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

Electrical Properties of Solids. XIV. Copolymers of Acrylonitrile and Ethyl Acrylate[1]

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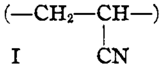
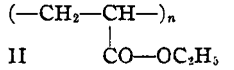
I. Introduction.—In preceding papers of this series, we have described the electrical properties of a number of systems containing polymers of high molecular weight. The general behavior includes a broad dispersion of dielectric constant and a maximum in absorption for power or audiofrequencies in the approximate range of 40–100°, the location depending on structure and molecular weight. For a given polymer, the location of the loss maximum is shifted to lower temperatures with increasing amounts of a second component of low molecular weight (plasticizer[2]). The plasticizer does not contribute to absorption in the range of variables where the polar groups on the polymeric chain respond; from the electrical point of view, the plasticizer acts like a volume diluent with fixed dielectric constant and zero loss (aside from any ionic conductance due to electrolytic impurities). On account of the small size of the plasticizer molecules, their maximum response (assuming a polar plasticizer) would be expected to appear at higher frequencies. It is, however, also possible to plasticize a polymer internally, by building a chain in which two monomers of different structure take part.[3,4] When both monomers are polar, the resulting copolymers might be expected to have properties intermediate between those of the two pure polymers, because the orientation of both types of polar groups would be subject to the restraints imposed by the chain structure.[5,6]

In this paper is presented a study of the electrical properties of a series of copolymers of acrylonitrile (I, vinyl cyanide) and ethyl acrylate (II). Both monomers


I

$(\text{—CH}_2\text{—}\underset{\text{CN}}{\text{CH}}\text{—})_n$


II

$(\text{—CH}_2\text{—}\underset{\text{CO—OC}_2\text{H}_5}{\text{CH}}\text{—})_n$

are of the $CH_2{:}CHX$ type; the dipole moment of the nitrile group is 3.2_1 Debye units,[7] nearly double that of the ester group. Polyacrylonitrile (P-ViCN) resembles polyvinyl chloride,[8] which also has the polar groups attached directly to the chain carbons, in that it is hard and brittle at room temperatures, and has its 60-cycle loss maximum at about 110°. Polyethylacrylate (P-$ViCO_2Et$), on the other hand, is soft and flexible, even more so than polymethylacrylate,[1] which has its 60-cycle maximum at 27°. Consequently we would expect a decrease in static dielectric constant, and a shift to lower temperatures of maximum absorption at a given frequency for acrylonitrile copolymerized with increasing amounts of ethyl acrylate. The experimental data agree with these qualitative statements: the maximum in 60-cycle absorption drops from 110° for P-ViCN to 45° as the $ViCO_2Et$ content of the copolymer increases from zero to 65% and the static dielectric constant decreases from 37 to 12. The average moment (averaged over both kinds of dipoles present) decreases linearly with composition from 4.6 to 3.4 over the same range.

II. Experimental.—We are indebted to the Pittsfield Plastics Laboratory for samples of the copolymers. The general method of preparation was to mix the monomers, add 0.25% benzoyl peroxide as polymerization catalyst and emulsify with about 5 volumes of water, using 0.5–1.0% emulsifying agent. The emulsion was heated to 60–80° with constant agitation under a reflux for fifteen to twenty-four hours, after which the polymer was separated and washed. Compositions were determined by analyses for nitrile and ethoxy groups in the final polymers.

The compounds were pressed for five minutes in a closed mold to discs 5 cm. in diameter and 2–3 mm. thick, at temperatures ranging from 140° for the 35% ViCN sample to 170° for the 100% ViCN sample. The densities are given by the formula

$$d = 1.190 - 0.0013\,p$$

where p is the percentage of ester in the copolymer. Cells, bridges and thermostats were the same as those used in previous work.

The loss factors and dielectric constants at 60 cycles are given in Tables I and II, for polymers containing from 35 to 100% ViCN. Measurements at the same temperatures were also made at 1000 cycles, and in the range of temperatures in which the loss factor maximum came in the 60 cycle–8 kilocycle band, measurements were made at 10° intervals, at 60, 120, 240, 480, 1000, 2000, 4000 and 8000 cycles.[9] The d. c. conductances are given in Table III, and Table IV gives the low temperature properties of polyacrylonitrile at three frequencies.

III. Discussion.—In Figs. 1 and 2 are shown the dielectric constants and loss factors at 60

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(1) Paper XIII. THIS JOURNAL, **64**, 2389 (1942).

(2) Mead, Tichenor and Fuoss, *ibid.*, **64**, 283 (1942).

(3) Ueberreiter, *Angew. Chem.*, **53**, 247 (1940).

(4) Würstlin, *Z. Elektrochem.*, **48**, 311 (1942).

(5) Fuoss and Kirkwood, THIS JOURNAL, **63**, 385 (1941).

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

(7) Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, N. Y., 1931, p. 193.

(8) Fuoss, THIS JOURNAL, **63**, 378 (1941).

(9) For a copy of these data, order Document 1800 from the American Documentation Institute, Offices of Science Service, 2101 Constitution Ave., Washington, D. C., remitting 50 cents for microfilm or 70 cents for photocopies readable without optical aid.

TABLE I

LOSS FACTORS AT 60 CYCLES OF ACRYLONITRILE–ETHYL ACRYLATE COPOLYMERS

t, °C.	34.5%	38.0%	43.6%	58.0%	65.2%	70.5%	76.5%	78.2%	85.2%	100%
20	0.25	0.14	0.05	..	0.11	..	..	..	..	0.27
25	0.47	0.52	..	..	..	..	..	..	..	..
30	0.87	1.06	.06	0.08	.12	0.10	0.16	0.18	0.19	.34
35	1.37	1.92	..	..	..	..	..	..	..	..
40	1.94	2.67	.19	.09	.17	.13	.19	.24	.20	.42
45	2.21	2.66	..	..	..	..	..	..	..	..
50	2.06	1.84	1.04	.20	.51	.19	.28	.35	.24	.55
55	1.56	1.08	2.02	.39	.92	.25	.39	..	..	..
60	1.07	0.66	2.71	.88	1.60	.39	.66	.58	.30	.72
65	0.86	.54	2.62	1.82	2.42	.77	1.31	.93	..	..
70	.80	.60	1.97	2.96	3.02	1.64	2.37	1.72	.40	.99
75	.93	.71	1.29	3.47	3.21	3.01	3.61	3.00	..	1.22
80	.95	.66	.77	2.90	2.86	4.10	4.14	4.23	1.00	1.56
85	..	..	.48	1.87	2.32	3.91	3.70	4.38	1.93	2.05
90	..	..	.33	1.10	1.90	2.79	2.89	3.86	3.23	2.84
95	..	..	.38	.69	1.79	1.85	2.42	3.38	4.19	3.83
100	..	..	.49	.59	2.01	1.40	2.29	3.46	4.21	5.04
105	..	..	.62	.66	1.88	1.45	2.47	4.76	3.87	6.39

TABLE II

DIELECTRIC CONSTANTS AT 60 CYCLES OF ACRYLONITRILE–ETHYL ACRYLATE COPOLYMERS

t, °C.	34.5%	38.0%	43.6%	58.0%	65.2%	70.5%	76.5%	78.2%	85.2%	100%
20	4.45	3.96	3.78	...	4.07	...	...	...	...	4.40
25	4.94	...	...	...	...	...	...	...	...	...
30	5.86	4.90	3.86	3.99	4.33	4.19	4.51	4.41	4.37	4.68
35	7.17	5.93	...	...	...	...	...	...	...	...
40	9.20	7.71	4.31	4.11	4.62	4.36	4.74	4.64	4.57	5.01
45	11.35	10.21	...	...	...	...	...	...	...	...
50	13.46	13.09	6.00	4.56	5.62	4.71	5.26	5.08	4.88	5.51
55	15.01	15.13	8.34	5.03	6.60	4.98	5.65	...	...	...
60	15.67	15.95	10.87	5.97	8.24	5.40	6.35	5.83	5.31	6.19
65	15.90	16.19	13.84	7.83	10.71	6.31	7.85	6.71	...	...
70	15.91	16.17	16.02	10.91	13.68	8.11	10.20	8.42	5.86	7.20
75	15.86	16.18	17.17	14.80	16.95	11.14	14.00	11.25	...	7.99
80	15.79	16.18	17.62	18.22	19.78	15.34	18.46	15.43	7.58	8.98
85	...	16.12	17.59	20.11	21.51	19.88	22.33	19.64	9.75	10.38
90	...	...	17.43	20.81	22.22	22.81	24.74	22.82	13.29	12.38
95	...	...	17.21	20.64	22.58	24.10	25.93	24.16	17.83	14.99
100	...	...	16.95	20.52	22.52	24.42	26.01	25.08	22.12	18.41
105	...	...	16.76	20.49	22.52	24.24	24.75	25.58	24.81	22.18

TABLE III

D. C. CONDUCTANCE OF COPOLYMERS

$\kappa \times 10^{10}$

t, °C.	34.5%	38.0%	43.6%	58.0%	65.2%	70.5%	76.5%	78.2%	85.2%	100%
50	0.029	0.021	...	...	...	...	...	...	...	...
55	.074	.054	...	...	...	...	...	...	...	...
60	.160	.129	0.001	...	0.003	0.001	...	...	...	...
65	.314	.277	.002	...	.010	.001	0.002	0.002	...	...
70	.633	.559	.008	0.001	.029	.002	.007	.007	...	0.001
75	1.141	1.040	.017	.004	.070	.007	.022	.023	...	.004
80	1.970	1.825	.039	.014	.159	.021	.056	.064	0.002	.007
85	...	3.13	.083	.031	.324	.058	.130	.153	.008	.018
90	...	...	.166	.070	.625	.137	.278	.332	.025	.046
95	...	...	.348	.148	1.16	.298	.527	.658	.068	.112
100	...	...	.665	.313	1.94	.620	.949	1.247	.175	.282
105	...	...	1.20	.587	3.30	1.11	1.42	1.907	.380	.635

cycles as functions of temperature for polymers containing 35, 44, 58, 78 and 100% ViCN. Increasing nitrile content in the copolymers causes the loss factor maximum and the dielectric con-

TABLE IV

ELECTRICAL PROPERTIES OF POLYACRYLONITRILE AT LOW TEMPERATURES

t, °C.	60~ ϵ'	60~ ϵ''	1000~ ϵ'	1000~ ϵ''	8000~ ϵ'	8000~ ϵ''
−60	3.530	0.031	3.475	0.020	3.461	0.014
−50	3.581	.045	3.517	.029	3.468	.020
−40	3.639	.058	3.545	.041	3.510	.025
−30	3.715	.075	3.621	.049	3.531	.034
−20	3.794	.095	3.642	.066	3.565	.045
−10	3.907	.124	3.718	.082	3.607	.059
0	4.042	.166	3.795	.106	3.663	.074
10	4.183	.205	3.816	.131	3.718	.092

stant to increase, corresponding to the higher dipole strength of the CN-group as compared to that of the ester group. The increase in ϵ' and ϵ'' is such that their ratio ($\epsilon''/\epsilon' = \tan \delta$, δ = loss angle) at the temperature where the 60-cycle maximum in loss factor appears is practically independent of composition, and averages to 0.22 in the range 35–85% ViCN. This average value is about double that of P-ViCO$_2$Me, and about two-thirds of that estimated for P-ViCN. At the same time the peak absorption and maximum dispersion shift to higher temperatures, indicating that the average relaxation rate constant[10] decreases as the nitrile content increases; or in terms of the former unsatisfactory hydrodynamic picture, the "internal viscosity" increases. In other words, the probability of rotation is less, the more nitrile groups there are on the chain, probably due to dipole–dipole interaction between chains. This shift of electrical properties with composition is paralleled by the change in mechanical properties: the copolymers become harder and less flexible at a given temperature as the nitrile content increases.

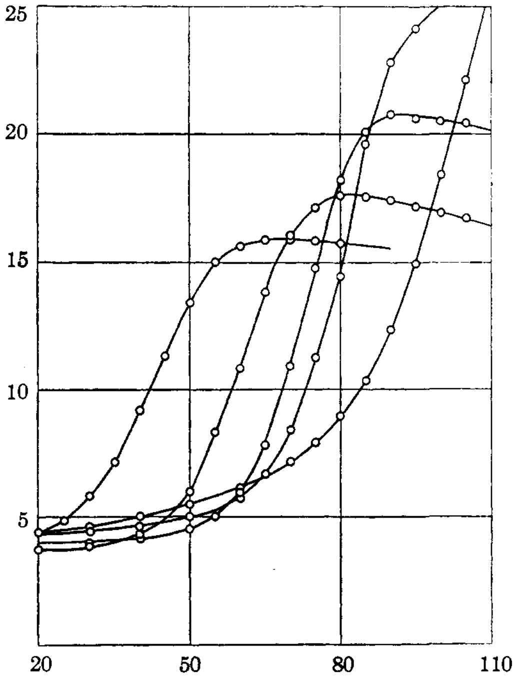

Fig. 1.—Dielectric constants at 60 cycles of copolymers containing 35 (left curve), 44, 58, 78 and 100% (right curve) acrylonitrile.

The Cole plots[11] are circular arcs, with centers below the ϵ'-axis, showing that a distribution of relaxation times[5,6] is necessary to describe the dielectric behavior of the copolymers. The distribution parameters (Cole's α) vary from 0.4 to 0.6, and exhibit no systematic dependence on composition; a plot on probability paper is linear, showing that the values are distributed according to the normal law of errors, and gives $\alpha = 0.48 \pm 0.05$. The ratio $R = \epsilon''_m/(\epsilon_0 - \epsilon_\infty)$ is also a measure of the width of the distribution of relaxation times (ϵ''_m = maximum loss factor, ϵ_0 = static dielectric constant and ϵ_∞ = high frequency dielectric constant). For a system describable in terms of a single relaxation time, $R = 0.5$; for these copolymers, R averages to 0.19.

The high frequency ends of the Cole arcs extrapolate to about 5.0 for all compositions. This value is considerably larger than the square of the index of refraction (n = 1.48 for P-ViCO$_2$Me, n = 1.49 for P-ViCN) and suggests that a second low temperature absorption mechanism is involved, as was found to be the case for polyvinyl acetate[12] and polyvinyl chloride.[13] Measurements were made down to −60° for P-ViCN and no secondary maximum was found; however, the curvature of the $\epsilon' - T$ and $\epsilon'' - T$ plots changes in the low temperature range, and a test plot[14] shows that different absorption mechanisms are acting at low and at high temperatures.

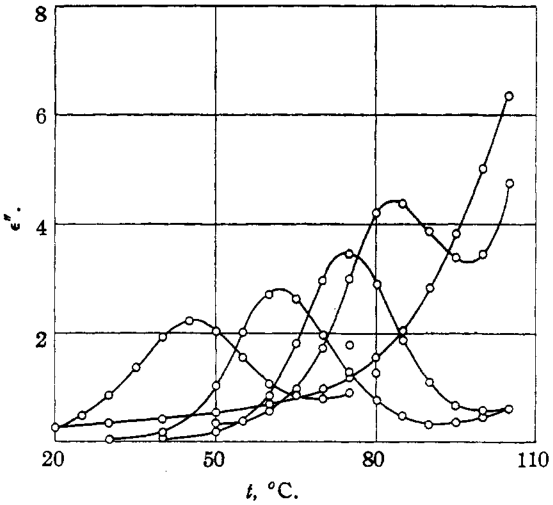

Fig. 2.—Loss factors at 60 cycles of copolymers containing 35 (left curve), 44, 58, 78 and 100% (right curve) acrylonitrile.

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[10] Kauzmann, *Rev. Mod. Phys.*, **14**, 12 (1942).

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

[12] Mead and Fuoss, THIS JOURNAL, **63**, 2832 (1941): Fig. 3.

[13] Ref. 8, Fig. 7.

[14] Fuoss, THIS JOURNAL, **63**, 369 (1941); Fig. 6.

The low frequency ends of the Cole arcs extrapolate to static dielectric constants which range from 16.4 at 60° for the 35% sample to 30.8 at 105° for the 85% sample. These limiting values may be used to calculate average moments per monomer unit,[5] if we average over both kinds of dipoles. The results of the calculation are shown in Fig. 3. Extrapolating linearly to 100% ViCN (our present upper limit of 105° did not permit determination of the 60-cycle maximum for P-ViCN) gives $\mu = 4.6$, from which a value of 37 for the static dielectric constant of polyacrylonitrile at 105° can be calculated.[5] This is the highest dielectric constant so far observed for a solid organic compound, and is about the same as that of the liquid nitriles.

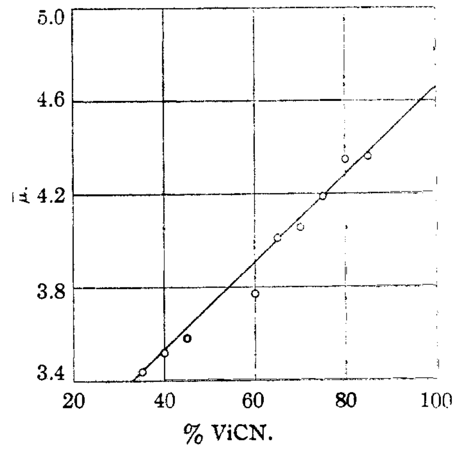

Fig. 3.—Average moments per monomer unit as function of nitrile content.

In Table III, it will be seen that the d. c. conductance reaches fairly high values. The logarithm of the conductance is approximately linear in $1/T$ and the slopes correspond to energies of 40 to 50 kilocalories. A direct comparison of conductances on the basis of nitrile content is not permissible, because the resistance to ionic motion depends on nitrile concentration. However, we may compare the d. c. conductances of different copolymers at temperatures at which they are hydrodynamically equivalent; for example, at the temperatures T_m at which the 60 cycle loss maximum appears. A plot of log κ_0 at the temperatures T_m where ϵ'' (60) is a maximum is approximately linear in % ViCN; the conductance increases by about three decades from 45 to 100% ViCN, showing that the presence of nitrile groups is largely responsible for the d. c. conductance. It is quite possible that a slight hydrolysis of some of the —CN groups to —CO_2NH_4 groups can account for the electrolyte present.

When the d. c. conductance becomes high (of the order of 10^{-10}), the now familiar secondary rise[15] in the ϵ''–T curves appears. The a. c. loss factors are computed from the difference between total measured a. c. conductance at a given frequency and the observed d. c. conductance. The branch of the ϵ''–T curve above the maximum is not symmetrical with the low temperature side, but goes through a minimum, and then rises very rapidly. This effect is necessarily due to the electrolyte present, and can only mean that ionic motion in these media of high viscosity is not in phase with the field. We have completed a preliminary study of the properties of known concentrations of known electrolytes (quaternary picrates) in polymers as the solvent medium, and hope to present these results when time permits. The electrolytic contribution to a. c. properties may be described empirically as a parallel admittance with constant phase angle ($\varphi = \pi/4$), whose components vary inversely as the square root of frequency and directly as the stoichiometric concentration of electrolyte.

Summary

1. The electrical properties of a series of acrylonitrile–ethyl acrylate copolymers have been measured at power and audiofrequencies in the temperature range 20–105°.

2. The copolymers have properties intermediate between those of the simple polymers; with increasing acrylonitrile content, the loss factor maximum at a given frequency increases and is displaced toward higher temperatures; simultaneously, the static dielectric constant increases from 12 to 37 in the range 35 to 100% acrylonitrile.

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[15] Fuoss, THIS JOURNAL, **61**, 2329 (1939). Figs. 6 and 7; Ref. 8, Fig. 2; Ref. 14, Fig. 5, and discussion, p. 376.