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

Electrical Properties of Solids. IX.[1] Dependence of Dispersion on Molecular Weight in the System Polyvinyl Chloride–Diphenyl

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I. Introduction

Results presented n previous papers of this series show that plastic solids containing polar polymers are characterized by a wide absorption and dispersion region. In the preceding paper,[1] this behavior was described empirically in terms of a distribution of relaxation times in the system, and a method for obtaining the distribution from electrical data was given. A consideration of the rotatory diffusion of long chain molecules[2] shows that such molecules necessarily exhibit a wide distribution of relaxation times as a consequence of their structure, and gives us an explanation, in terms of a molecular model, of the observed electrical properties of polar polymers.

The theoretical treatment for a dilute solution of a monodisperse polymer of the type $(CH_2CHX)_n$, where X is a simple polar group, leads to a distribution function $G(\tau)$ which satisfies the equations

$$G(\tau) = \tau_0/(\tau + \tau_0)^2;\ 4\tau_0/n\pi^2 \leq \tau \leq n\tau_0/6 \quad (1)$$
$$G(\tau) = 0 \quad \text{elsewhere.}$$

$$\int_0^\infty G(\tau)d\tau = 1 \quad (2)$$

The most probable time of relaxation τ_0 is given by $1/2\pi f$, where f_m is the frequency corresponding to the maximum in $H(x)$. (This function is the in-phase component of the reduced polarization, and to a close approximation, is proportional to the maximum in the loss factor ϵ'' as a function of frequency.) The resulting dispersion range is much broader than that corresponding to a system characterized by a single time of relaxation; for the former, $H(x)$ drops to only 57% of its peak value in one decade change of frequency from f_m, while for the latter, $H(x)$ has dropped to 20% of its maximum in the first decade. The broader curve necessarily[3] gives a lower maximum in the $H(x) - \log f$ curve; the values are, respectively, 0.500 and 0.286 at $f = f_m$.

The quantity τ_0 is related to the parameters describing the polymeric molecule by the equation

$$\tau_0 = 3\pi na^2b\eta/kT \quad (3)$$

where n is the number of monomer units in the chain, a is the carbon–carbon distance, b is $(3v/8\pi)^{1/3}$, v is the volume of a monomer unit, η is the viscosity of the medium, k is Boltzmann's constant and T is the temperature. In order of magnitude, τ_0 equals the product of degree of polymerization into the time of relaxation of a single monomeric unit in a medium of the same viscosity.

Equation (3) states a proportionality between the molecular weight ($M = nm_0$, where m_0 is the molecular weight of the monomer unit) and the reciprocal of the frequency of maximum absorption and hence offers a method of determining the size of linear macromolecules by fairly simple electrical measurements. Absolute values cannot yet be obtained for plastic solids because their viscosities have not been determined, and because the concentrations in the systems studied so far are too high to meet the approximations made in the theoretical treatment. However, Eq. (3) may still be used to test the general theory, by considering electrical data for polymers of different molecular weights.

Staudinger[4] has shown that the intrinsic viscosity $[\eta]$ is proportional to the molecular weight of polymers in a homologous series. The quantity $[\eta]$ is defined[5] as

$$[\eta] = [d(\eta/\eta_0)/dc]_{c=0} \quad (4)$$

where η is the viscosity of a solution containing c monomoles of polymer per liter in a solvent of viscosity η_0. Combining Staudinger's result with (3), we have

$$\tau_0 = 1/2\pi f_m = A[\eta] \quad (5)$$

That is, the reciprocal of the frequency of maximum absorption should be a proportional to the intrinsic viscosity.

In this paper, data will be presented for PVi-Cl-Ph_2 80:20 systems which verify Eq. (5), both for the case of fractionated and for polydisperse polymers. It will also be shown that the dipole moment per monomer unit[1] is independent of molecular weight, as might be expected if the

(1) Paper VIII, Fuoss and Kirkwood, THIS JOURNAL, **63**, 385 (1941).

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

(3) Kramers, *Atti Congr. dei Fisici, Como*, 545 (1927); Gorter and Kronig, *Physica*, **3**, 1009 (1936).

(4) Staudinger, "Die hochmolekularen organischen Verbindungen," J. Springer, Berlin, 1932.

(5) Kraemer and Lansing, *J. Phys. Chem.*, **39**, 153 (1935); Kraemer and Van Natta, *ibid.*, **36**, 3175 (1932); Flory and Stickney, THIS JOURNAL, **62**, 3032 (1940).

method and assumptions used in its computation from the data are correct. These results confirm the theory that in the high temperature range[6] the electrical properties of systems containing polar polymers are due to dipole rotation in the impressed field. The average polar response differs from that obtaining in simple polar liquids on account of the distribution of relaxation times produced by the convolutions of the chains carrying the dipoles.

II. Materials, Apparatus and Procedure

The experimental methods were practically the same as those used in the previous work on poly-*p*-chlorostyrene[6] and polyvinyl chloride–diphenyl systems.[7] One change in method in preparing some of the disks was made which requires comment: plasticizer was added in petroleum ether solution as before, but the solvent was removed by drying in a vacuum oven at 60°. This procedure was much more rapid than evaporation at room temperature, but some diphenyl was also lost. The amount lost was determined by difference between the weights of polymer plus diphenyl taken initially and the final dry weight of the aggregate. Uniformity of the samples was ensured by sheeting at 100° and milling at 60° after cold pressing the mixture obtained by evaporation of the solvent. The samples (3–7 g.) were weighed to mg. after every step, so that correction could be made for any diphenyl lost. The final samples were prepared in the form of 5-cm. disks by pressing for five minutes at 120° in a closed mold.

Eight different samples of polyvinyl chloride were used. The corresponding disk numbers and polymer designations are given in the first two columns of Table I. For use in discussion, a previously reported[6] sample (No. 605) is also included. The third column gives the diphenyl content.

TABLE I

DESCRIPTION OF SAMPLES

No.	PViCl	% Ph_2	$[\eta]$	$\log f_m$ (55°)	β (55°)	$\tilde{\mu}$
605	1.05	20.0	6.26[b]	3.48	0.460	2.13
659	XS161	20.0	9.15[b]	3.23	.348	2.30
661	XS162	20.0	6.98[b]	3.44	.402	2.22
664	XS168	20.0	11.50[b]	3.09	.376	2.29
676	7.1	19.31	5.78[a]	3.20	.399	2.18
677	3,4–1.1	19.11	3.64[a]	3.25	.461	2.11
678	3,4–4.1	18.77	2.21[a]	3.26	.479	2.12
679	7.1	19.39	5.78[a]	3.24	.419	2.09
680	A5	19.33	5.44[a]	3.19	.411	2.14

[a] In methyl amyl ketone at 40°. [b] In cyclohexanone at 25°.

The samples are characterized by their intrinsic viscosities, which are given in the fourth column of Table I. All viscosity determinations were made by Dr. D. J. Mead of this Laboratory, to whom grateful acknowledgment is made. The details of the method, and a report on a systematic study of the viscosity of polyvinyl chloride solutions are given in a separate paper by Dr. Mead.[8] Briefly, the determinations were made in a Bingham viscometer at concentrations in the range 0.02–0.05 monomole per liter, and extrapolated to zero pressure to eliminate errors due to uncoiling chains by velocity gradients in the capillary.[9] In Table I, $[\eta]$ is the limit slope at zero concentration of the $(\eta/\eta_0)-c$ plot, where c is here in monomoles per *kilogram* of solution.

Sample 1.05 is the low viscosity polymer used in much of the previous work.[6,7] Samples XS 161, 162 and 168 are materials polymerized at different rates; in general the higher the rate of polymerization, the lower the intrinsic viscosity. This effect can be due to one of two causes: either a lower most probable molecular weight at the higher rates, or else a higher degree of branching at the higher rate. (More branching gives on the average a more spherical molecule, and for the same molecular weight, the sphere has the smaller intrinsic viscosity.[10]) We are indebted to the Dow Chemical Company for these four samples.

Sample A5 was obtained from the L38 polymer previously used for the tricresyl phosphate work.[11] One hundred grams was stirred for two hours at 40° with 2 liters of acetone, and centrifuged. The solid residue was reëxtracted with warm acetone as before and, after centrifuging, was extracted a third time. The third acetone extract gave only a very faint turbidity on dilution with twice its volume of water, which indicates that the polymer was free of acetone-soluble polyvinyl chloride. The acetone-wet material was swollen, and would have given horny lumps on drying. In order to obtain the polymer in powder form, the material from the third centrifuging was suspended in acetone, and, with motor-stirring, methyl alcohol was added slowly until the alcohol content was 50%. This procedure coagulated the swollen polymer as a fine precipitate, which was put to soak overnight in methyl alcohol. The next day it was filtered, washed with methyl alcohol and dried in a vacuum oven at 85°. The yield was 70.4 g., with $[\eta] = 5.44$. The original material had an intrinsic viscosity in methyl amyl ketone at 40° equal to 4.75; calculations based on these three data, and making no correction for mechanical loss, gives $[\eta] = 3.1$ for the acetone-soluble material, as compared with 2.72 observed for the material in the first extract. As the work on frac-

(6) Fuoss, THIS JOURNAL, 63, 369 (1941).
(7) Fuoss, *ibid.*, 63, 378 (1941).
(8) Mead, unpublished work.
(9) Mark, *J. Appl. Phys.*, 12, 41 (1941).
(10) H. Mark, "Physical Chemistry of High Polymeric Systems," Interscience Publishers, New York, N. Y., 1940, p. 258ff.
(11) Fuoss, THIS JOURNAL, 60, 451 (1938); *ibid.*, 61, 2334 (1939).

tionation will show, sample A5 is much less polydisperse than unfractionated L38, because it contains none of the low molecular weight material which is acetone soluble, and the cut-off on the higher molecular weight side of the distribution curve is fairly sharp.

The polymers used in making samples 676–679 were refractionated fractions obtained from L38 by the methods described in the next section. They cover a range of about three to one in weight-average molecular weight.

III. Fractionation of Polyvinyl Chloride.—After a number of preliminary experiments, two general procedures were developed: the first is an analytical method, requiring 1–2 g. of polymer, and was used to determine the distribution curve of the polymer. It was applied to a variety of polyvinyl chloride samples, but results for only L38 will be given here in order to save space. After the micromethod had determined the precipitation range of a given polymer, and its viscosity distribution, the second method was used in order to obtain sufficient material in the different fractions to permit preparation of samples for electrical measurements. The micro-method was quantitative (average recovery 98%); in the preparative method; speed and convenience in manipulation were the controlling factors.

The general method consists in dissolving the polymer in a mixture of a solvent and a low-boiling swelling agent (or non-precipitant), and then gradually adding a precipitating agent in successive portions, centrifuging out the precipitate after each addition of precipitant. For low average molecular weight polyvinyl chloride, mesityl oxide was used as solvent; for higher, cyclohexanone. Acetone was used as diluent and methyl alcohol as precipitant.

Micro Method.—Between 1 and 2 g. of polymer was weighed into a weighed wide-mouth 200-cc. centrifuge bottle, and wet out with five to ten times its weight of acetone. (Wetting with acetone prevents the polymer from coalescing to a single lump when solvent is added; omission of this step gives "fish-eggs" which are extremely slow to dissolve.) Then 10–40 times the polymer weight of solvent was added, with stirring. The mixture was heated on the steam-bath under a reflux until all the polymer was in solution. The solution was diluted with acetone to give 1–2.5% polymer in the final solution: in general, the more dilute the solution, the better the fractionation.

Precipitation was then started. The solution was set refluxing under a vertical condenser which had several jogs in the lower end of the condenser tube, at a rate which kept liquid acetone bubbling in the bottom of the condenser. The indentations in the condenser are made so that liquid running in from above must strike condenser surface, and cannot fall directly into the contents of the flask beneath. A weighed portion of methyl alcohol was added from a weight buret through a capillary funnel; it ran slowly into the acetone in the splash-pot in the condenser, and then *diluted with acetone*, ran into the solution. This procedure permits the *addition of diluted precipitant to the solution without increasing the total volume* more than that corresponding to the volume of the precipitant. (If methyl alcohol is simply poured in, even with very efficient stirring, clots of total precipitate form. The method in which the alcohol concentration in the solution rises very gradually, so that the local concentration is at no time very high, is therefore recommended.)

After the alcohol had been added, the solution was allowed to cool slowly and was finally chilled in ice, after which it was centrifuged. The supernatant liquid was carefully decanted into a second weighed centrifuge bottle, and a second portion of alcohol added to give the next fraction; this procedure was repeated until the alcohol concentration reached 50%, which usually leaves only a trace of material in solution.

The curve (% polymer precipitated) *vs.* (% methyl alcohol in solution) is an S-curve, as will be seen in the examples given. In the inflection range of the curve, *i. e.*, where large precipitates are formed by small increments of precipitant, it is advisable to raise the alcohol concentration by not more than 2.0–2.5% steps, and to cool quite slowly. Before and after the inflection region, larger concentration changes may be made. Even so, each precipitate, especially the heavy ones in the critical region, usually brings down some material of lower molecular weight; this effect can produce a fictitious minimum in the distribution curve, but refractionation of the middle fractions corrects the error.

Each precipitate was broken up in a small amount of acetone–alcohol of the same alcohol weight concentration as the solution from which it was precipitated. A small grid of 20-mesh nickel screen, 1.5-cm. square, welded to a 1-mm. nickel wire support and handle is very convenient for cutting up the gelatinous precipitates. Then more acetone–alcohol was added and, after stirring, an excess of alcohol was added slowly to coagulate the precipitate. After standing for an hour, with occasional stirring, the liquid was decanted, and alcohol added to complete the coagulation. With a little practice, fine flocculent precipitates can be obtained. After soaking in alcohol for at least several hours, the precipitate was filtered on a small hard filter, sucked "dry," broken up, and vacuum-dried at 100°. The precipitates were then weighed, and samples taken for viscosity determinations. It is for rapid and complete solubility in the viscosity work that care is taken to obtain fine precipitates rather than hard lumps of polymer. Also, it is extremely difficult to remove the solvent (mesityl oxide or cyclohexanone) from the original gelatinous precipitates but two hours of vacuum drying at 100° brings the fine precipitates to constant weight.

The results for the fractionation of the L38 polyvinyl chloride are given in Table II. Half of the material was still soluble in mesityl oxide–acetone (1:3) containing 20% methyl alcohol by weight, but precipitated on raising the alcohol to 25%. As the viscosities show, the high molecular weight material is the least soluble and precipi-

TABLE II

FRACTIONATION OF L38 POLYVINYL CHLORIDE

% MeOH	% ppt.	$[\eta]$
20.0	16.7	6.1
25.0	49.9	5.5
32.5	17.4	4.5
40.0	12.3	2.9
50.0	3.5	1.8

tates first. The resulting distribution curve is shown in Fig. 1, where the areas of the rectangles are chosen such that the total area is 100. It will be seen that this polymer contains polyvinyl chloride molecules distributed around a most probable size which has an intrinsic viscosity of 5.5 in methyl amyl ketone at 40°. This corresponds roughly to a molecular weight of about 30,000; the estimate is based on values of the Staudinger constant[4] for other polymers.

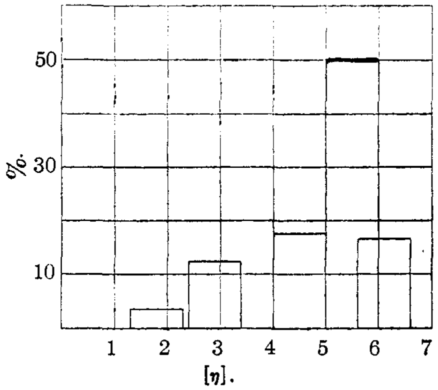

Fig. 1.—Distribution curve for L38 polyvinyl chloride.

Preparation of Fractions in Quantity.—Polymer 7.1 was the middle fraction of L38. Twenty grams of L38 was dissolved in 200 g. of mesityl oxide after wetting with 100 g. of acetone. After solution was complete, the mixture was diluted with acetone to 2.5% polymer by weight, and then methyl alcohol was added through the reflux to give 20% alcohol by weight. The precipitate was centrifuged out, and the middle fraction was then separated by bringing the alcohol concentration to 25%. This fraction was washed with 25% alcohol–75% acetone, then broken up, coagulated, filtered and dried as described in the preceding section. Three batches were run, giving a total of 38.37 g. of once fractionated polyvinyl chloride, with $[\eta] = 5.44$. These were combined and redissolved in the mesityl oxide–acetone mixture, and reprecipitated at 21.1% methyl alcohol. This precipitate was washed, etc., and after drying was used to make disks 676 and 679. The data for the fractionations are given in Table III; data for only one of the three initial 20-g. lots are given, because the other two gave much the same result.

The two low molecular weight samples (for disks 677 and 678) were obtained by fractional precipitation of an acetone extract of L38. Four 100-g. batches were extracted with 2 liters of acetone each at 40° for one and one-half hours and centrifuged. After preliminary tests to locate the inflection in the precipitation curve of the solution, the extract was divided into two portions for convenience and precipitated as shown in Table IV.

TABLE III

PREPARATION OF 7.1 FRACTION

% MeOH	Wt. ppt.	[η]
	First Fractionation	
20.0	4.52	5.44
25.0	11.34	4.94
50.0	3.12	2.33
	Fractionation of Middle Fractions	
21.1	32.65	5.78
25.0	2.04	4.46
50.0	2.70	2.92

TABLE IV

FRACTIONATION OF ACETONE EXTRACT

% MeOH	First portion Wt. ppt.	First portion [η]	Second portion Wt. ppt.	Second portion [η]
10	0	..	0	...
12	11.18	3.25	11.05	3.56
15	2.20	3.16	1.45	3.27
20	4.69	2.86	5.49	2.89
25	3.65	2.11	3.68	2.13
35	3.06	1.54	3.18	1.51

The 12% and 25% precipitates from the extract were then refractionated as shown in Table V.

TABLE V

REFRACTIONATION OF ACETONE SOLUBLE POLYMERS

% MeOH	12% Ppt. Wt. ppt.	[η]	% MeOH	25% Ppt. Wt. ppt.	[η]
16	10.85	3.64	25	3.39	2.21
20	6.30	3.47	35	2.22	2.14
30	2.68	2.95			

IV. Experimental Results.—The electrical properties at 55° for the samples of Table I are summarized in Table VI. The data cover the frequency range 60 to 10,000 cycles; for the PViCl–Ph_2 80:20 systems, the maximum loss factor comes near the center of this range at 55°.[12] The main uncertainty in absolute value is due to warping, with attendant changes in cell constant, and in unfavorable cases, may amount to several per cent.; but relative values for a given sample, on which most of the arguments are based, are probably reliable to better than 0.5%.

In order to determine whether the thermal

(12) Measurements were made at other temperatures, but in order to save space are omitted here. For a copy of these data, order Document 1561 from the American Documentation Institute, Offices of Science Service, 2101 Constitution Ave., Washington, D. C., remitting 23c for microfilm or 50c for photocopies readable without optical aid.

TABLE VI

ELECTRICAL PROPERTIES OF PViCl–Ph_2 80:20 SYSTEMS AT 55°

f	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
	No. 661		No. 659		No. 664		No. 680	
60	8.54	0.699	8.15	0.728	8.28	0.785	8.26	0.698
120	8.23	.775	7.82	.797	7.92	.874	7.94	.806
240	7.88	.867	7.44	.871	7.50	.949	7.55	.910
500	7.44	.980	7.01	.941	7.02	1.022	7.11	.985
1000	6.95	1.040	6.53	.965	6.51	1.045	6.54	1.061
2000	6.40	1.094	6.05	.986	5.99	1.036	5.96	1.073
3000	6.06	1.102	5.75	.980	5.69	1.019	5.64	1.058
6000	5.44	1.072	5.23	.942	5.14	0.953	5.05	0.999
10,000	4.94	0.999	4.80	.877	4.73	.878	4.63	.920
	No. 676		No. 679		No. 677		No. 678	
60	8.37	0.710	8.24	0.669	8.66	0.668	9.03	0.668
120	8.03	.813	7.93	.776	8.34	.811	8.69	.830
240	7.64	.917	7.56	.899	7.95	.953	8.29	1.007
480	7.20	.993	7.14	.976	7.47	1.082	7.78	1.168
1000	6.66	1.045	6.60	1.040	6.86	1.164	7.09	1.275
2000	6.11	1.065	6.05	1.063	6.24	1.193	6.40	1.305
3000	5.79	1.055	5.73	1.050	5.86	1.180	5.99	1.284
6000	5.21	0.993	5.15	0.999	5.21	1.102	5.26	1.192
10,000	4.76	.918	4.70	.925	4.71	1.009	4.73	1.082

treatment involved in preparing the samples for electrical measurements (sheeting, milling and pressing) had made any permanent change in the structure of the polymers, several of the samples were dissolved in mesityl oxide and acetone after the electrical measurements were completed. The polymer was then precipitated with methyl alcohol, washed and dried. Viscosities were then determined with the following results: no. 677, initial $[\eta]$ 3.64, final $[\eta]$ 3.55; no. 678, 2.21 and 2.20; no. 679, 5.79 and 5.97; no. 680, 5.44 and 5.72. These figures indicate that the average molecular weight was unchanged during the manipulation.

In order to determine accurately the frequency of the maximum, $\cosh^{-1}(\epsilon''_m/\epsilon'')$ was plotted[1] against the logarithm of the frequency. The data for all the samples studied gave good straight lines; a typical example (no. 676) is shown in Fig. 2. The values of $\log f_m$ were interpolated as the intersection of these lines with the horizontal axis, and are given in the fourth column of Table I. A plot of $\log f_m$ against weight per cent. of diphenyl,[7] at different temperatures, is very nearly linear, and gives $(\Delta \log f_m/\Delta\%)_{55°} = 0.276$; that is, an increase in diphenyl content of 1% nearly doubles the frequency for the maximum in ϵ'' at a given temperature in the composition range 10–20% Ph_2. This coefficient was used to calculate the values of $\log f_m$ at 20% Ph_2 for samples 676–680 from the observed values given for slightly lower diphenyl concentrations in Table I. The corrected values are as follows: no. 676, $\log f_m$ (20%, 55°) = 3.39; 677, 3.50; 678, 3.60; 679, 3.41; 680, 3.37.

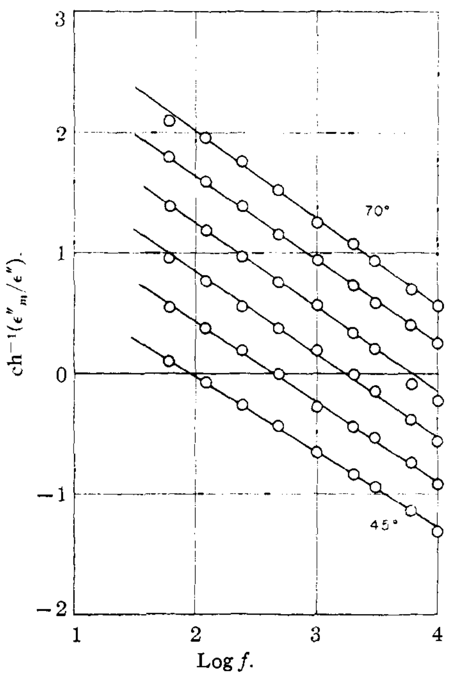

Fig. 2.—Test plot for PViCl–Ph_2, 80:20.

V. Discussion

The most significant result of this investigation is the verification of Eq. 3. As outlined in the introduction, a theoretical consideration of the behavior of long chain polymers leads to a distribution of relaxation times about a most probable time τ_0, which is proportional to the degree of polymerization. The reciprocal of the frequency f_m for maximum absorption is equal to $2\pi\tau_0$, and the molecular weight is proportional to $[\eta]$, the intrinsic viscosity. In Fig. 3, the values of $10^4/f_m$ at 55° for the different samples, fractionated and polydisperse, of Table I are plotted against the corresponding values of $[\eta]$.[13] A straight line through the origin averages the points quite satisfactorily, considering the fact that the ordinates are obtained through the logarithm of a frequency. (Any error here is much magnified, of course, because the $\mathrm{ch}^{-1}(\epsilon''_m/\epsilon'') - \log f$ plots determined $\log f_m$, and in Fig. 3, the ordinates are the antilogarithms of the *mantissas* of the interpolared logarithms whose characteristic is 3.)

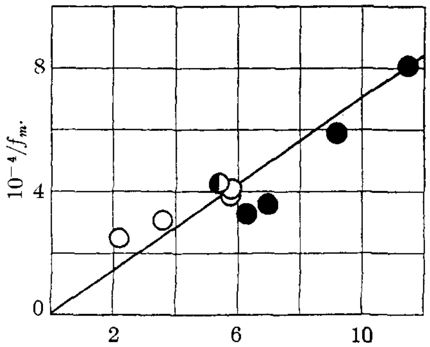

Fig. 3.—Proportionality between relaxation time and molecular weight.

Straight lines are also obtained when $1/f_m$ for the other temperatures measured is plotted against $[\eta]$. As might be expected from Eq. (3), the slopes decrease with increasing temperature, corresponding to a decrease of the internal viscosity of the plastic with increasing temperature. This decrease of viscosity causes the frequency for maximum absorption to increase with increasing temperature for a given composition. A plot of $\log f_m$ against $1/T$ is linear, and gives a molar energy of the order of 55–60 kcal, which is the same as that obtained for the coefficient of the d. c. conductance. This result suggests that internal viscosities in plastics might be very conveniently measured by following the d. c. conductance of known concentrations of known electrolytes added to them.

The fact that the fractionated and the polydisperse polymers both give approximately the same proportionality between τ_0 and $[\eta]$ is not surprising. For a system with a single time of relaxation, the maximum in $H(x)$, the in-phase component of the reduced polarization, is 0.500. For a monodisperse dilute polar polymer, $H_{\max.}$ drops to 0.286; that is, the distribution of relaxation times due to the convolutions of the polymeric chain lowers and broadens the absorption curve markedly. If a polydisperse polymer is assumed, with a chain length distribution given by

$$\phi(n) = e^{-n/\bar{n}}/\bar{n} \qquad (6)$$

the superposition of this distribution on the τ-distribution lowers H by only a small amount, *viz.*, to 0.267. In other words, the fact that *a* chain polymer is present is the important factor in determining the absorption; if the system is monodisperse, τ_0 and $[\eta]$ are proportional to the chain length n; for a polydisperse system, τ_0 and $[\eta]$ are proportional to the *average* chain length $\bar{n}$, and otherwise, little is changed.

As a matter of fact, the actual distribution in the systems described here is broader than either of the theoretical ones; the maximum H values are about 70% of the theoretical. Chain interaction, which was neglected in the theory by the assumption of dilute solutions, would further broaden the distribution of relaxation times beyond those calculated, because mechanical coupling by two chains crossing, for example, would give a structure in which the movement of either chain would affect the other, and the pair would have many more possible relaxation times than merely twice those for one of the chains.

The different polyvinyl chloride samples of Table I include a fairly wide variety of polymers, fractionated and polydisperse, covering a range of about five to one in average molecular weight. The one invariant physically is the presence of –C–Cl dipoles in all the polymers. We shall next calculate the moments $\tilde{\mu}$ per monomer unit,[1] and demonstrate that they are independent of the nature of the polymer.

In order to calculate the polarization P_2', values of the static dielectric constants ϵ_0 are necessary, and since they were not measured they must be obtained by extrapolation of the data to

(13) Some viscosities were determined in methyl amyl ketone and others in cyclohexanone. The absolute viscosities were, of course, quite different, but the values of $[\eta]$, which is essentially a per cent. viscosity change per mole, in the two solvents for the same polymer do not differ enough[6] to affect the argument here.

zero frequency. In the preceding paper of this series, it was shown that

$$\epsilon'' = \epsilon''_m \operatorname{sech} \alpha x \quad (7)$$

where

$$x = \ln f_m/f \quad (8)$$

and α is a distribution parameter, gave a satisfactory empirical representation of the data[7] for polyvinyl chloride systems (*cf.* Fig. 2). Then, given values of ϵ''_m and α, it was possible to compute ϵ_0, P_2' and hence $\tilde{\mu}$.

Recently, Cole has demonstrated that a method[14] which he applied to biological systems could also be used for other dielectric systems.[15] The Cole relationship is

$$(\epsilon - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty) = [1 + (i\omega\tau_0)^\beta]^{-1} \quad (9)$$

where

$$\epsilon = \epsilon' - i\epsilon'' \quad (10)$$

and β is a constant. (We have replaced Cole's $[1 - \alpha]$ by β, in order to prevent confusion with the α of Eq. 7.) Separating (9) into its two components, defined by (10), we obtain

$$\frac{2(\epsilon' - \epsilon_\infty)}{\epsilon_0 - \epsilon_\infty} = 1 - \frac{\sinh \beta x}{\cosh \beta x + \cos \beta\pi/2} \quad (11)$$

and

$$\frac{2\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{\sin \beta\pi/2}{\cosh \beta x + \cos \beta\pi/2} \quad (12)$$

with

$$\epsilon''_m/\epsilon'' = \frac{\cosh \beta x + \cos \beta\pi/2}{1 + \cos \beta\pi/2} \quad (13)$$

Data which fit (9) give a circular arc when ϵ'' is plotted against ϵ' at constant temperature. Examples are shown in Fig. 4 for several of the samples of Table I; in the figure, the ordinate scale is shifted two units for each curve to prevent crossing. Either (9) or (7) fits these data satisfactorily and extrapolates to nearly the same values of ϵ_0 and ϵ_∞, but for systems with a sharper distribution[16] of relaxation times, the hyperbolic secant plot shows distinct curvature while the Cole arc function still fits the data in the high temperature–low frequency range. The difference between the two functions is that (7) leads to

$$(\epsilon - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty) = [1 + i\,(\omega\tau_0)^\alpha]^{-1} \quad (14)$$

in place of (9); in view of Cole's argument that linear operations on a field $Ee^{i\omega t}$ should give the same functional behavior of i as of ω, (9) is preferable on theoretical as well as empirical grounds. We shall therefore use the arc function in obtaining ϵ_0 from the data.

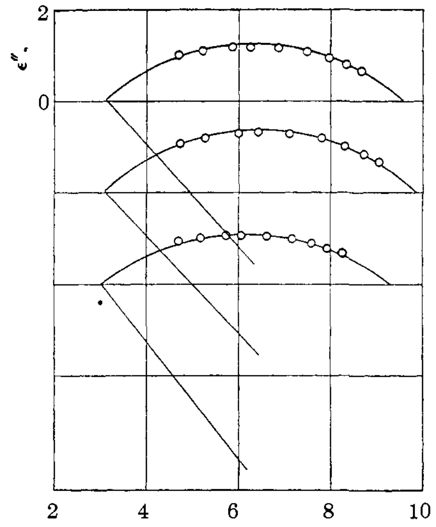

Fig. 4.—Test plots for Eq. (9), samples 677, 678 and 679.

The parameter β of (9) is the distribution parameter[17] of the system, and can be used to calculate the distribution function by the method of Fourier inversion.[1] When the parameter is small (wide distribution), and the frequency range covered by the data is not very wide (in our case, about 2.5 decades), Cole's graphical method of determining β is not very accurate. We present herewith two analytical methods of determining β, ϵ_0 and ϵ_∞ from the data.

The approximate linearity of the hyperbolic anticosine plots suggests one method, and since this plot is the best method for obtaining an accurate value of $\log f_m$, a method of obtaining β from it also seems worth while. If we assume that the loss factors fit (13), then a plot of ch^{-1}-$(e\epsilon\ /\epsilon'')$ against $\log f$ is a plot of the function $G(x)$, where

$$G(x) = \mathrm{ch}^{-1}\left[\frac{\mathrm{ch}\, \beta x + \cos \beta\pi/2}{1 + \cos \beta\pi/2}\right] = \mathrm{ch}^{-1}(\epsilon''_m/\epsilon'') \quad (15)$$

It can be shown that

$$(\mathrm{d}G/\mathrm{d}x)_{x=0} = \beta/\sqrt{2} \cos \beta\pi/4 \quad (16)$$

Hence if we plot $\mathrm{ch}^{-1}(\epsilon''_m/\epsilon'')$ against $\log f$, and determine the slope α where the curve (usually

(14) K. S. Cole, *J. Gen. Physiol.*, **12**, 37 (1928).

(15) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

(16) Unpublished observations on polyvinyl acetate, polyvinyl chloracetate and polymethyl methacrylate.

(17) Our work[2] on distribution functions was not available when Cole objected to the distribution interpretation of (9), on the grounds that a distribution was merely another empirical representation of the data, without physical significance. It has since been shown, however, that a distribution of relaxation times is a necessary physical consequence of polymeric structure.

nearly linear) crosses the log f axis (*i. e.*, at log f_m where $x = 0$), we have

$$\beta = \alpha \sqrt{2} \cos \beta\pi/4 \qquad (17)$$

Solutions of this transcendental equation are given in Table VII for the useful range of the variables.

TABLE VII

SOLUTIONS OF EQ. 17

β	α	β	α	β	α
0.10	0.0709	0.34	0.2492	0.58	0.4567
.12	.0852	.36	.2651	.60	.4762
.14	.0996	.38	.2811	.62	.4960
.16	.1140	.40	.2974	.64	.5164
.18	.1286	.42	.3139	.66	.5372
.20	.1432	.44	.3307	.68	.5586
.22	.1579	.46	.3477	.70	.5805
.24	.1728	.48	.3650	.72	.6030
.26	.1878	.50	.3827	.74	.6260
.28	.2029	.52	.4006	.76	.6497
.30	.2182	.54	.4189	.78	.6742
.32	.2336	.56	.4376	.80	.6992

A second method of determining the distribution parameter from the data is to use the logarithmic decrement of the $\epsilon'' - \log f$ curve, because this curve uniquely determines the distribution function through the Fourier transform.[18] After determining log f_m from a $\mathrm{ch}^{-1}(\epsilon''_m/\epsilon'') - \log f$ plot, the value ϵ''_{10} of ϵ'' at ($\log f_m \pm 1$) is interpolated on an $\epsilon'' - \log f$ plot. The value of ϵ'' at the maximum and its value one decade away determines β, because

$$P(\beta) = \epsilon''_{10}/\epsilon''_m = \frac{1 + \cos \beta\pi/2}{\cosh 2.303\beta + \cos \beta\pi/2} \qquad (18)$$

and given $P(\beta)$, we can solve the transcendental (18) for β. Solutions of this equation are given in Table VIII.

TABLE VIII

SOLUTIONS OF EQ. (18)

β	$P(\beta)$	β	$P(\beta)$	β	$P(\beta)$
0.20	0.9475	0.34	0.8522	0.48	0.7190
.22	.9366	.36	.8352	.50	.6977
.24	.9248	.38	.8174	.52	.6760
.26	.9121	.40	.7989	.54	.6542
.28	.8984	.42	.7798	.56	.6319
.30	.8839	.44	.7600	.58	.6096
.32	.8684	.46	.7397	.60	.5871

Having determined β by one of the above methods, ϵ_0 and ϵ_∞ are readily obtained. The equation

$$\epsilon_0 - \epsilon_\infty = 2\epsilon''_m \operatorname{ctn} \beta\pi/4 \qquad (19)$$

evaluates the difference between the static dielectric constant ϵ_0 and the square of the index of refraction ϵ_∞. Then

$$(\epsilon'_m - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty) = 1/2 \qquad (20)$$

where ϵ'_m is the dielectric constant at the frequency where ϵ'' reaches a maximum, evaluates ϵ_∞, which, with (19), determines ϵ_0. The three constants β, ϵ_0 and ϵ_∞ are thus determined from three data: the loss factor and dielectric constant at f_m and one other value of ϵ''.

In order to draw the graphs of Fig. 4, one simply marks ϵ_∞ and ϵ_0 on the ϵ' axis, and draws a circular arc connecting them, with its center at the point $[\epsilon'_m, -(\epsilon'_m - \epsilon_\infty) \operatorname{ctn} \beta\pi/2]$ in the $\epsilon' - \epsilon''$ plane. In all the cases investigated, the experimental points fell on the arcs so determined, which is excellent confirmation of (9), because a curve determined from three data fits all the data. The values of β for 55° are given in the sixth column of Table I.

Detailed results of the calculation outlined above for several of the samples are given in Table IX; similar results were obtained for the other samples. The last column gives the values of the moments $\tilde{\mu}$ per monomer unit.[19] As was observed before[7] in the previous study of PViCl–Ph_2 systems at different diphenyl concentrations, the values of $\tilde{\mu}$ are independent of temperature in the high temperature range. The average values of the moments for the different samples are given in the last column of Table I. The over-all average

TABLE IX

CONSTANTS FOR PViCl–Ph_2 80:20 SYSTEMS

	β	ϵ_0	ϵ_∞	μ
		No. 676		
50°	0.386	9.59	3.02	2.13
55	.399	9.62	2.97	2.16
60	.411	9.37	2.72	2.18
65	.407	9.24	2.25	2.26
		No. 677		
45	0.416	10.09	3.16	2.16
50	.442	9.67	3.17	2.12
55	.461	9.48	3.18	2.10
60	.477	9.08	2.94	2.07
65	.487	8.85	2.74	2.10
		No. 678		
50	0.464	10.22	3.22	2.20
55	.479	9.76	3.14	2.15
60	.512	9.31	3.25	2.07
65	.529	8.98	3.22	2.05

(18) If the approximation $H(x) = A\epsilon''$ is not justified, then a slightly more complicated calculation must be made. For the systems discussed here, however, $\epsilon'^2 >> \epsilon''^2$; see Eq. (20), ref. 1.

(19) The moments were calculated from ϵ_0 and ϵ_∞, using Equations (13), (74), (75) and (76) of ref. 1. For V, the molar volume, we used 53.3 cc.; the densities of the samples of Table I averaged to 1.33.

is $\tilde{\mu} = 2.17$, with a maximum deviation of 0.13. Within the experimental error, $\tilde{\mu}$ is independent of molecular weight, as anticipated.

The distribution parameters do not differ much from polymer to polymer. Except for no. 605, the fractionated polymers perhaps average to a slightly sharper distribution than the unfractionated; in view of the small theoretical difference between the values of H_{max} for the two cases[2] treated, this result seems reasonable. It is significant to note that β increases with increasing temperature; if the broadening of the experimental distribution over the theoretical is due to chain interaction, increased temperature would decrease interaction and hence sharpen the empirical distribution. It is interesting to compare the theoretical and empirical distributions. By applying the Fourier transform to (12), assuming that H and ϵ'' are proportional,[18] we obtain for systems satisfying (9)

$$2\pi F(s) = \sin \beta\pi/(\cosh \beta s + \cos \beta\pi) \qquad (21)$$

where $s = \ln \tau/\tau_0$. For most of the samples studied, β is about one-half; for the round value, the distribution function (21) becomes simply

$$2\pi F(s) = \operatorname{sech} s/2 \qquad (22)$$

as compared with the theoretical[2]

$$4F(s) = \operatorname{sech}^2 s/2 \qquad (23)$$

As can be seen in Fig. 5, the empirical curve is broader and lower than the one calculated for a monodisperse polar polymer in dilute solution. Further investigations of these systems should therefore be directed along two lines: experimental studies of more dilute systems, and a theoretical investigation of interaction in the more concentrated systems.

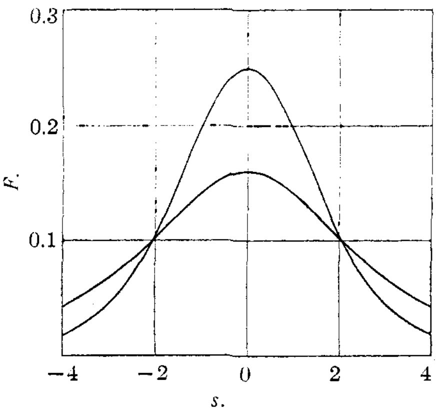

Fig. 5.—Distribution of relaxation times: upper curve, theoretical; lower curve, empirical.

Summary

1. The fractionation of polyvinyl chloride is described.

2. Electrical data over the frequency range 60–10,000 cycles at a number of temperatures are reported for different fractions of polyvinyl chloride, plasticized with 20% diphenyl. Data are also given for a number of unfractionated polymers of different average molecular weight. A range of about five to one in molecular weight was covered.

3. The most probable relaxation time of a polar polymer, as measured by the reciprocal of the frequency of maximum absorption at a given temperature, is proportional to the degree of polymerization.

4. The dipole moment per monomer unit in a linear polymer of the type $(\text{-}CH_2CHX\text{-})_n$ is independent of the degree of polymerization.

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