by volume, respectively, of tricresyl phosphate and dioctyl phthalate. While the hardness of these two compounds is about the same, the dioctyl phthalate sample has a lower brittleness point, and a lower loss factor than the tricresyl phosphate sample at all temperatures above 20°, making it of interest as a practical wire insulation compound. Additional data on this system will be published elsewhere.

V. Conclusions

The power loss in polyvinyl chloride–plasticizer systems can be separated into two parts: a loss due to dipole rotation and a loss due to ionic conduction—only the latter being reduced by the addition of stabilizers which prevent or retard the evolution of hydrogen chloride, or which neutralize hydrochloric acid.

A study of the effect of plasticizer content and temperature on the hardness and the dipole rotation loss suggests that mechanical deformation and dipole rotation involve activation energies of about the same order of magnitude. The size of the chain units that move as a unit in mechanical deformations appears to be of the same order of magnitude as the size of the chain units that move with the dipole rotations.

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

Electrical Properties of Solids. VI.[1] Dipole Rotation in High Polymers[2]

BY RAYMOND M. FUOSS

I. Introduction

As far as their electrical properties are concerned, linear polymers can be divided into two groups, polar and non-polar. The latter include hydrocarbons such as rubber, polyisobutylene, polystyrene and so on. Their dielectric constants are low and are insensitive to frequency and temperature; when free from polar or electrolytic impurities, they show no power absorption. Polar polymers form a much more interesting group: they include polymers in which dipoles are attached directly to the chain carbon atoms, such as in polyvinyl chloride and polyacrylonitrile, and polymers in which the dipoles are carried on side chains, such as in polyvinyl chloroacetate and polymethyl methacrylate. Their properties depend markedly on temperature and frequency. In general, the dielectric constant and loss factor are low at low temperatures or high frequencies. With increasing temperature or decreasing frequency, the dielectric constant goes through an inflection increase and the loss factor through a maximum. The height, width and location of the dispersion is determined by the chemical structure of the polymer and by the nature and amount of any second component present as plasticizer.

In this paper are presented the results of an experimental study of several polymeric systems. Polyvinyl chloride was chosen as an example of the polar polymer with chain dipoles, and poly-*p*-chlorostyrene as an example in which the dipoles are off-chain, that is, coupled to the polymer chain carbons by other atoms. These are in turn compared with a polar substance, *p*-chlorodiphenyl, dissolved in a linear non-polar polymer, polystyrene. The purpose of the work was to obtain an empirical description of several simple polymeric systems on which a theoretical explanation may eventually be built. Based on this work and work still in progress, we conclude that the dispersion and absorption in polar polymers is due to the motion of dipoles in what is effectively a medium of high viscosity.

Linear polymers represent a state of matter quite different from those dealt with in conventional physical chemistry: superficially, they appear to be solids, but they are neither crystalline solids nor glasses. In either of the latter solids, we can go from a given atom (or ion) to any other along electronic or ionic bond lines in a three dimensional network. (In molecular crystalline solids, there exists a three dimensional van der Waals bond network.) In the linear polymer, however, there are terminating sequences of primary valence bonds, and neighboring chains are held together by mechanical entanglement, although in some cases there may also be bonding

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[1] Paper V, THIS JOURNAL, **61**, 2334 (1939).

[2] A part of the material in this paper was presented at the Cincinnati meeting of the American Chemical Society, April 9, 1940.

of the magnitude of van der Waals forces between neighboring chains. The result is that locally the plastics behave in many ways like liquids while from the point of view of bulk properties, they are solids.

Qualitatively we can understand some of the properties of polar polymers. In a normal polar liquid, individual dipoles are in molecules which are mechanically free from one another, and we find the normal distribution of dipole orientations produced by the equilibrium between their mutual energies and the Brownian motion of the molecules carrying them. In the polar polymer, on the other hand, the dipoles of a given chain have a distribution of orientations which is determined by the spatial convolutions of that chain, and on which Brownian motion in the ordinary sense has little effect. The perturbation produced by an external field will then necessarily give different frequency properties for polar polymers as contrasted with polar liquids. Also, mutual compensation of dipoles by interaction of their fields ("association") will be impossible for dipoles on the same polymeric chain, unless they are off-chain dipoles carried on long side chains, and, even then, interaction will be hindered. For this reason, we expect and find higher static dielectric constants in linear polymeric solids than in the corresponding monomeric polar liquids in which there is no tie line of fixed length between dipoles.

Plasticization is the addition of a substance of relatively low molecular weight to a high polymer. The first thing which strikes one's attention is the specificity of polymer–plasticizer systems: for example, aromatic hydrocarbons and many esters, ethers and ketones are readily compatible with polyvinyl chloride, but aliphatic hydrocarbons or alcohols and polyvinyl chloride mix only like so much water and sand. Other analogies to liquid solutions have been observed and probably the analogs of saturation, consolute temperatures and the like exist for the polymer–plasticizer systems. Locally, at least, polyvinyl chloride–diphenyl or polystyrene–chlorodiphenyl behave much more like true solutions than mere mechanical mixtures, because the presence of the plasticizer greatly reduces resistance to molecular motion. Dipole rotation and ionic migration increase in freedom with increasing plasticizer content and simultaneously the resistance to bulk motion is decreased. A correlation between macroscopic mechanical properties and internal molecular dynamics is one of the most fascinating problems of the many yet unexplored in the field of high polymers.

The linear polymers possess another property which gives a clue to their structure. Below a definite temperature, called the brittle point, they break suddenly under an increasing tensile load, with no preliminary stretching. Above the brittle point, they stretch before breaking, in amounts which increase with increasing temperature. Preliminary experiments show that there is a discontinuity in the specific heat and density–temperature coefficient at this temperature. Electrically, the behavior is quite different in the brittle and the elastic ranges, as will be discussed in detail in a later section. At low temperatures, the polymeric chains seem to be tightly and closely interwoven, so that a disturbance of any sort is propagated readily throughout the volume, as in ordinary solids. Above the brittle point, internal motion becomes much freer, and individual parts of chains are able to move independently. To use the analogy with liquid systems, at the brittle point, an internal melting occurs, so that the polymer changes from a three-dimensional solid to a one-dimensional solid: that is, along the chain axis, the molecules behave like molecules in a solid, while perpendicular to the chain, they behave like liquids, so that superficially they appear to be solids, while, insofar as molecular motion is concerned, they are essentially liquids, with many of the properties of normal liquids.

II. Materials, Apparatus and Procedure.—The **polyvinyl chloride** was a sample of moderately low molecular weight. A solution in methyl *n*-amyl ketone at 20° had a viscosity of 1.05 cps. at a concentration of 0.05 m N (weight of polymer equal to 0.05 formula weights of monomer per liter of solution).[3] It was washed with hot alcohol to remove traces of hydrogen chloride and benzoyl peroxide or benzoic acid which might have been present. **Polystyrene** was used as received; according to the manufacturer, it had an average molecular weight of 80,000. **Poly-*p*-chlorostyrene** was prepared for us at the University of Illinois. The material as received was dissolved in toluene and precipitated from dilute solution by alcohol in order to separate unpolymerized monomer and probably some of the low molecular weight material. Three successive precipitations were made. From the viscosity of a benzene solution, the molecular weight of the crude material was reported as 26,000; that of the reprecipitated polymer was naturally larger.[4] The writer is indebted to

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(3) We are grateful to the Dow Chemical Company for this information.

(4) We gratefully acknowledge the coöperation of Professor C. S. Marvel in this work.

TABLE I

PREPARATION OF SAMPLES

Composition											
PViCl	PSt	PClSt	Ph_2	o-Cl	p-Cl	Times sheeted	Sheeting temp., °C.	Press time	Press temp.	ρ	n
100	0	0	0	0	0	0	...	4	150	1.41	1.57
80	0	0	20	0	0	2	110	5	130	1.30	1.55
0	80	0	0	0	20	4	70	2	80	1.06	1.60
0	90	0	0	0	10	4	100	8	120	1.06	1.60
0	0	100	0	0	0	0	...	5	135	1.21	1.61
0	0	91	9	0	0	0	...	5	125	1.21	..
0	0	80	20	0	0	0	...	3	120	1.21	..
0	0	89	0	5.5	5.5	2	100	5	120	1.21	..
0	0	80	0	10	10	4	70	5	80	1.21	..
0	0	80	0	20	0	0	...	4	95	1.21	1.58
0	0	80	0	0	20	0	...	4	120	1.21	1.58

Mr. E. H. Winslow of this Laboratory for analyses of the precipitated polymer. Samples were fused in the Parr bomb with sodium peroxide, and after the chloride was precipitated by silver nitrate, excess silver was determined by Volhard titration. Found: 25.1, 25.3% Cl; calcd. 25.6.

The plasticizers used were all recrystallized: diphenyl, m. p. 69.0°; *o*-chlorodiphenyl, m. p. 32.0°; *p*-chlorodiphenyl, m. p. 77.0°.

For electrical measurements, disks of the polymers 5 cm. in diameter and 1–2 mm. thick were made by hot-pressing the powders. In the case of the plasticized samples, weighed amounts of the plasticizers were dissolved in petroleum ether (b. p. <50°) and this solution was added to the polymer. Evaporation (finished by pumping as a precaution against entrapped solvent) of the ether gave a uniform distribution of the plasticizer through the polymer. The mixture was then hot-pressed into 10 mil sheets, cut, stacked and repressed several times in order to complete plasticization and to ensure thorough mixing. Then the test disks were pressed. Details of the thermal history involved in the preparation of the samples are summarized in Table I, where compositions are given as weight per cent. In order to make the table compact, the following abbreviations are used in the headings of the columns giving composition: PViCl, polyvinyl chloride; PSt, polystyrene, PClSt, poly-*p*-chlorostyrene; Ph_2, diphenyl; *o*-Cl, *o*-chlorodiphenyl; and *p*-Cl, *p*-chlorodiphenyl. Press times are given in minutes. The number of sheeting operations is given; each sheeting exposed the sample to press temperature for two minutes.

Densities (g./cc. at 30°) are given in the eleventh column. They were determined from the dimensions of the samples, measured by micrometer and vernier, and their weights. The last column gives the indices of refraction, measured on a Benford refractometer.[4a]

In order to obtain good electrical contact with the electrodes of the measuring cell, aqua-dag electrodes were painted onto the samples for the determinations in the 60–10,000 cycle range.

When the petroleum ether solutions of the plasticizers were added to polystyrene or poly-*p*-chlorostyrene, the powdered polymer soaked up the solution, and then within about thirty seconds turned into a rubbery mass from which ether, much depleted in solute, was exuded. The process reminds one very much of the partition of a solute between two solvents or possibly an adsorption. Either 10 or 20% diphenyl in polychlorostyrene gives transparent plastics at room temperature; equal parts by weight of diphenyl and polymer are transparent when hot but, on cooling, the diphenyl crystallizes out, giving an opaque white aggregate. Since diphenyl melts at 69°, the 10 and 20% samples are the analogs in polymeric systems of ordinary solutions. Further quantitative work is planned on these systems; the temperature coefficients of solubility will, of course, be particularly interesting.

The electrical measurements were made in a three terminal cell, similar in general design to one already described.[5] Copper was used in place of steel, for better heat conductance, and in order to maintain an inert surface, the electrodes were faced with thin sheet platinum. The copper electrodes were machined flat, and laid on a heavy copper block, which was heated until soft solder would flow on the electrodes. A layer of solder was wiped on, the 6-mil platinum sheet (previously pressed flat) was laid on the tinned surface of the electrode, and a hot block laid on top of the assembly, which was then allowed to cool. The platinum sheet was made slightly over-size, so that the final edge machining could be done on the faced electrodes. Finally the surfaces of the electrodes were polished flat.

For work in the range 20–105°, an oil-filled thermostat was used, where the temperature was held within ±0.02°. For lower temperatures, a petroleum ether-bath chilled by manual addition of solid carbon dioxide was used; the temperature fluctuations were at worst about one degree, which, however, were not serious, because the electrical properties changed only slowly with temperature in the low temperature range.

The bridges have already been described: the Schering bridge[6] was used for 60 to 1000 cycles, and the parallel bridge[7] for one to 10 kilocycles. One group of measurements were made on the radio-frequency bridge[8]; the help of Mr. S. I. Reynolds is gratefully acknowledged. All readings were made at fairly low voltages: up to 10 volts on the audio and radio frequency bridges, and up to 300 volts on the Schering bridge. In no case was the voltage high enough to cause heating effects.[9]

One experimental precaution is particularly important

[4a] Benford, *J. Optical Soc. Am.*, **29**, 352 (1939).

[5] Fuoss, *Trans. Electrochem. Soc.*, **74**, 91 (1938).

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

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

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

[9] Fuoss, THIS JOURNAL, **60**, 456 (1938).

All the compositions studied were thermoplastic, that is, flow when hot under pressure. Since the cell clamps exert a moderate pressure on the disk samples, some of them were compressed during measurement at higher temperatures. Also, due to elastic memory, distortion occurred in some cases. The initial cell constant was determined from the weight and diameter of the sample and its density. Its capacity and loss angle were determined at 60 cycles and 40°, where no change in dimensions with time was observed. Then electrical measurements at other temperatures were made, alternating with 40°–60 cycle readings. The loss angle is independent of sample geometry, and as long as it remained unchanged, assurance was given that no chemical change occurred in the sample. Capacity changes in the 40° checks were then taken to mean dimensional changes, and from the 40° capacity, the equivalent air capacity for the deformed sample could be calculated.

III. Experimental Results.—In order to show the properties of several typical systems, the 60-cycle temperature curves for polyvinyl chloride, for polyvinyl chloride–diphenyl, 80:20 and for poly-*p*-chlorostyrene–diphenyl 80:20 are given in Table II. Space is not available here for reproduction of the data at all frequencies and temperatures covered for the eleven systems investigated; they may be obtained, however, in tabular form as American Documentation Institute Document No. 1460*.

The samples containing polyvinyl chloride showed d. c. conductances which were measured on our d. c. bridge[10] when they were large enough to detect ($\gtrless 10^{-13}$ mho). Before calculating ϵ'', the a. c. loss factor, the d. c. conductance was subtracted from the total a. c. conductance at a given frequency; as previously pointed out,[11] this procedure assumes that the ionic conductance is independent of frequency. This assumption is only a first approximation, as will be shown later in the discussion. The d. c. conductances are given in Table III.

IV. Discussion.—The general dependence of the dielectric constants and loss factors on frequency and temperature of the systems investigated seems at first glance familiar: maxima in loss factors appear at definite frequency and temperature, accompanied by sigmoid increases in dielectric constant. More careful examination, however, shows that the dispersion and absorption are not describable by a simple Debye mechanism; four differences appear: (1) the decrement of the ϵ''–log f curves is too small; (2) the inflection slope of the ϵ'–log f curves is too small; (3) the maximum value of ϵ'' is much less than half the difference between the static dielectric constant and the square of the index of refraction and (4) the ϵ''–T and ϵ'–T curves for low temperatures are entirely different from the curves obtained by extrapolation of data from higher temperatures.

TABLE II

ELECTRICAL PROPERTIES OF POLYMERIC SYSTEMS AT 60 CYCLES

	PViCl		PViCl-Ph$_2$ 80:20		PClSt-Ph$_2$ 80:20	
t	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
−30	3.038	0.0538	2.820	0.0138	...	...
−20	3.092	.0587	2.836	.0162	...	...
−10	3.149	.0617	2.856	.0194	...	...
0	3.209	.0629	2.884	.0236	...	...
10	3.270	.0611	2.927	.0316	...	...
20	3.330	.0586	3.046	.0688	...	...
25	....	....	3.271	.173	...	...
30	3.395	.0543	3.709	.367	...	...
35	....	....	4.536	.714	...	...
40	3.456	.0494	5.85	1.034	2.790	0.053
45	....	....	7.08	1.043	...	...
50	3.525	.0444	8.02	0.810	3.008	.176
55	....	....	8.52	.563	3.211	.255
60	3.600	.0405	8.74	.395	3.477	.309
65	3.637	.0386	8.82	.322	3.748	.285
70	3.69	.041	8.82	.314	3.927	.186
75	3.81	.060	...	....	3.987	.091
80	4.12	.142	...	....	3.971	.039
85	4.73	.340	...	....	3.936	.017
90	5.95	.735	...	....	...	...
95	7.70	1.149	...	....	...	...
100	9.27	1.204	...	....	...	...
105	10.35	1.020	...	....	...	...

TABLE III

D. C. CONDUCTANCES

	PViCl—No. 601		PViCl-Ph$_2$
	$10^{10}\kappa_0$	t	$10^{10}\kappa_0$
100	0.032	45	0.0015
105	.142	50	.0054
PViCl	No. 604	55	.0154
95	0.0056	60	.039
100	.022	65	.088
105	.067	70	.188

Figures 1 and 2 summarize the 60-cycle data for unplasticized polyvinyl chloride. The loss factor reaches a maximum of only 1.22 at 98°; the low temperature dielectric constant in Fig. 1 apparently levels off at about 3.6, which is much higher than 2.6, the square of the index of refraction, and estimating by symmetry from Fig. 1, the static dielectric constant is at least 13. As a function of frequency, the 100° data are shown as the top curve of Fig. 3, where $\epsilon''/\epsilon''_{\max}$ is plotted

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* For a copy of the tables, order Document 1460 from the American Documentation Institute, Offices of Science Service, 2101 Constitution Ave., Washington, D. C., remitting 33¢ for microfilm or $1.50 for photocopies readable without optical aid.

(10) Fuoss, THIS JOURNAL, **60**, 451 (1938).

(11) Fuoss, *ibid.*, **61**, 2329 (1939).

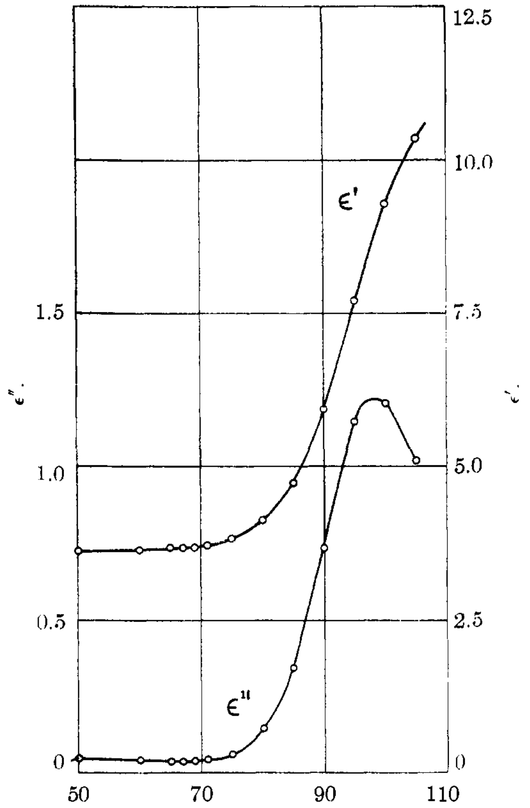

Fig. 1.—Properties of polyvinyl chloride at 60 cycles.

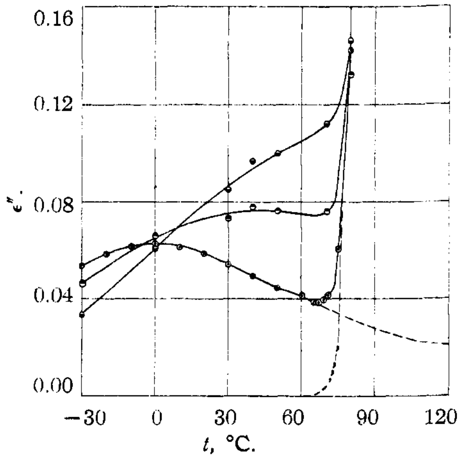

Fig. 2.—Low temperature properties of polyvinyl chloride: O, 60 cycles; ●, 1000 cycles; ◒, 10,000 cycles.

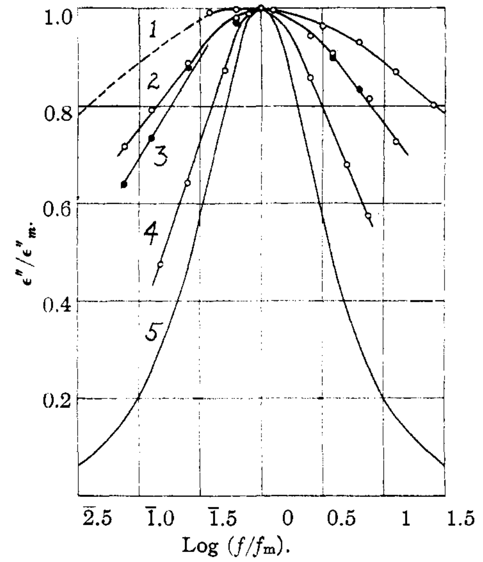

Fig. 3.—Frequency curves: 1, polyvinyl chloride; 2, polyvinyl chloride–diphenyl 80:20; 3, polychlorostyrene–diphenyl 80:20; 4, polyvinyl chloroacetate; 5, Debye absorption curve.

against log f/f_m. It is immediately obvious that the absorption curve is much blunter for polyvinyl chloride than that corresponding to a Debye dispersion, which is shown in the same figure as the innermost (and sharpest) curve.

Examination of the low temperature data (shown in Figs. 2 and 4) shows that a complete change in the electrical properties occurs at about 70°. The rate of decrease of ε' with decreasing temperature suddenly slows down to a practically linear dependence, and the 60-cycle loss factor goes through a distinct minimum. Toward lower temperatures, ε'' slowly rises again to a blunt maxi-

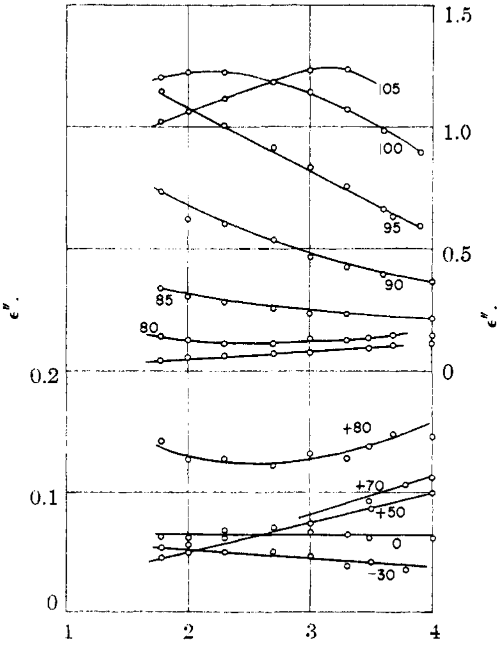

Fig. 4.—Loss factors of polyvinyl chloride as functions of temperature and frequency.

mum at zero, which is quite unlike the sharp maximum at 98°. An idea of the width of the dispersion can be had from the fact that ϵ' decreases from 3.395 at 30° and 60 cycles to 3.038 at $-30°$, or only about 10%, and the square of the index of refraction is 2.6. The low temperature maximum shifts to higher temperature and becomes higher with increasing frequency; at about 2000 cycles, a horizontal inflection appears, where minimum and maximum have coalesced and above 2000 cycles, only a change of curvature is visible. The curves of Fig. 2 are strongly reminiscent of critical curves. The interval 60–80° contains a transition point for polyvinyl chloride: above 80°, the properties are sharply sensitive to temperature, while below 60° they change only slowly. Now 80° is the brittle point of polyvinyl chloride.[12] In the low temperature range which is defined by the electrical properties, internal motion is obviously much restricted and, macroscopically, the solid is brittle. In the high temperature range, the chlorine dipoles are free to follow an external field; if the static dielectric constant were measured, one would predict from the behavior under alternating fields a sudden increase in it at the brittle point because ϵ'' shows an almost exponential increase at all frequencies at that temperature.[12a] Macroscopically, the solid becomes elastic and plastic above the brittle point, showing that increased internal freedom of motion is mirrored by decreased bulk rigidity.

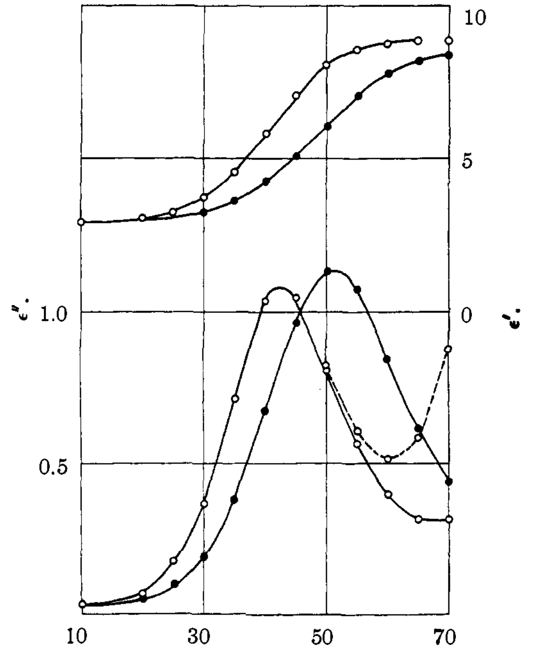

Fig. 5.—Polyvinyl chloride–diphenyl 80:20; ○, 60 cycles; ●, 1000 cycles.

The thermal behavior of the material in the transition range is extremely interesting. Outside this range, a change of thermostat temperature is accompanied by a change of ϵ' and ϵ'', the rate of which is determined by the heat conductivity of cell and sample. (We recall that the samples are thin disks in a copper cell immersed in oil.) But if the temperature is changed from, say, 70 to 75°, the dielectric constant and loss factor take nearly an hour after the regulator is set for 75° to approach steady values. Similar drifts in density have been observed for polystyrene[13] in the range of temperature where the density–temperature coefficient shows a discontinuity, and Russell[12] has shown that this temperature also coincides within the experimental error with the brittle point of polystyrene. If one visualizes the process as a distribution of thermal energy over the chains, the effects can be understood. At low temperatures, the chains are closely packed and tightly coupled, so that kinetic energy is easily transferred; at high temperatures, kinetic energy is transferred readily along chains, but different chains are no longer closely coupled, and it requires a long time (diffusion rate) for energies to average themselves out. Normal Brownian motion in the case of long linear polymers is clearly impossible: instead we find local fluctuations in energy passing along the chains. The loosening of structure at the brittle point is probably also visible in the specific heat; the writer hopes to test this hypothesis experimentally.

The properties of polyvinyl chloride plasticized with 20% diphenyl are shown in Fig. 5. We note first that the 60 cycle maximum in ϵ'' now appears at 43°, as compared with 98° for the pure polymer, and the static dielectric constant drops to about 9. Also the width of the dispersion is narrower (Fig. 3). The effect of the plasticizer can be described as a very great reduction in in-

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(12) J. J. Russell, *Ind. Eng. Chem.*, **32**, 509 (1940).

(12a) After this paper was submitted for publication, the writer's attention was called to a comprehensive study of a glycol phthalate resin by C. G. Garton, *J. Inst. Elec. Engrs.*, **85**, 625 (1939). Garton observed a rapid increase in the static dielectric constant of his resin from 3.75 to 8.90 in the temperature range where his a. c. properties indicate a transition of the type reported here for polyvinyl chloride.

(13) Patnode and Scheiber, THIS JOURNAL, **61**, 3449 (1939).

ternal viscosity. In order to analyze the data, we may define a variable x by the equation

$$\epsilon''/\epsilon''_{\max} = 2x/(1 + x^2) \qquad (1)$$

As is seen in Fig. 3, the absorption obviously does not satisfy a Debye mechanism, but we may use the form of Equation (1), provided x is not given the simple Debye value of $\omega\tau$. However, x will still be a measure of resistance to dipole motion, and we shall investigate the properties of the quantity so defined.

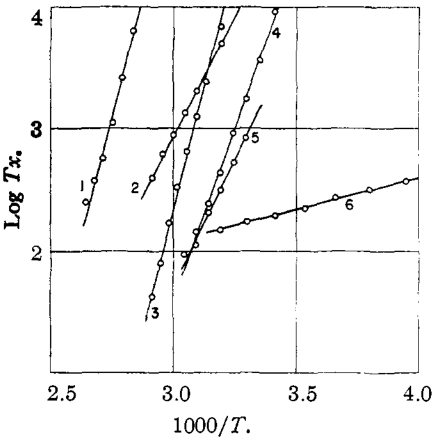

Fig. 6.—Test plots for: 1, polyvinyl chloride; 2, polychlorostyrene-*p*-chlorodiphenyl 80:20; 3, polyvinyl chloroacetate; 4, polyvinyl chloride–diphenyl 80:20; 5, polychlorostyrene-*o*-chlorodiphenyl-*p*-chlorodiphenyl 80:10:10; 6, polyvinyl chloride at low temperatures.

For many liquids, the logarithm of the viscosity is a linear function of reciprocal absolute temperature. If we calculate x from the 60-cycle data of Table II for polyvinyl chloride–diphenyl 80:20, and plot log Tx against $1/T$, we obtain the straight line 2 of Fig. 6. In other words, x defined by (1) satisfies the empirical relationship

$$\log Tx = A + B/T \qquad (2)$$

If we define an energy Q by the usual equation $Q = BR$, we find for curve 2 of Fig. 6 $Q = 27$ kcal., which is the order of a viscosity "energy of activation." A similar plot for unplasticized polyvinyl chloride gives line 1 in Fig. 6; its slope corresponds to $Q = 43$ kcal. In fact, all the systems studied give linear log Tx–$1/T$ plots. Our hypothesis that x of Eq. (1) is a measure of internal viscosity thus seems justified. Further confirmation is found in the temperature dependence of the d. c. conductance κ_0, which is a measure of the internal resistance to translational motion. In Fig. 7, log κ_0 for the 80:20 sample is plotted against $1/T$. The plasticized polyvinyl chloride gives a slightly concave-down curve, for which an average Q of about 40 kcal. can be calculated. (The d. c. conductance is presumably due to traces of hydrogen chloride released by pyrolysis of the polyvinyl chloride during preparation of the sample[5,11].) Polyvinyl chloroacetate[14] gives an excellent straight line on the same plot. We therefore conclude that the electrical properties of the polar polymer are due to relaxation effects of its dipoles, because the temperature dependence of the loss factor is describable by a variable which behaves like a viscosity.

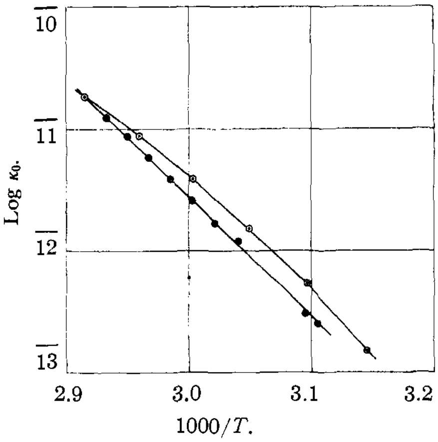

Fig. 7.—D. c. conductances: ⊙, polyvinyl chloride–diphenyl 80:20; ●, polyvinyl chloroacetate.

A similar analysis also can be made for the low temperature maximum: again we can calculate x values from the definition of Eq. (1), and again log Tx–$1/T$ is linear, as is shown by curve 6 of Fig. 6. But its striking difference from the high temperature maxima is obvious: it is best shown by the fact that for it, $Q = 2.45$ kcal., which is of the order of the energy associated with van der Waals forces. When this figure is compared with the 43 kcal. associated with the high temperature maximum, the conclusion is inescapable that the low temperature state is physically entirely different from the high temperature state of the polymer. The transition temperature can be interpreted physically as the one at which the chains become free to slip past each other.

As stated above, however, the high temperature dispersion is not due to a simple Debye mechanism, in which only one time of relaxation is present. This is clearly shown in Fig. 3: the ϵ''–frequency curves for the polar polymers are

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[14] Details to be presented in a later communication.

all much wider than the Debye curve. Wagner[15] proposed a gaussian distribution of times of relaxation about a most probable value in order to describe absorption currents in dielectrics, and Yager[16] developed a method of calculating the distribution coefficient b from the frequency dependence of ϵ' and ϵ''. For polyvinyl chloride, Yager's test plots are approximately linear; the distribution coefficient obtained is 0.17. This value corresponds to an extremely broad distribution; if τ_0 is the most probable time of relaxation of Wagner's equations, then for polyvinyl chloride, we would have only 42% of all the times in the range $10\ \tau_0 \geqslant \tau \geqslant \tau_0/10$ and for $100\ \tau_0 \geqslant \tau \geqslant \tau_0/100$, 27% of the total number of dipoles are still unaccounted for. There are, however, practical difficulties in the use of the Wagner distribution: the static dielectric constant determined by extrapolation of Yager's equations is considerably larger than the square of the index of refraction, and the test plots show systematic deviations from linearity. The latter objection can, of course, be met by assuming an unsymmetrical distribution function, but such *post factum* assumptions involving more arbitrary constants reduce in last analysis to exercises in arithmetic. In any case, the first objection is fundamental.

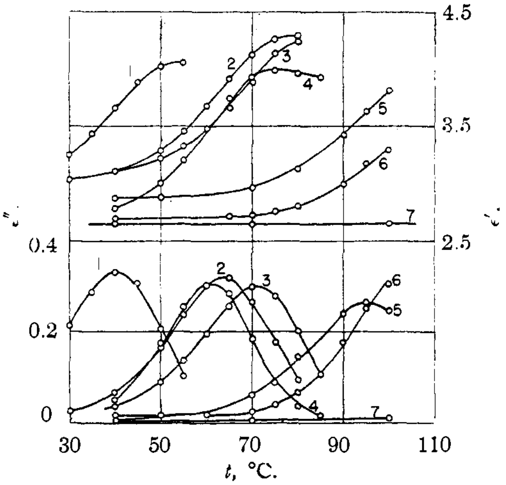

Fig. 8.—Electrical properties at 60 cycles of polychlorostyrene: 1, 10 *o*-chlorodiphenyl plus 10 *p*-chlorodiphenyl; 2, 20 *o*-chlorodiphenyl; 3, 20 *p*-chlorodiphenyl; 4, 20 diphenyl; 5, 5 *o*-chlorodiphenyl plus 5 *p*-chlorodiphenyl; 6, 9 diphenyl; 7, unplasticized.

A distribution of relaxations may well be involved, but the correct one remains to be proposed. The phenomenological objection to the Wagner theory is that it implies a physical system in which we have a distribution of times of relaxation, each characteristic of a group of dipoles *which individually behave normally;* the broad dispersion is simply the resultant of their simultaneous response to an electric field. But for reasons which have already been given, it seems impossible to have normal dipole behavior in polar polymers: the dipoles are anchored to the chain instead of being on free rotors, and the fundamental Boltzmann equilibrium underlying Debye's theory for polar liquids must be replaced by the proper orientation distribution for dipoles on a random polymer chain.

Returning now to the data for plasticized polyvinyl chloride (Fig. 5), another very interesting property is found. The dotted curve represents the loss factors calculated from the *total* a. c. conductance. If the measured d. c. conductance is subtracted from the a. c. conductance, the solid curve is obtained. But the resulting curve at 60 cycles *is not symmetrical* about its bisector through the apex: the high temperature side still shows a tendency to a minimum. With increasing frequency, the curves become more symmetrical. This lack of symmetry at low frequencies is directly traceable to the previously observed[17] correlation between a. c. properties and d. c. conductance in the system polyvinyl chloride–tricresyl phosphate. There it was found that both ϵ' and ϵ'' were linear in the square root of d. c. conductance. The only possible conclusion is that the ionic motion is not in phase with the field and consequently ionic behavior in plastic solids differs markedly from that in liquid solutions. A possible explanation is that the ions in these media of extremely high viscosity are, for low frequency fields, effectively bound to equilibrium positions; another is that they do not reach terminal velocity in a quarter cycle. More data bearing on this problem are emphatically needed.

In Fig. 8 are shown the results for poly-*p*-chlorostyrene, where ϵ' and ϵ'' for 60 cycles are plotted against temperature. Over the temperature range covered, the pure polymer has a dielectric constant practically equal to the square of the index of refraction, and loss factor is small. However, it shows signs of an accelerated increase at 100°; the 60-cycle maximum is prob-

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(15) Wagner, *Ann. Physik*, **40**, 817 (1913).

(16) Yager, *Physics*, **7**, 434 (1936).

(17) Fuoss, This Journal, **61**, 2334 (1939).

ably at about 150°. If the internal viscosity is decreased by adding plasticizer, the maximum appears at lower temperatures. With 9% diphenyl, it appears at 100°, and with 20% diphenyl at 62°. The corresponding log Tx–$1/T$ plots (Fig. 6) are linear, with Q values in the range 20–30 kcal. It is interesting and significant that the chlorodiphenyls, which are polar, have about the same effect on the polymer as diphenyl which is non-polar. If $\epsilon''/\epsilon''_{\max}$ is plotted against $(T - T_{\max})$, the different polychlorostyrene systems give points all of which lie practically on the same curve. As far as the dipoles of polychlorostyrene are concerned, the effect of the plasticizer is simply to reduce the internal viscosity; the response of the plasticizer dipoles comes at quite a different set of independent variables, as the work on chlorodiphenyl in polystyrene will show.

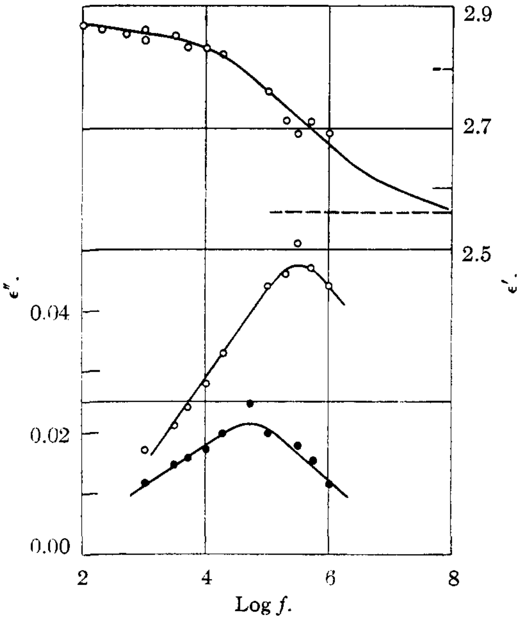

Fig. 9.—Polystyrene with p-chlorodiphenyl: ●, 10%, O, 20%.

The ϵ''-frequency curves for the polychlorostyrene systems are uniformly sharper than those for the polyvinyl chloride systems; this difference is undoubtedly due to the fact that the dipoles in polyvinyl chloride are attached directly to the chain carbons, while in the polychlorostyrene, they are attached to the chain through a benzene ring, which gives them more freedom of motion with respect to the chain. In polyvinyl chloroacetate,[14] where the dipole is carried on a still more flexible side chain, the ϵ''-frequency curves are very sharp, almost as sharp in fact as in a polar liquid (Fig. 3). It was also noted that the ϵ''-frequency curves become sharper with increasing temperature, as might be expected from the hypothesis that the properties are due to the motion of dipoles bound to a long carbon chain. Another generalization can be made: when the ϵ''–T curve is blunt, the ϵ''–f curve is sharp, and *vice versa.*

If we dissolve a polar substance of low molecular weight, such as p-chlorodiphenyl, in a non-polar polymer, we would expect a dispersion region at a higher frequency for a given temperature than for dipoles attached to the polymeric chain by primary valence bonds. The data for p-chlorodiphenyl in polystyrene bear this out. As shown in Fig. 9, 10% chlorodiphenyl in polystyrene has its maximum in absorption at room temperature at about 50 kilocycles and 20% at 300 kilocycles. The maximum for 20% comes at a higher frequency than for 10% because the viscosity is lower in the former. Now if $\epsilon''/\epsilon''_{\max}$ is plotted against $\log f/f_{\max}$ for these two systems, and also for plasticized polychlorostyrene, all the points lie on one curve. Consequently, the same mechanism is operating in both cases: a chlorine attached to a benzene ring is moving in an a. c. field, in a medium of very high viscosity. If we plot log $f_{\max}$, which is also a measure of viscosity against $1/T$, a significant difference appears: the effective viscosity for the chain dipoles is higher at ordinary temperatures and has a much higher temperature coefficient than that for the dissolved dipoles. This is to be expected, but the coincidence of the $\epsilon''/\epsilon''_{\max}$–log $f/f_{\max}$ curves for the two systems shows that the mechanics of di-

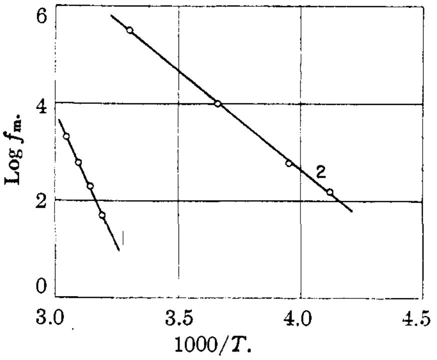

Fig. 10.—Temperature dependence of frequency for absorption maximum: 1, polychlorostyrene–o-chlorodiphenyl-p-chlorodiphenyl 80:10:10; 2, polystyrene–p-chlorodiphenyl 80:20.

pole rotation are the same in both cases. Apparently the chlorodiphenyl molecules are locked into an arbitrary distribution by the surrounding polymeric chains. It will be interesting to study other polar solutes in non-polar polymers in order to determine the effect of size and shape of the solute molecule on a. c. properties.

The identity of the field sensitive groups in the two systems discussed above is confirmed by the heights of the absorption maxima: they are proportional to the chlorine content, as shown in Table IV. This result is clear proof that the a. c. properties of polar polymers are due to the response of the dipoles to the field, and the identity of the polar group in the polymer is established.

TABLE IV

ABSORPTION MAXIMA IN CHLORINE SYSTEMS

System	% Cl	$\epsilon''_{\max}$	$\epsilon''/\%$
Polystyrene–chlorodiphenyl 90:10	1.88	0.021	1.12
Polystyrene–chlorodiphenyl 80:20	3.76	0.047	1.25
Polychlorostyrene–diphenyl 80:20	20.5	0.305	1.50

Summary

1. The a. c. properties at 60–10,000 cycles over a wide temperature range have been determined for the following systems: polyvinyl chloride; polyvinyl chloride–diphenyl 80:20; polystyrene; polystyrene–*p*-chlorodiphenyl 90:10 and 80:20; poly-*p*-chlorostyrene, alone and with various amounts of diphenyl, *o*-chlorodiphenyl, *p*-chlorodiphenyl and mixtures of the last two.

2. The above systems show characteristic maxima in absorption and dispersion in dielectric constant, which are determined by the size and strength of the polar group, by the length and flexibility of the bond of the polar group to the polymer chain, and by the nature and amount of a second component present as plasticizer.

3. The fundamental mechanism of a. c. response is dipole rotation in a medium of high viscosity; it differs from the mechanism obtaining in ordinary polar liquids in that simple rotatory Brownian motion must be replaced by internal rotatory Brownian motion related to the change in convolutions of the polymeric chain.

4. The primary effect of changing temperature is to change the internal viscosity.

5. A transition temperature has been found in the case of polyvinyl chloride at which a process best described as an internal melting occurs.

SCHENECTADY, N. Y. RECEIVED MAY 7, 1940

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Electrical Properties of Solids. VII. The System Polyvinyl Chloride–Diphenyl

BY RAYMOND M. FUOSS

I. Introduction

A plastic containing 20 parts diphenyl and 80 parts polyvinyl chloride by weight was described in the previous paper of this series.[1] Its properties differed markedly from those of polyvinyl chloride alone: The value of the high temperature–low frequency dielectric constant was lowered, the absorption peak for a given frequency was shifted to lower temperatures by about 60° (which corresponds to many decades change in viscosity), and the shapes of the low temperature dielectric constant and loss factor curves were completely altered. Polyvinyl chloride shows a minimum in 60 cycle loss factor at 65° which is located between a broad low maximum at 0° and a sharp high one at 98°, while the curve for P-ViCl-Ph$_2$ 80:20 has a sharp high maximum at 42.5°, and is monotone, descending from there to $-70°$, with no indication of a low temperature maximum. These differences all suggested that it would be interesting to explore the range 0–20% diphenyl in some detail, in order to see how the transitions occurred.

The most striking result of the investigation was the non-linearity of the properties of the system in composition. As far as the low temperature changes are concerned, about half of the transition from the curve characteristic of polyvinyl chloride to that for the 80:20 system occurs with the addition of the first 5% diphenyl, and about one-third with only the first 1% diphenyl in the plastic. One per cent. diphenyl corresponds roughly to one diphenyl molecule to 250 monomeric (—CH$_2$CHCl—) units. The high temperature properties also change rapidly with the first

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[1] Fuoss, THIS JOURNAL, **63**, 369 (1941).