

Summary

1. The acid catalyzed hydrogen exchange reaction of 1-dimethylaminonaphthalene is greatly retarded by a chloro or nitro group in the 8 position. 1,8 - Bis - dimethylaminonaphthalene exchanges hydrogen more slowly than the 1,5 isomer. These observations support a mechanism previously advanced.

2. Carbazole and acridane derivatives are less reactive in hydrogen exchange than the corresponding diphenylamine derivatives. The role of steric factors is discussed.

3. N-Methylacridane also exhibits a base catalyzed exchange reaction which is thought to involve the methylene hydrogen atoms.

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Dielectric Properties of Plasticized Polyvinyl Chloride

By J. M. DAVIES, R. F. MILLER AND W. F. BUSSE

I. Introduction

Plasticized γ -polyvinyl chloride¹ (Koroseal) has physical properties such as toughness, flexibility, oil-resistance, non-inflammability, as well as high electrical resistance, which make it very valuable as an insulator and a protecting sheath for electrical conductors.^{2,3,4} It is also important from the scientific standpoint because changes in each of three variables—frequency of the current, temperature and ratio of γ -polyvinyl chloride to plasticizer in the sample—can be made to produce roughly equivalent changes in dielectric properties. This offers the possibility of using this system to gain more information about the general theories of energy loss in dielectrics, and, perhaps, also of using the available theories of dielectric loss to get information about the molecular structure of the γ -polyvinyl chloride-plasticizer systems.

In general, the dielectric constant of these systems is about 3 at sufficiently low temperatures, or low plasticizer contents, or high frequencies. If the temperature or the plasticizer content is raised, or the frequency lowered enough, the dielectric constant increases to a high value of 8 to 12, depending on the kind and amount of plasticizer. In the region where the dielectric constant changes most rapidly, the loss factor reaches a maximum, as required by all theories of dielectric loss.

Previous work⁵ on the dielectric properties of

(1) Semon, U. S. Patent 1,929,453, October 10 (1933).

(2) Brous and Semon, *Ind. Eng. Chem.*, **27**, 667 (1935).

(3) Schoenfeld, *Trans. Am. Inst. Chem. Eng.*, **35**, 447 (1939).

(4) Schoenfeld, Browne and Brous, *Ind. Eng. Chem.*, **31**, 964 (1939).

(5) Davies and Busse, "Conference on Electrical Insulation," National Research Council, Cambridge, Mass., meeting, 1939 Annual Report, p. 30.

samples having a wide range of plasticizer (tricresyl phosphate) content at a wide range of temperatures, suggested that there might be a relation between the dielectric properties and the mechanical flexibility of the samples having various amounts of any one plasticizer. By varying the plasticizer content at any one temperature, or varying the temperature at any one plasticizer content, the hardness can be varied over a very wide range—from a hard, tough, horny product to one that is soft, flexible and elastic. However, when the samples of different plasticizer contents were compared at the respective temperatures at which each showed its dielectric loss maximum, the hardness of the samples, as measured by a durometer, was found to be roughly the same.

Because the dielectric measurements were made on unstabilized samples, and because the durometer is not an ideal hardness measuring instrument, this work was repeated and extended using stabilized samples, and measuring the hardness in absolute units by a method developed in this Laboratory.⁶ In addition, data are presented on the direct current resistance of these systems, and on the dielectric properties of some samples with plasticizers other than tricresyl phosphate. Some more fundamental interpretations of the data are suggested.

II. Preparation of Samples.—Three series of samples were prepared by adding commercial γ -polyvinyl chloride to dimethylthianthrene, tricresyl phosphate, and, in a few cases, dioctyl phthalate, as plasticizers. Samples containing 46%, by volume, dimethylthianthrene were prepared with and without the addition of 0.8%, by volume, of lead silicate as stabilizer. Seven concentrations of tri-

(6) Larrick, Meeting of the Rheology Society, Akron, Ohio, 1937; *Phys. Rev.*, **57**, 358 (1940). In this reference the equation is misprinted.

creryl phosphate were used varying in 10% steps from 0 to 60%, by volume, with 100 to 40%, respectively, of polyvinyl chloride. Each sample also contained about 0.5%, by volume, of litharge. A few samples were prepared with dioctyl phthalate as plasticizer and 1.5% lead silicate as stabilizer.

The powdered γ -polyvinyl chloride was first mixed with stabilizer and plasticizer in a mixing-bowl, and then milled and molded to the proper shape in a press at a suitable temperature. The unplasticized samples were molded by pressing the unmilled powder for ten minutes at 310°F. between flat plates with 0.1 inch stops. The plasticized samples were milled fifteen minutes at 240°F. and molded ten minutes at 297°F. to give sheets 0.1 inch thick and 6 inches in diameter for the electrical tests. The hardness tests were made on samples 0.5 inch thick and 2 inches in diameter, molded fifteen minutes at 297°F.

III. Testing Procedure.—The measurements on these samples included dielectric constant and loss factor at 15, 60 and 1000 cycles per second, direct current resistivity and hardness at various temperatures from -15 to 120° .

Most of the alternating current measurements were made with a General Electric Schering bridge^{7,8} at 15, 60 and 1000 cycles per second with 100 volts across the sample. A General Radio beat frequency oscillator was the source for 1000 and 15 cycle-per-second currents, using a filter at the lower frequency, while the 60 cycle-per-second current was obtained from the power line. The direct current measurements were made at 225 volts, using a high-sensitivity galvanometer circuit. The dimethylthianthrene stocks were measured at 1000 cycles per second with a General Radio capacity bridge.

The dimethylthianthrene stocks were measured without surface treatment and without a guard ring. The tricresyl phosphate and dioctyl phthalate stocks were coated with Aquadag and a guard ring was provided on one side by cutting a ring about 0.02 inch wide at a diameter of 3.5 inches. The electrodes consisted of an unguarded top electrode 4.5 inches in diameter, and a bottom assembly of an inner guarded electrode 3.45 inches in diameter and

an outer guard electrode 3.64 inches inside diameter, and 4.5 inches outside diameter, all gold-plated. These electrodes were mounted in a circulating air oven, with the leads and the lower electrodes completely shielded. The oven was heated electrically or cooled with air passed through coils in a low temperature bath. At temperatures above about 75° , some mechanical distortion and shrinking of the samples occurred, so the dimensions of the samples were remeasured after tests at the higher temperatures.

The hardness measurements were made using a dead-load indenter with 2 to 4 lb. on a $1/2$ -inch diameter ball.⁹

IV. Results

The dielectric constant and loss factor of the two dimethylthianthrene stocks are given in Fig. 1. The rise in the dielectric constant and the accompanying maximum in the loss factor are typical of results obtained with many solid waxes and resins which contain polar groups.^{9,10} While this loss undoubtedly is due to rotation of dipoles, it is much more difficult to determine the precise mechanism of the loss in solid bodies than it is in liquids.^{11,12,13}

The second rise in the power loss curve at higher temperatures is due to ionic conduction, as evidenced by the accompanying rise in direct current conductivity. The addition of lead silicate to this compound reduces the ionic conductivity considerably without appreciably affecting the dipole loss or dielectric constant. The amount of stabilizer used in these tests was not the optimum for minimum ionic conductivity, but it was enough to separate the two types of losses and permit a better study of the dipole action.

The effect of frequency on the dielectric properties of a typical sample containing 40 parts of tricresyl phosphate and 60 parts of γ -polyvinyl chloride by volume plus one-half part by volume of lead oxide is shown in Fig. 2. A change in frequency from 15 to 1000 cycles per second shifts the position of maximum slope in the dielectric constant curves from about 25° to 39° , or about 14° . The peaks of the loss curves are shifted from about 28° for the same change in frequency, again a difference of about 14° . However, the high temperature rise in the loss curve is shifted by over 50° , again indicating the loss in this part of the curve is due to a different mechanism from that which produces the peak at lower temperatures.

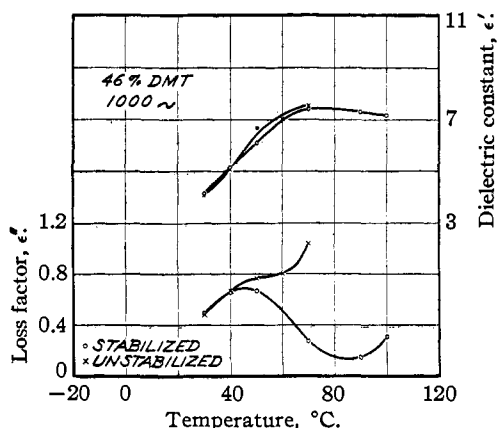


Fig. 1.—Variation in dielectric constant and loss factor of a polyvinyl chloride-dimethylthianthrene system with temperature.

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

(8) Fuoss, *ibid.*, **60**, 451 (1938).

(9) White and Bishop, *ibid.*, **62**, 8 (1940).

(10) White, Biggs and Morgan, *ibid.*, **62**, 16 (1940).

(11) Fuoss, *ibid.*, **60**, 456 (1938).

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

(13) Fuoss, *ibid.*, **61**, 2334 (1939).

The effects of the ratio of the γ -polyvinyl chloride to tricresyl phosphate on the dielectric constant and loss factor at 15, 60 and 1000 cycles per second are shown in Figs. 3 to 8. Figure 9 shows the logarithm of the direct current resistivity plotted against the reciprocal of the absolute temperature.

At any one frequency and composition the changes in dielectric constant with temperature are similar to the changes that would be obtained at any one temperature by varying the concentration of plasticizer in this system. The irregularities in the 15 cycle-per-second dielectric constant data for the 60% plasticizer system at higher temperatures (40 to 70°) possibly are due to interfacial polarizations at the surface of the sample.

The temperatures of maximum slope in the dielectric constant curves are shifted approximately 16° for each 10% increase in the volume of plasticizer and there is about the same change with composition for the temperatures of loss factor peaks. In general, a 10° change in temperature has about the same effect on dielectric properties as a 6% change in plasticizer content, or a 2-decade change in frequency, although there are small differences which show that these three changes are not precisely equivalent. The maximum dielectric constant, for example, decreases slightly with plasticizer content, due to the fact that the tricresyl phosphate has a dielectric constant of only 7.4 at 60 cycles per second and 25°, compared to the high temperature value of about 12 for the pure polyvinyl chloride. Also, the low temperature loss factors of the 100% polyvinyl chloride are higher than those of the plasticized compounds, perhaps due to the low temperature dielectric constant and loss factor maximum at 0° reported by Fuoss.¹⁴

Although the change in the alternating current peak with composition is quite uniform, this is not true of the change in the ionic conductance at high temperatures. At 60 cycles per second the change from 10 to 20% plasticizer produces a shift of only about half as much in this part of the curve as does a change from 50 to 60%. This result may be related to the fact that the temperature coefficients of resistance tend to decrease with increased plasticizer content at any one temperature. It should be noted that the curves (Fig. 9) for the logarithm of the direct current resistivity vs. the reciprocal of the absolute temperature are

not linear over the temperature range covered in this work, especially for the samples containing the larger amounts of plasticizer.

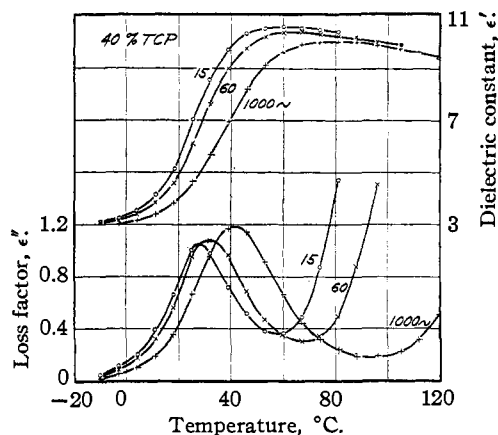


Fig. 2.—Variation in dielectric constant and loss factor of a stabilized 60% polyvinyl chloride-40% tricresyl phosphate system.

The simple theories of change in dielectric constant with frequency (or temperature) usually imply the existence of a single relaxation time τ .¹⁵ If the polarization is assumed to be due to the motion of bound charges, then τ is given by the ratio r/f , from the equation

$$r \frac{ds}{dt} + fs = eF \quad (1)$$

where F is electric field, e the charge, s the displacement of the charged particle, and r and f the friction and elastic coefficients, respectively. In Debye's¹⁶ original interpretation the force tending to return the dipoles to random orientation is due to thermal motion. He derives the equation

$$\tau = \zeta/2kT \quad (2)$$

where ζ is the viscous force retarding the motion of the dipole, T the absolute temperature, and k is Boltzmann's constant. On this basis τ is $1/e$ of the time required for the dipoles to return to random orientation after removal of the electric field.

A study of scale models of the polyvinyl chloride molecules shows that only at the end of the chain is there any chance of free rotation of a single H-C-Cl dipole about the adjoining C-C single valence bond. Everywhere else the rotation of the H-C-Cl dipole is hindered by the requirement of fixed valence angles for the two adjacent chain carbon atoms.

(15) Murphy and Morgan, *Bell System Tech. J.*, **17**, 640 (1938).

(16) Debye, "Polar Molecules," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 84.

(14) Fuoss, Am. Chem. Soc. Meeting, Cincinnati, Ohio, 1940.

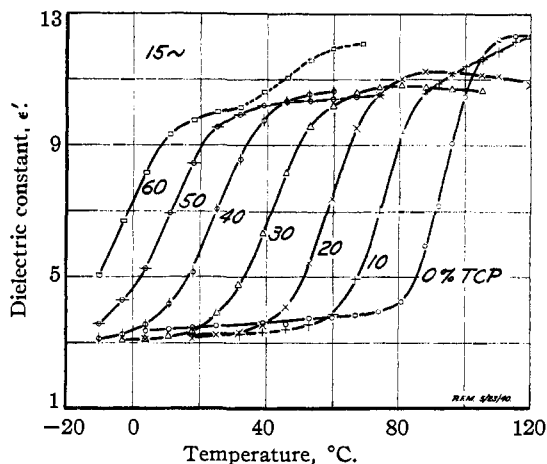


Fig. 3.—Effect of temperature on the 15 cps. dielectric constant of stabilized polyvinyl chloride-tricresyl phosphate systems.

It seems very improbable that a change in dielectric constant from 3 to 12 could be produced by the very slight angular motion of the dipoles permitted by the deformation of the adjoining valence angles. If something approaching complete rotation of the dipoles is required, it can be obtained only by the rotation of large segments of the chain. Since the chains of polyvinyl chloride will have a more or less random, kinky shape, the size of the segments which tend to rotate as a unit will vary over a wide range. This would lead one to expect a wide range of relaxation times.

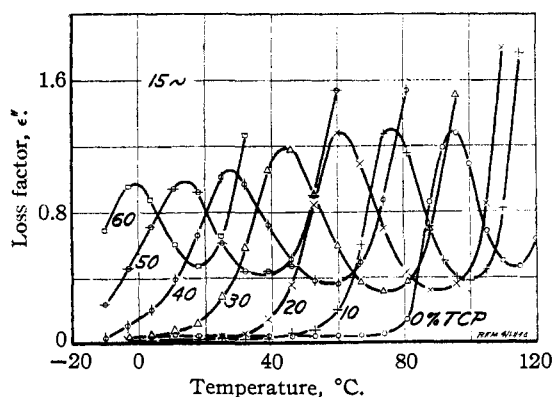


Fig. 4.—Effect of temperature on the 15 cps. loss factor of stabilized polyvinyl chloride-tricresyl phosphate systems.

This view is confirmed by a study of the height of the loss factor peaks. If there were a single relaxation time, the maximum in the loss factor curve, ϵ''_{\max} would be

$$\epsilon''_{\max} = \frac{\epsilon_0 - \epsilon_{\infty}}{2} \quad (3)$$

where ϵ_0 and ϵ_{∞} are the values of the dielectric constants at very low and very high frequencies. The observed values of ϵ''_{\max} are only about one-third the values calculated from the above equation, indicating that the material has a range of relaxation times. Yager¹⁷ developed a method of applying Wagner's theory to determine the range of relaxation times. He expressed the results in terms of a factor b , which is ∞ for a single relaxation time, and is 0 for an infinite range of relaxation times. He found experimentally that b varied from about 1.2 for glycerol at -44° to 0.147 for Vinsol, an oxidized rosin, at 129° and 0.135 for polystyrene plasticized with Arochlor 1254 at 25° .

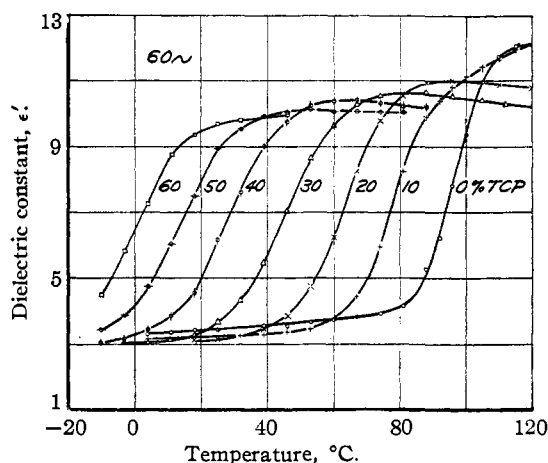


Fig. 5.—Effect of temperature on the 60 cps. dielectric constant of stabilized polyvinyl chloride-tricresyl phosphate systems.

The values of b were calculated for the Koroseal data shown in Figs. 3 to 8, assuming changes in temperature were equivalent to changes in frequency. The results showed that b was about 0.15 for all samples, suggesting that the relaxation times range from 3 to 4 decades on each side of the peak.

In using equation (2) Debye assumed that Stokes' law was valid for rotation of dipoles, *i. e.*

$$\zeta = 8\pi\eta a^3 \quad (4)$$

and

$$\tau = \frac{4\pi\eta a^2}{kT} \quad (5)$$

where η is the coefficient of viscosity and a the radius of a spherical dipole. Using equation (5) to calculate the size of dipoles rotating in dilute liquid solutions, reasonable values are obtained if the macroscopic viscosity of the liquid is used for η . However, when it is applied to polar solids,

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

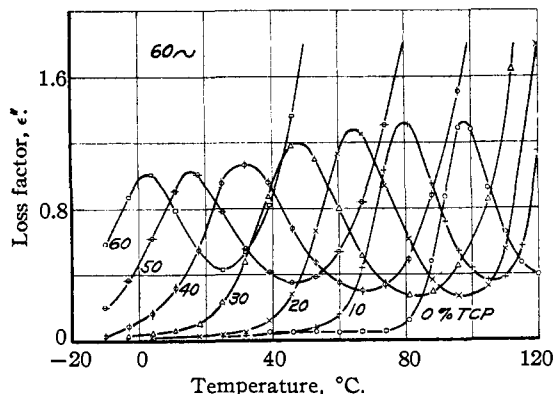


Fig. 6.—Effect of temperature on the 60 cps. loss factor of stabilized polyvinyl chloride–tricresyl phosphate systems.

or solid solutions, unreasonably low values of dipole radius are obtained if the macroscopic viscosity is assumed. Methylpentachlorobenzene, for example, is a solid melting at $+224^\circ$ and is reported to have a relaxation time of 10^{-6} second at 10° .¹² The value of η calculated from Debye's formula is of the order of magnitude of 25 poises, which is only about the viscosity of castor oil at this temperature. Jackson¹⁸ studied the dielectric properties of solutions of cetyl palmitate in paraffin. Assuming that only the polar ester group rotated, he calculated the inner viscosity of paraffin wax to be about that of castor oil. If he assumed that the whole ester molecule rotated, he obtained a lower and still less reasonable value of the apparent viscosity. Sillars¹⁹ found that for normal esters dissolved in paraffin wax, the

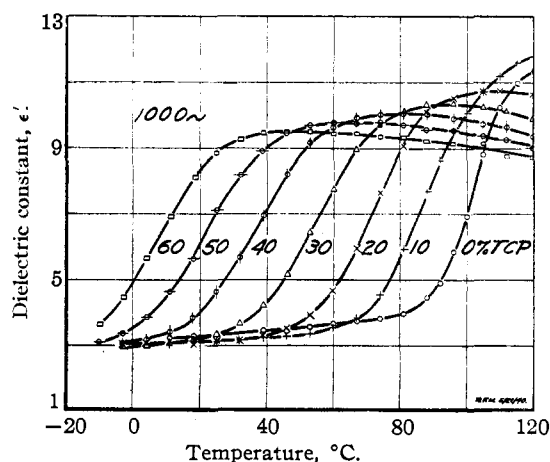


Fig. 7.—Effect of temperature on the 1000 cps. dielectric constant of stabilized polyvinyl chloride–tricresyl phosphate systems.

(18) Jackson, *Proc. Roy. Soc. (London)*, **A150**, 197 (1935).

(19) Sillars, *ibid.*, **A169**, 66 (1938).

relaxation time changed enormously with chain length, indicating that the whole molecules do rotate about their long axes in the solid state. Pelmore²⁰ also found that the relaxation time was a function of the melting point, and presumably the molecular weight, of the paraffin.

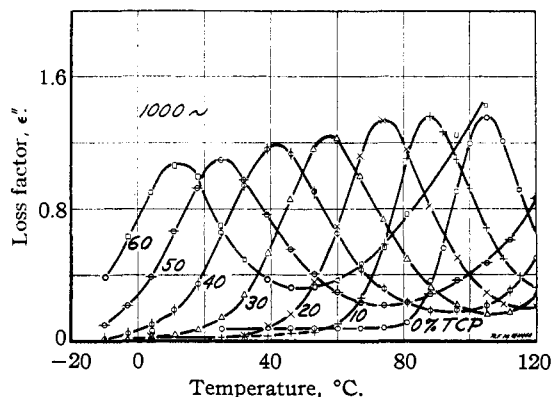


Fig. 8.—Effect of temperature on the 1000 cps. loss factor of stabilized polyvinyl chloride–tricresyl phosphate systems.

It is not necessary to assume Stokes' law and some particular value of the size of the rotating unit to get a measure of the resistance to dipole rotation. Fuoss¹⁴ assumed merely that the Debye friction factor ζ was proportional to the viscosity, and that the viscosity could be expressed by the equation^{21,22}

$$\log \eta = q/kT + B = Q/RT + B \quad (6)$$

where Q is the molar activation energy and R is the molar gas constant. Then the relaxation time of the dipoles, τ , is given by

$$\tau = \zeta/2kT = C\eta/T \quad (7)$$

where C is a constant. The loss factor ϵ'' is related to the relaxation time of the dielectric, τ^* , $[=(\epsilon_0 + 2)\tau/(\epsilon_\infty + 2)]$, where τ is relaxation time of dipole],²³ by the relation

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)\omega\tau^*}{1 + \omega^2\tau^{*2}} = 2\epsilon''_{\max} \frac{\omega\tau^*}{1 + \omega^2\tau^{*2}} \quad (8)$$

The relaxation time of the dipoles at any temperature where substantially all of the loss is due to dipole rotation can then be calculated from the observed loss factor by the equation:

$$\tau = \frac{1}{\omega\epsilon''} \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \left[\epsilon''_{\max} \pm \sqrt{\epsilon''_{\max}^2 - \epsilon''^2} \right] \quad (9)$$

(20) Pelmore, *ibid.*, **A172**, 502 (1939).

(21) Andrade, *Phil. Mag. (Series 7)*, **17**, 497 and 698 (1934).

(22) Eyring, *J. Chem. Phys.*, **3**, 107 (1935); **4**, 283 (1936).

(23) The τ used here and as originally used by Debye¹⁶ refers to the relaxation time of an individual dipole. τ^* refers to the dielectric as a whole. Murphy and Morgan¹⁶ and Yager¹⁷ use τ' for the individual dipole and τ for the dielectric.

Then from (7) and (6)

$$T\tau = C\eta \quad (10)$$

and

$$\log T\tau = q/kT + B' = Q/RT + B' \quad (11)$$

where Q is the activation energy needed to permit rotation of the dipoles in the electric field.

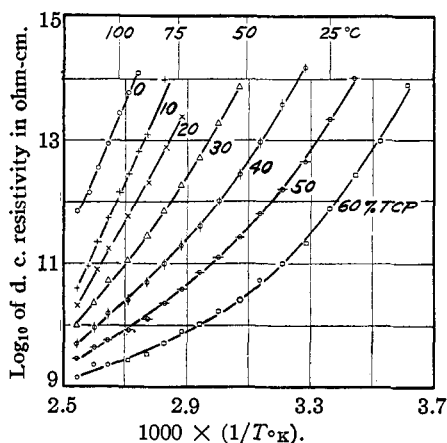


Fig. 9.—Variation in direct current resistivity with temperature and plasticizer content for stabilized polyvinyl chloride-tricresyl phosphate systems.

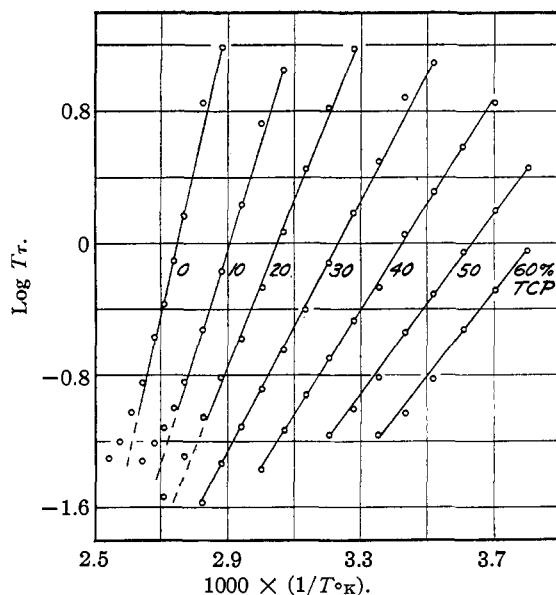


Fig. 10.—The relation between relaxation time τ and temperature T for stabilized polyvinyl chloride-tricresyl phosphate systems.

The values of τ were calculated by equation (9) from the loss factor data for the temperature range of the loss factor peaks. Figure 10 shows the straight lines obtained when $\log T\tau$ was plotted against $1/T$ for the 60 cycle-per-second data. The small direct current conductance had a negligible effect on the slope of the curves over the

greater part of the temperature range, although it did cause some deviations from the straight lines at the higher temperatures. Since the results are straight lines over a considerable range of temperatures, it looks as though the average activation energy, Q , for dipole rotation does not change much with temperature. The values of Q at 15, 60 and 1000 cycles per second for samples with different amounts of tricresyl phosphate are shown in Table I, together with Fuoss' value for a sample of 100% polyvinyl chloride measured at 60 cycles per second. It is interesting to note that the activation energy which Fuoss found for a sample which may have been made from polyvinyl chloride of a considerably lower molecular weight agrees closely with that found here for γ -polyvinyl chloride, since the tensile strengths of the polymers increase with molecular weight. This indicates that the size of the rotating units must be considerably less than the length of the polyvinyl chloride chains. This view is confirmed by the results of Flory²⁴ discussed below.

Table I also shows the Q values calculated from the direct current conductivity data both at 110° and at the respective temperatures where the resistivities of the samples are 3×10^{13} ohm-cm. These temperatures were chosen because they agreed approximately with the temperatures for the 1000 cycles per second loss factor maxima. At these temperatures the Q values for direct current conductivity are from one and one-half to three times greater than the Q values for the intra-molecular rotations producing the 1000 cycle-per-second alternating current loss factors. This does not necessarily mean that the activation energy for the translation of a single ion is greater than the activation energy for the rotation of a section of a chain, although the latter is not impossible. If the number of ions, N_1 , were an exponential function of the temperature, $N_1 = C_1 e^{-q_1/kT}$ and the mobility M (proportional to $1/\eta$) of each ion increased in the same way, $M = C_2 e^{-q_2/kT}$, then the conductance κ is the product of these two factors or

$$\kappa = C_1 C_2 e^{\frac{-(q_1 + q_2)}{kT}} = C e^{-q/kT}$$

It is also possible that the range of size of the rotating segments of the chain reduces the Q values for rotation.

The view that steric hindrance prevents single dipoles from rotating in the long chains implies

(24) Flory, THIS JOURNAL, 62, 1057 (1940).

TABLE I
APPARENT ACTIVATION ENERGIES FOR POLYVINYL CHLORIDE-TRICRESYL PHOSPHATE SYSTEMS

% Tricresyl phosphate by volume	Temperature of ϵ''_{max} , °C.			Q in kcal. from a. c. data			Q in kcal. from d. c. data	
	15 cps.	60 cps.	1000 cps.	15 cps.	60 cps.	1000 cps.	At 110°C.	at 3×10^{11} ohm-cm.
0 ^a		99 ^a			43.0 ^a			65.0 ^a
0	95	98	105	44.9	40.7	30.0	55.5	55.5 at 99°C.
10	76	80	88	32.4	29.2	24.9	51.0	51.4 83
20	61	65	74	25.0	22.7	20.0	39.5	41.9 72
30	44	48	57	19.1	17.6	16.0	28.7	41.1 57
40	28	32	42	15.0	14.2	13.7	21.2	38.7 40
50	14	16	25	12.8	12.6	12.1	14.0	36.8 23
60	-1	3	12	12.8	12.1	11.6	9.2	39.2 7

^a Fuoss' results.¹⁴

TABLE II
HARDNESS OF POLYVINYL CHLORIDE-TRICRESYL PHOSPHATE SYSTEMS.

% Tricresyl phosphate by volume	Modulus of elasticity, E , in psi						
	-10	At various temperatures, °C.			At temperatures of the loss factor maxima		
		32	70	105	15 cps.	60 cps.	1000 cps.
0		180,000	97,000	3000	5600	4500	3000
10		130,000	9,700	1000	5000	3250	1650
20		91,000	1,400		3500	2200	1250
30	250,000	17,000	850		2400	1650	1000
40	52,000	1,100	440		1500	1100	770
50	17,000	460	290		930	830	560
60	1,100	170	160		630	500	330

another interesting consequence. If relatively large sections of the chain must rotate as a unit, one might expect to find some relation between the resistance to this rotation and the resistance to mechanical deformation such as bending. Previous results⁵ indicated that such a relation might exist. To check these preliminary results, the absolute hardness of each sample was determined over a wide temperature range by an indentation method that permits calculation of Young's modulus from the results. Dr. Larrick,⁶ of this Laboratory, showed that by using spherical indentors with weights small enough to keep the indentations less than 10% of the diameter of the indenter, Young's modulus, E , or hardness of the samples, can be calculated from the equation

$$E = 0.795 \times \frac{L}{d^{3/2}D^{1/2}} \quad (12)$$

where L is the load in pounds, D is the diameter of the ball in inches, d the indentation in inches. The results depended to some extent on the time of application of load, so in most of this work the indentation after five seconds was used. Sometimes the agreement of check results was not as good as might be desired, due to effects of the previous thermal and mechanical history of the sample, slight variations from point to point on the surface due to molding imperfections, molding strains, etc. However, the variations in repeat

readings were small in relation to the total range of hardnesses covered in this series.

Table II shows that the values of E for this series of samples at room temperature (32°) range from about 170 up to 180,000 lb./sq. in., a range of over 1000-fold. However, the values of E at the temperature of the 60 cycle-per-second loss factor peak for example, are all between 500 and 4500, a range of only nine-fold. While this change of about nine-fold in the hardness at power factor maximum appears to be rather large, it is less than 1% of the total change in hardness of these samples at one temperature or of any one sample at the range of temperatures studied. Considering the large differences in the rate of deformation produced by the electric fields and by the indentors, even this close agreement is rather surprising.

Since the mechanical deformation must involve the relative motion of large segments of the chains, this agreement seems to be convincing evidence that the power loss due to dipole rotation involves movement of rather large segments of the γ -polyvinyl chloride molecules.

It is of interest to note that direct measurements of the modulus of a sample having 60 parts of polyvinyl chloride and 40 parts of tricresyl phosphate by weight²⁵ give a value of about 1200

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

± 200 psi for the modulus E at 30° and zero load. The interpolated value found in this work was about 800 ± 200 psi, which is a fair agreement considering total range of hardness changes, and the sensitiveness of the mechanical properties to previous thermal history of the sample and to rate of application of load.

The change of stress, E , at 112% elongation, with temperature over the range from 30 to 70° in this compound is reported to follow the equation $\log E = Q/RT + B$, giving a value of $Q = 4.93$ kg./cal. for the energy of activation of elastic displacement. The corresponding values for some metals are reported to range from 4.35 kg./cal. for lead to 13.8 kg./cal. for nickel. The hardness data found by the indentation method form sigmoid curves rather than straight lines when $\log E$ is plotted against $1/T$ for wide ranges of temperature, as shown in Fig. 11. However, over the range from 30 to 70° the values interpolated from this work do not deviate much from the straight line, giving $Q = 5$ kg./cal., which was reported by Russell.²⁵

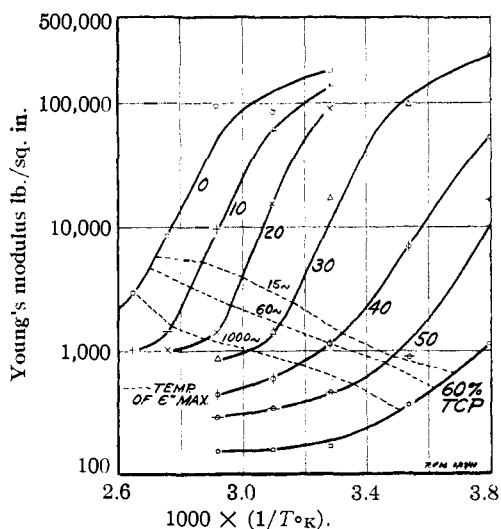


Fig. 11.—The variation in hardness with temperature for stabilized tricresyl phosphate systems.

The curves of $\log E$ vs. $1/T$ for each sample usually change their slope most rapidly in the regions of temperatures of the loss factor peaks, which are shown by the dotted lines in Fig. 11. This makes it impossible to get accurate or significant activation energies for mechanical deformations at these temperatures. However, tangents drawn to the smoothed curves in these regions suggest that the apparent activation energies (Q values) for mechanical deformation de-

crease with increasing plasticizer content, and are about one-half to one-third the corresponding values calculated from the loss factor peaks. The lower values might possibly be due to the fact that there are more possible degrees of freedom for mechanical deformations than for dipole rotations.

The activation energies for small mechanical deformations of dipole rotations would not be expected to have any relation to the molecular weight or tensile strength of the polymers, since the tensile strength may depend on the number of rotating or sliding segments which are present in each molecule. Flory²⁴ studied the viscosity of melted linear polyesters and found that the activation energy for viscous flow for polyesters was the order of 8 to 8.5 kg./cal., which was only two to three times the values for the simple esters, and for a series of polymers of molecular weights ranging from about 1000 to 7000 the activation energy was independent of molecular weight. He states: "The conclusion that the elementary flow properties of low and high molecular weight polyesters are identical is virtually unavoidable," the elementary flow processes being the displacement of small segments of the molecule rather than the displacement of the whole molecule at one time in the direction of shearing stress. Ewell²⁶ reached a similar conclusion regarding the flowing process in rubber and other highly elastic materials.

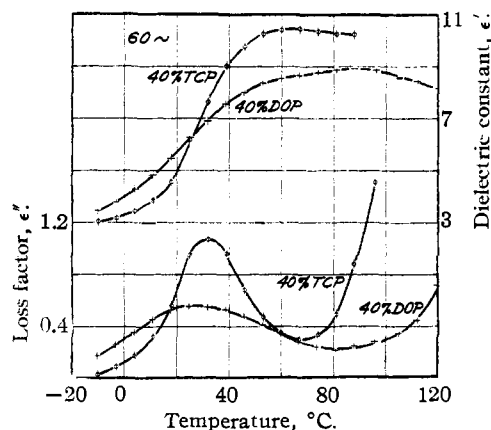


Fig. 12.—Comparison of the dielectric properties of polyvinyl chloride plasticized with tricresyl phosphate and dioctyl phthalate.

As an example of the results obtained with another plasticizer, Fig. 12 gives a comparison of the electrical properties of two compounds containing 60 parts of γ -polyvinyl chloride and 40 parts.

(26) Ewell, *J. Applied Physics*, **9**, 252 (1938).

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 con-

duction—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.

AKRON, OHIO

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

Electrical Properties of Solids. VI.¹ Dipole Rotation in High Polymers²

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

(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.

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