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Electrical Properties of Solids. XVI.[1] Polytrifluoromonochloroethylene as a Polyphase Dielectric

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Liquid and plastic polytrifluoromonochloroethylene polymers exhibit similar electrical behavior as a function of temperature and frequency. As the temperature is lowered, one passes from a single phase (either solid or liquid depending on the average molecular weight) to a two-phase state characterized by the appearance of crystallites in the material. The temperature at which crystals appear depends on the average molecular weight of the polymer and is governed by the solubility of the longer chain material in the shorter chain length "mother liquor," ranging from *ca.* 200° for the plastic material to −10° for a liquid sample. In each case the appearance of the crystalline phase is accompanied by a sharp rise in the dielectric constant to a peak value governed by the volume per cent. of crystals. There appear to be two distinct relaxation processes involved: (1) a low frequency two-phase dispersion where the solid has a high dielectric constant and (2) a broad dipole dispersion in the liquid (or glassy, depending on the temperature) phase occurring in a higher but overlapping frequency range. Although the loss factor (ϵ'') maxima occur at markedly different temperatures (for a given frequency), the activation energies derived from the data are the same.

I. Introduction

Previous studies of the electrical properties of polar polymers has established a general pattern of behavior: dispersion occurs, just as in polar liquids, but the width of the dispersion region may be many decades wide in the case of polymers. Polytrifluoromonochloroethylene (polytrifluorovinyl chloride), $(CF_2CFCl)_n$, has recently become available and represents an unusually interesting case, because both liquid polymers of low (average) molecular weight and thermoplastic polymers of much higher molecular weight can be prepared. As the results herewith reported will show, both the liquid fraction and the plastic are characterized by fairly broad distributions of relaxation times, and hence distribution rather than magnitude of molecular weight is necessary for a broad dispersion range.

It has been observed that polar polymers frequently show a transition in their electrical properties at low temperatures[3] which is characterized by an asymmetric Cole plot. Now, if the more volatile fractions of liquid polytrifluoromonochloroethylene are distilled off, the distribution of molecular weights in such a distillate is naturally different from that in the starting material. For example, in one case a distillate separated into two phases on cooling below 22° while the original unfractionated liquid mixture had to be cooled below −10° before the second phase appeared. The amount of solid phase depended upon the temperature. The electrical properties of such a distillate resemble those of polymeric systems at low temperatures previously mentioned. We are, therefore, led to the conclusion that the secondary maxima for polyvinylacetate, etc., and the resulting asymmetric Cole plots may be the consequence of the overlapping of dispersion regions of a two-phase system where each component has its own dipole dispersion. The purpose of this paper is to present experimental results bearing on this hypothesis.

II. Experimental

Materials.—Sample 1 was a fraction of polytrifluoromonochloroethylene[4] collected over the range 100–200° at 1 mm.; refractive index at 20°, 1.394; density at 25°, 1.93. On cooling, the viscosity increases and turbidity appears at −10°. Sample 2 was obtained from Sample 1 by redistillation; it represents 38% of the original starting material, and was collected over the range 190° (10 mm.) to 230° (2 mm.). On cooling, crystallites appear sharply at 22° (see Fig. 8); their relative amount increases on further cooling, but not on standing at a fixed temperature below 22°. In other words, the ***amount*** of solid phase depends on the temperature. The (number average) molecular weight of sample 2, as determined cryoscopically in cyclohexane, was found to be 980. Sample 3 was a sheet of F-1113, a polymer of unknown, but high molecular weight of the same empirical formula, $(CF_2\text{-}CFCl)_x$, as samples 1 and 2. Sample 4 was a high-boiling fraction of sample 2 collected between 205° (5 mm.) and 230° (2 mm.).

Apparatus and Methods.—The liquid samples (1, 2 and 4) were measured in a guarded platinum cell.[5] The solid sample (3) was measured as a disc (5 cm. diameter, *ca.* 2 mm. thick) in a guarded copper cell with platinum electrode faces.[6] Measurements in the power and low audio frequency were made with the General Electric Schering Bridge; in the range 1–300 kc., a General Radio 716C bridge was used. The latter was modified to accommodate a guard circuit.[7,8] The cells in a shielded can were placed in a dewar flask filled with cold acetone, and temperatures were regulated to ±0.2° by manual addition of small pieces of solid carbon dioxide. For measurements above room temperatures, the cell was placed in an air thermostat. Measurements above 300 kc. were made in a susceptance variation circuit as described by Hartshorn and Ward.[9]

Results

At 28.5°, Fluorolube Standard (sample 1) has a dielectric constant (ϵ') of 2.74, substantially independent of frequency in the range 1–300 kc. and the loss factor (ϵ'') is less than 0.001 up to 100 kc. As the temperature is lowered, dispersion begins to

TABLE I

ELECTRICAL PROPERTIES OF FLUOROLUBE (SAMPLE I)

	1 kc.		10 kc.		100 kc.	
t, °C.	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
28.5	2.75	0.000	2.75	0.000	2.73	0.001
0	2.88	.000	2.87	.001	2.88	.012
−21	2.98	.002	2.98	.016	2.92	.083
−39	3.14	.055	3.02	.126	2.77	.161
−50	3.09	.135	2.82	.159	2.61	.124
−60	2.84	.147	2.65	.117	2.51	.086
−74	2.53	.066	2.45	.053	2.37	.050
−78	2.48	.036	2.42	.038	2.37	.041

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[1] Paper XV, THIS JOURNAL, **67**, 1566 (1945).

[2] Yale University, New Haven, Connecticut.

[3] (a) Polyvinylchloride–diphenyl, R. M. Fuoss, THIS JOURNAL, **63**, 378 (1941), Fig. 6; (b) polyvinyl acetate and chloroacetate, D. J. Mead and R. M. Fuoss, *ibid.*, **63**, 2832 (1941), Figs. 3 and 7.

[4] "Fluorolube Standard" as supplied by the Hooker Electrochemical Co., Niagara Falls, N. Y.

[5] D. J. Mead and R. M. Fuoss, THIS JOURNAL, **61**, 2047 (1939).

[6] R. M. Fuoss, *ibid.*, **63**, 369 (1941).

[7] R. F. Field, *General Radio Exptr.*, **14**, No. 10 (1940).

[8] S. I. Reynolds, *Science*, **110**, 693 (1949).

[9] L. Hartshorn and W. H. Ward, *J. Inst. Elect. Eng.*, **79**, 597 (1936).

appear, as shown in Fig. 1. Table I gives an abstract of the numerical results at round frequencies.

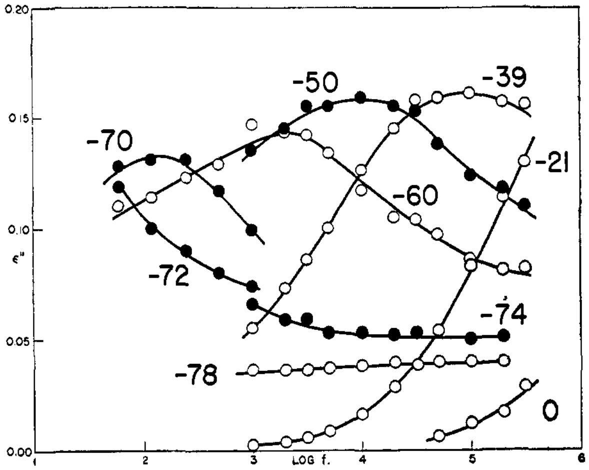

Fig. 1.—Loss factor as a function of frequency and temperature for liquid polytrifluorochloroethylene (sample No. 1).

Loss factor as a function of frequency and temperature for sample 2 is shown in Fig. 2 and for sample 3 in Fig. 3. An excerpt of the numerical results is given in Tables II and III.

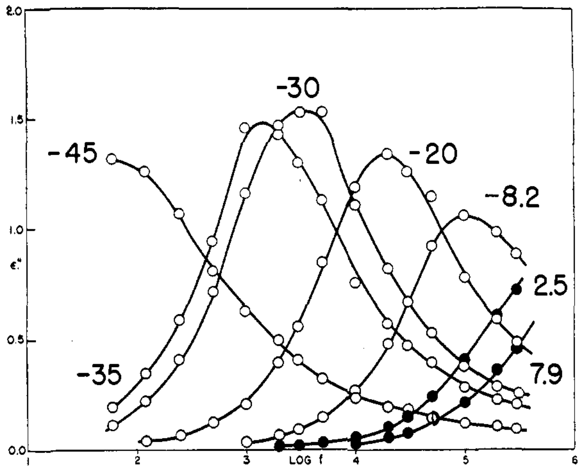

Fig. 2.—Loss factor as a function of frequency and temperature for the volatile fraction (sample 2).

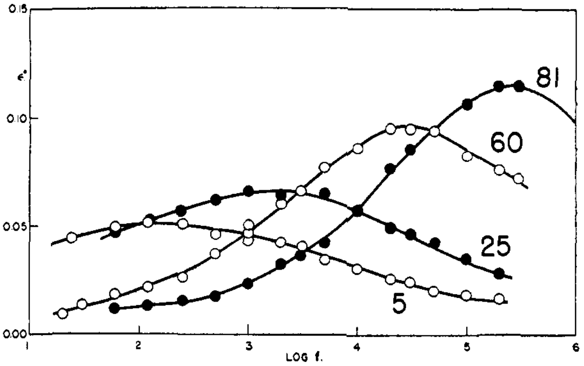

Fig. 3.—Loss factor as a function of frequency and temperature for plastic polytrifluorochloroethylene (sample 3).

TABLE II

ELECTRICAL PROPERTIES OF SAMPLE 2

	1 kc.		10 kc.		100 kc.	
t, °C.	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
−45.0	3.30	0.626	2.80	0.238	2.55	0.120
−35.0	5.53	1.46	3.60	0.756	2.82	.283
−30.0	6.25	1.16	4.00	1.11	2.95	.376
−20.0	6.05	0.205	5.50	1.19	3.55	.781
− 8.2	5.40	.033	5.37	0.270	4.55	1.06
2.5	4.48	.0108	4.48	.056	4.32	0.406
7.9	4.10	.0056	4.10	.0266	4.06	.215
19.6	3.25	.0026	3.25	.0049	3.25	.044
28.0	2.96	.000	2.96	.0015	2.96	.0145
36.0	..	....	3.06	.0015	3.05	.0015

TABLE III

ELECTRICAL PROPERTIES OF F-1113 PLASTIC (SAMPLE 3)

t,	1 kc.		10 kc.		100 kc.	
°C.	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
5	2.41	0.0470	2.35	0.0303	2.32	0.0187
25	2.50	.0652	2.39	.0576	2.32	.0355
60	2.72	.0504	2.62	.0870	2.46	.0834
81	2.77	.0270	2.73	.0579	2.59	.1070

III. Discussion

The three systems, liquid (sample 1), fractionated liquid (sample 2) and plastic (sample 3) exhibit electrical properties not unlike those of the polar polymers which have been described in this series of papers. As seen in Figs. 1, 2 and 3, the loss factor goes through a maximum as a function of frequency, and the location of the maximum is temperature dependent. The breadth of the maxima for samples 1 and 3 corresponds to a wide distribution of relaxation times,[10,11] while sample 2 has somewhat sharper maxima as might be expected as a result of the repeated distillation. The breadth is seen also to increase with decreasing temperature as has been observed with polyvinyl chloride.

The striking difference between the three samples is in the location of the dispersion range: for samples 1, 2 and 3, the 10 kilocycle maximum, for example, appears at −50°, −25° and +50°, respectively. Despite these differences, however, the fundamental energetic step involved in the low frequency relaxation process, whatever it may be, is the same in all three samples. This is shown by the parallelism of the plots of $\log f_{\max}$ *vs.* $1/T$ in Fig. 4; in fact, from the equation $f_{\max} = A \exp Q/RT$, we compute $Q = 19$ kcal., a value of the same order of magnitude as that observed for other polymeric systems.

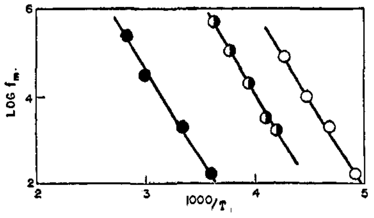

Fig. 4.—Dependence of maximum loss frequency on temperature; open circles, sample 1; half-black circles, sample 2; solid circles, sample 3.

In Fig. 7 are presented the Cole plots of the data obtained on sample 2. Reference to these curves

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

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

shows that, while the low-frequency range is satisfactorily described by a narrow band of relaxation frequencies, the high frequency end departs more and more from a semi-circular arc; and furthermore the curves appear to be tending toward the square of the index of refraction as their limit (as, indeed, they should). This asymmetry is present, although less apparent, in the plots of ϵ'' and ϵ' *vs.* frequency (see Fig. 2). One might consider the possibility that this asymmetry is caused by the asymmetrical distribution of molecular weights due to the manner in which Sample 2 was distilled from Sample 1. This seems to be ruled out because Cole plots of Samples 1 and 3 display the same asymmetry (with reduced magnitudes of ϵ' and ϵ'') and there is no reason to expect anything but a symmetrical distribution of chain lengths for these samples. As we proceed to temperatures above $-30°$, it is noted that the low frequency limit and height of the semicircular portion of the plots becomes smaller. At the temperature of $+36.0°$ where no solid phase was present, an extension of the frequency range shows that the liquid itself has a small and broad absorption maximum at about 40 mc. From this observation we would conclude that the asymmetry of plots is, at least, partially due to a superposition of this liquid (or glassy) dipole absorption curve on another relaxation associated with the presence of solid. This conclusion is reinforced by the parallelism of the log $f_{\max}$ *vs.* $1/T$ plots for the three samples, all of which contain a solid phase.

The resemblance of the complex locus data to those reported recently for glycerol must be only superficial[12] because it is almost certain that these measurements were made on a one-phase liquid system.[13]

In Fig. 5 is shown the dependence of ϵ' on temperature at the constant frequency of 10 kc. for samples 1, 2 and 4. As we proceed from higher to lower temperatures, these three liquids exhibit the same general behavior. First of all, there is a small linear increase of the dielectric constant due to density change; then suddenly at the precise temperature where crystals begin to form, ϵ' rises sharply above the extrapolated liquid values. From visual observations of the turbidity, the rate of rise is governed by the volume fraction of solid present. Thus, the dielectric constant of sample 1, which has a very small percentage of crystals, rises negligibly at $-10°$ where solid begins to form. In contrast, Sample 4, which represents the most nearly monodisperse system due to repeated fractionation, rises at the most rapid rate.

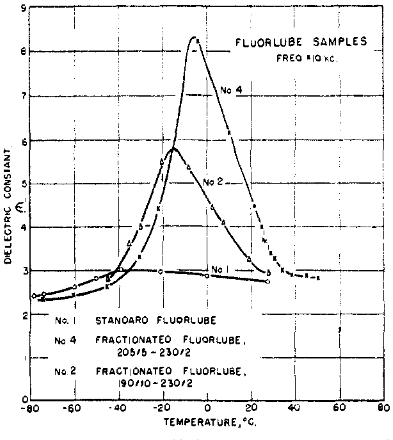

Fig. 5.—Dependence on dielectric constant of temperature at 10 kc.; liquid Fluorolube samples 1, 2 and 4.

Sample 3, the plastic, similarly shows a sudden rise in ϵ' as the temperature is lowered through the value where crystals appear. In this case, however, the crystals form at a considerably higher temperature, *ca.* 183°; where ϵ' rises from 1.95 to 2.25 as the temperature is lowered over a few degrees range.

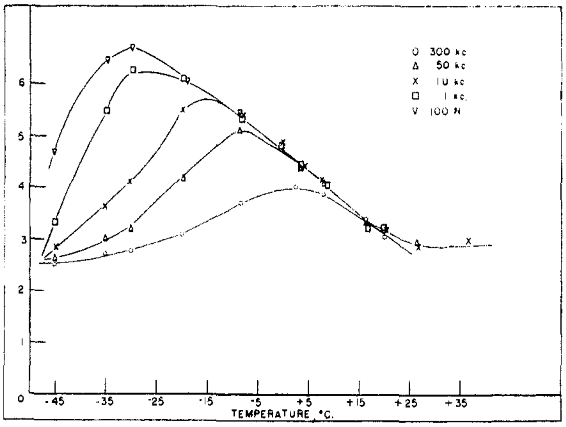

Fig. 6.—Dependence of dielectric constant on temperature at several different frequencies for the volatile fraction (sample 2).

Figure 6 shows for sample 2 the complete family of curves of ϵ' *vs.* T for a number of different frequencies. It is seen that the initial rate of rise is frequency independent and depends only on the volume fraction of crystals present, completely in accord with the conclusions drawn from Fig. 5.

Using X-ray, nuclear magnetic resonance, and dielectric studies, much conclusive experimental evidence for hindered rotation of long-chain compounds in the solid state has been advanced by a number of investigators.[14] It is to be understood that the word rotation, as used in this paper, does not mean *free* rotation as in ordinary gases,

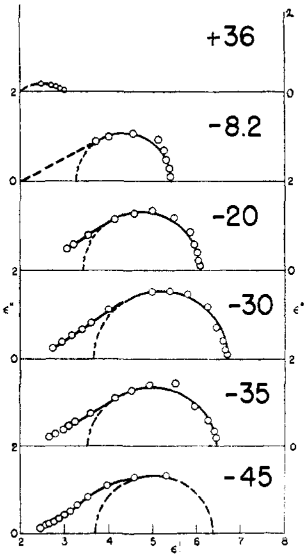

Fig. 7.—Cole plots for distilled sample (sample 2).

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(12) D. W. Davidson and R. H. Cole, *J. Chem. Physics*, **18**, 1417 (1950).

(13) Private communication from R. H. Cole.

(14) For example, long-chain alcohols, Hoffman and Smyth, This Journal, **71**, 3591 (1949); long-chain bromides, Hoffman and Smyth, *ibid.*, **72**, 171 (1950); long-chain paraffins, Muller, *Proc. Roy. Soc.* (*London*), **A138**, 514 (1932); solid hydrocarbons, Andrew, *J. Chem. Phys.*, **18**, 607 (1950).

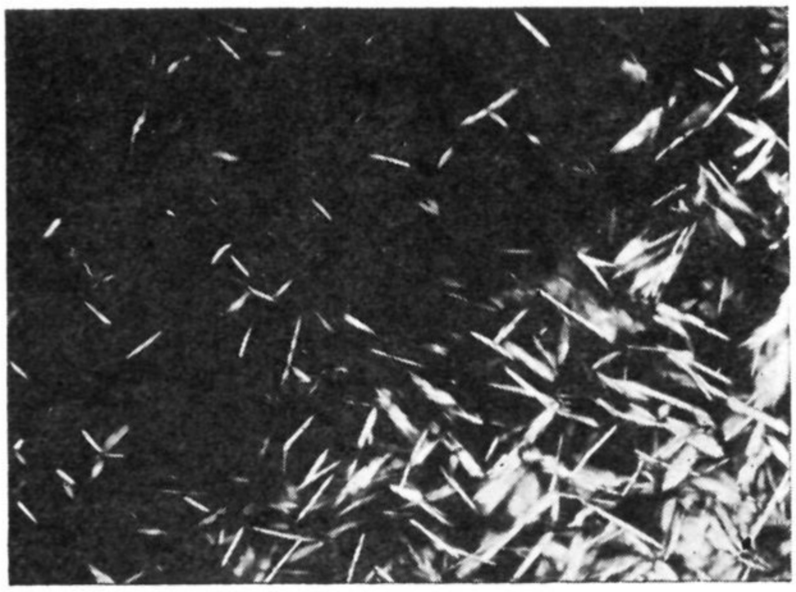

Fig. 8.—Photograph of crystals appearing below 22° in distilled Fluorolube liquid (sample 2), magnification 50 ×; polarized light.

but rather *hindered* rotation about a molecular axis as observed, for example, in ethane. Experimental results on the solid state hindered dipole rotator, dodecyl stearate,[15] yield a semi-circular Cole plot having a large dielectric constant and low loss factor at low frequencies. Thus, it appears reasonable to suppose that such a dipole rotation about the long axis of the $-(CF_2CFCl)_x$ polymer might occur. Viewing such a chain endwise, we see considerable cylindrical symmetry similar to the long chain compounds previously cited, which would certainly favor rotation. Because of the high degree of electrical symmetry, one would expect only a small dipole moment, and consequently small dielectric constant, for the monomer trifluoromonochloroethylene. However, with the head-to-tail polymerization which exists in this polymer, one effectively has dipoles on alternate carbon atoms which are oriented in the same direction (see Fig. 9). If the chain is constrained to a linear configuration the individual dipoles of the ordered crystalline state will be additive resulting in large dipole moments and dielectric constant ($\epsilon' \approx 8$ at 10 kc.). Therefore, we have established that the observed high dielectric constant could arise in a reasonable manner from the solid phase of our two-phase system. It must be pointed out, however, that a conducting solid phase immersed in a relatively loss-free liquid phase would exhibit the same behavior and so, in the absence of measurements on the pure solid state, we cannot prove which picture is the correct one. However, in view of the arguments mentioned above, and the fact that we know of no good reason why the crystals should have a high conductivity, we prefer the hindered solid rotator point of view.

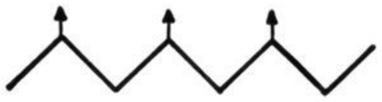

Fig. 9.—A polytrifluoromonochloroethylene chain showing the addition of resultant dipoles on alternate carbon atoms.

In summary, we may say that the preferred physical picture which could account for the observed dielectric behavior in this system is (1) at the onset of crystallization we have a two-phase system satisfying the condition for Maxwell–Wagner polarization, *viz.*, $\kappa_1\epsilon_2' \dot{\pm} \kappa_2\epsilon_1'$, (2) the liquid phase has a broad dispersion which occurs in an overlapping but higher frequency range than that of the two-phase dispersion and thus makes the Cole plots asymmetrical and (3) that the high dielectric constant of the composite at low frequencies is probably caused by hindered dipole rotation in the solid phase. Measurements on the pure solid phase would be necessary to establish definitely this last point. Considering the similarity of molecular structures and the likelihood of having two phases, it is very possible that the same mechanism is responsible for the dielectric behavior observed earlier for polyvinyl acetate, etc.[3]

Grateful acknowledgment is made to Dr. J. D. Hoffman and Dr. S. Roberts of this Laboratory for their helpful discussions concerning this paper.

SCHENECTADY, N. Y. RECEIVED JANUARY 12, 1951

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(15) Private communication, R. W. Crowe and C. P. Smyth.