.32. The moment per monomer unit is independent of the degree of polymerization, and equals 2.3. If we compare this with $\mu_0 = 1.80$ for ethyl acetate,[13] we see that in the unplasticized polymer, the value of the moment $\tilde{\mu}$ per monomer unit is somewhat larger than μ_0, that of the corresponding molecule in the gas phase, just as was observed in the case of unplasticized polyvinyl chloride. For the chloride, the ratio $\tilde{\mu}/\mu_0$ was found[1,14] to be $\sqrt{3}/2$. In the case of the acetate, the component of moment normal to the chain will be multiplied by the same reduction factor, while the component parallel to the chain will be unaffected, on account of the free rotation at the oxygen bond. An approximate calculation gives $\tilde{\mu}/\mu_0 = 0.935$ for this case. The observed ratio is $2.3/1.8 = 1.28$; as has already been mentioned, the average moment in unplasticized polymers is expected to be higher than in dilute systems.[14]

Polyvinyl chloroacetate was very similar in its behavior to the polyvinyl acetates, except that its loss factor–temperature curves were somewhat sharper, corresponding to the increased freedom of rotation with respect to the chain of the Cl-component of the net dipole. This is also shown by the fact that the ratio $\epsilon''_{\text{max.}}/(\epsilon_0 - n^2)$ is larger for the chloroacetate than for the acetates. A plot of $\log f_{\text{max.}}$ against $1/T$ gave $Q = 52.7$ kcal. Excellent evidence that the high temperature electrical properties were determined by a relaxation mechanism controlled by the internal viscosity is given in Fig. 5, where $\log f_m$ at a series of temperatures is plotted against the logarithm of κ_0, the d. c. conductance measured at the same temperatures. The dotted line is drawn at 45° to the axis. To a fairly close approximation, f_m is proportional to κ_0. The latter is inversely propor-

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(13) Smyth, "Dielectric Constant and Molecular Structure," A. C. S. Monograph, Reinhold Publishing Corporation, New York, N. Y., 1930.

(14) Fuoss, THIS JOURNAL, **63**, 2410 (1941).

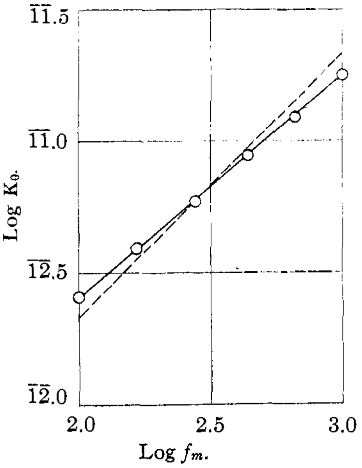

Fig. 5.—Correlation between relaxation and viscosity in polyvinyl chloroacetate.

tional to η, the internal viscosity, while the former is inversely proportional to τ_m, the most probable time of relaxation. Hence $\tau_m \sim \eta$, and the coefficient of resistance to the translational motion of ions is approximately equal to the coefficient of resistance to the rotational motion of the dipoles.

The ϵ''–ϵ' maps for polyvinyl chloroacetate are circular arcs in the high temperature–low frequency range, and were used to extrapolate for ϵ_0. At 70°, ϵ_0 was found to be 25.5, and using equations (3) and (5), this value gives $\tilde{\mu} = 4.9$, which looks reasonable.

What has been said so far in this discussion refers to the range of variables where the electrical properties can be interpreted in terms of a relaxation mechanism in which the dipoles exhibit a distribution of relaxation times; that is, where the ϵ''–ϵ' locus is a circular arc. Physically, this corresponds to properties measured at "low frequencies and high temperatures." Both these terms are relative, of course, and the "high temperature" range is different from polymer to polymer. Based on experience to date, the high temperature range is roughly the range of temperatures above that at which the loss factor at 60 cycles reaches its dipole maximum. Until more information on the suspected transition in polymers is available, we have no choice and must use this admittedly arbitrary definition.

In Fig. 3, we have a series of ϵ''–ϵ' plots for Gelva 60 at different temperatures. At 80°, the data lie on a circular arc with center at (5.95, −0.65) and radius 5.98, which gives $\tan \beta\pi/2 = 9.20$ and $\beta = 0.93$. The low frequency end of the arc extrapolates to $\epsilon_0 = 8.10$, which checks the observed value obtained from the envelope of the ϵ'–T curves. But the high frequency end extrapolates to a value of $\epsilon_\infty = 3.55$, which is much larger than 2.16, the square of the index of refraction. This suggests that the ϵ''–ϵ' locus is unsymmetrical, as shown by the dotted curve in Fig. 3a. At 69°, the dissymmetry is clearly visible in the observed points: the low frequency end is a circular arc, but in the neighborhood of the maximum, the radius of curvature begins to increase, and the ϵ''–ϵ' points approach a straight line which extrapolates to n^2. But data at lower temperatures show that the behavior is even more complicated: at 60°, the linear section extrapolates to $\epsilon_\infty = 3.00$. Consequently there must be a concave-up section in the ϵ''–ϵ' locus, in order that the observed curve terminate at the observed ϵ_∞ point. The data at still lower temperatures[11] indicate an absorption mechanism which is quite different from that obtaining at higher temperatures: in Fig. 2, it is seen that the slope of the ϵ'–T curves becomes very small while the dielectric constant is still greater than 3 (*i. e.* $\gg n^2$) and the loss factor decelerates in its decrease in the low temperature range.

In Table VII are given some high frequency data at 33°. These data show that over the four decades from one kilocycle to ten megacycles, the dielectric constant is decreasing slowly, while the loss factor remains substantially constant; in other words, we have here an extremely broad dispersion region.

TABLE VII

GELVA 60 AT HIGH FREQUENCIES

f, kc.	ϵ'	ϵ''
1	3.08	0.022
5	3.06	.021
20	3.03	.020
50	3.02	.022
100	3.00	.022
500	2.98	.025
1,000	2.97	.021
10,000	2.92	.019

If the whole ϵ''–ϵ' curve had the course indicated by the dotted line of Fig. 3a, an empirical description could be given on the assumption that the distribution function for the relaxation times was unsymmetrical. Side chains due to branching, for example, would give a contribution in the range of short relaxation times, which would be superimposed on the distribution of times characteristic of the backbone of the polymer. An alternative is to assume that the distribution parameter β is a function of frequency. At high temperatures and low frequencies, the molecules have time to redistribute themselves during a quarter cycle, because the viscosity is low and the times of relaxation are short. But for measurements at high frequency, the average for the distribution of the times of relaxation is taken in a time which is long compared to the period of the field, and consequently fluctuations will be more and more pronounced with increasing frequency. Indeed, by drawing normals to curves of the type of Fig. 3, it is possible to obtain from their intersections with a perpendicular through the maximum of the $\epsilon''-\epsilon'$ plot a series of distribution parameters as a function of frequency. The values so obtained approach unity for zero frequency and zero for infinite frequency; that is, the system behaves as if it were characterized by a single relaxation time (or by a rather narrow bond) at high temperatures and low frequencies and by an infinitely broad distribution when the frequency is high or the temperature low. These two extremes correspond, respectively, to periods very long and very short compared to the time of relaxation within the polymer.

In the case of polyvinyl chloroacetate, where the data were extended to very low temperatures, a second maximum in absorption in our frequency band appears, as is shown in Fig. 6. This is similar to the low temperature maximum observed for polyvinyl chloride[4]; since it can be eliminated by dilution of the polymer with a substance of low molecular weight[14,15] it is clearly due to an interaction between chain molecules. Although low temperature measurements on the polyvinyl acetates were not made, the shape of the $\epsilon'-T$ and $\epsilon''-T$ curves, as well as the data of Table VI, all indicate that they too have a secondary maximum.

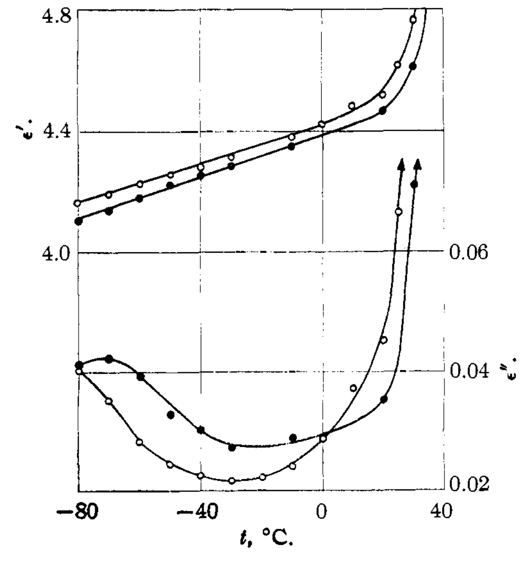

Fig. 6.—Electrical properties of polyvinyl chloroacetate at low temperatures: O, 60 cycles; ●, 500 cycles.

If a Cole plot is made for polyvinyl chloroacetate in the low temperature range, a minimum appears at −10°, as is shown in Fig. 7. The general $\epsilon''-\epsilon'$ curve therefore cannot have the form shown as the dotted curve of Fig. 3a, but must have the form shown by the dotted curve of Fig. 3b. There is another possibility, which is shown as the dotted curve of Fig. 3c. The double maximum may be present for all polar polymers at all temperatures as we go from zero to infinity on the frequency scale, as is suggested by the data for the polyvinyl chloroacetate and for polyvinyl chloride (Case 3b). Or else there may exist a true transition temperature,[4] T_c, for these substances, such that the small arc of Fig. 3c is covered by the zero to infinity frequency range at temperatures below the transition temperature, and the large arc is covered by the whole frequency range at temperatures above the transition temperature. This is equivalent to saying that the polymers exist in two forms, which are characterized by two static dielectric constants, and two ϵ_∞ values: for $T < T_c$, ϵ_∞ is the square of the index of refraction, and ϵ_0 is the value given by the cusp in Fig. 3c. For $T > T_c$, ϵ_∞ is the square of the index of refraction plus the term arising from the polarization responsible for the small arc, and the static dielectric constant is these two terms plus the contribution due to polarization of the permanent dipoles.

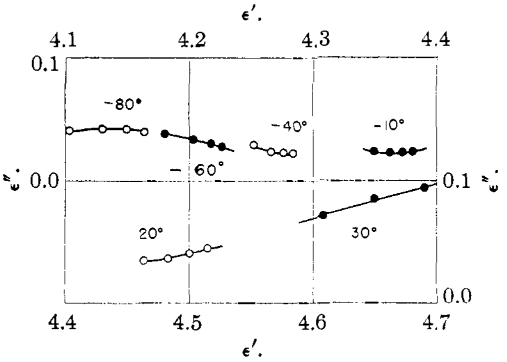

Fig. 7.—Low temperature loci for polyvinyl chloroacetate.

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(15) Fuoss, This Journal, **63**, 378 (1941).

The fact that the data for polyvinyl chloride and polyvinyl chloroacetate (Fig. 7) give curves of the type of Fig. 3b does not eliminate the possibility shown by the dotted extrapolation in Fig. 3c, because times of relaxation are extremely long in the low temperature range, and the possibility is not excluded that the samples were not in thermal equilibrium when the measurements were made. Some creep[4] in the bridge balance for the chloroacetate samples in the neighborhood of 20° was observed, and the values reported are the apparent asymptotic values based on several hours of observation. But really long-time observations were not made, because no necessity for them was suspected. The most direct answer to the various questions raised here can probably be obtained by making measurements at ultra-high frequencies in the high temperature range. Theoretically, a study of static dielectric constants in the low temperature range should give the same information, but in view of the long times of relaxation involved, transients would probably make for considerable experimental difficulty.

In conclusion, then, we can say that the high temperature–low frequency properties of polar polymers or of plasticized polymers over the whole range of variables can be accounted for on the fairly simple mechanism of dipole orientation subject to the restrictions imposed by the fact that the dipoles are attached to a long flexible carbon chain. Much, however, remains to be done in the high frequency–low temperature range, that is, where the period of the impressed field is short compared to the times of relaxation of the polymeric system.

Summary

1. The electrical properties of polyvinyl chloroacetate from -80 to $+70°$ are given for the (approximate) frequency range 60 cycles to 10 kilocycles. The moment per monomer unit was found to be 4.9×10^{-18}.

2. The electrical properties of two polyvinyl acetates (Gelva) of different molecular weights are given for 30 to 100° over the same frequency range. The moment per monomer unit was found to be 2.3×10^{-18} for both polymers.

3. These polymers, in the high temperature range, exhibit absorption due to dipole rotation. The times of relaxation are distributed about a value which is proportional to the molecular weight of the polymer.

4. The distribution is much sharper than for polymers of the type $(CH_2CHCl)_n$, because rotation about the oxygen atoms linking the dipoles to the polymeric chain frees the dipoles from many restrictions imposed by the convolutions of the chain.

5. Static dielectric constants much larger than the dielectric constants of the corresponding monomers are interpreted as diminished association of dipoles in the polymers, produced by the restrictions on translational motion imposed by the bond to the chain.

6. Further evidence is advanced that the d. c. conductance can be used as a measure of the internal viscosity of plastics: both the d. c. conductance and the time of polar relaxation are exponential in $1/T$ and have approximately the same temperature coefficient.

7. A number of puzzling features in the electrical properties, which appear when the period of the impressed field is short compared to the time of elastic relaxation in the system, are pointed out. Some tentative explanations are proposed, and an experimental attack is suggested.

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