Electrical Properties of Solids. XIII. Polymethyl Acrylate, Polymethyl Methacrylate, Polymethyl-α-chloracrylate and Polychloroethyl Methacrylate[1]

BY DARWIN J. MEAD AND RAYMOND M. FUOSS

1. **Introduction.**—In a recent paper,[2] we presented some measurements on several high polymers in which the polar groups were attached to chain carbons by flexible bonds. In this paper, we present data covering the following four systems: I, polymethyl acrylate; II, polymethyl methacrylate; III, polymethyl-α-chloracrylate and IV, polychloroethyl methacrylate.

—CH₂CH—   —CH₂C(CH₃)—
(structures I and II, III and IV)

—CH₂CH—   —CH₂C(CH₃)—
        | |
       CO   CO
        | |
      OCH₃   OCH₃
       I   II

 CH₂CCl—   —CH₂C(CH₃)—
        | |
       CO   CO
        | |
      OCH₃   OCH₂CH₂Cl
      III   IV
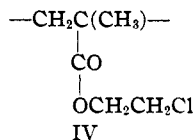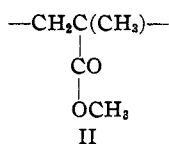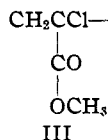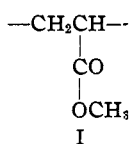
In these, the polar carbonyl group is attached to a chain carbon, and then a second polar group is attached to the carbonyl. In addition, two of them contain C–Cl dipoles. These compounds are the first of a series of polymers of the general type $(—CH_2 \cdot CXY—)_n$ which we planned to investigate.

Polymethyl acrylate is an isomer of polyvinyl acetate. The reversal of position of the —CO·O— group with respect to the chain produces several distinct changes in the electrical properties. The static dielectric constant of polymethyl acrylate is lower than that of polyvinyl acetate at a given temperature, and the peak loss factor is much lower. The distribution of relaxation times[3] is wider for the acrylate, because the highly polar carbonyl group is attached to the chain carbon, and only the weaker methoxy group is relatively free from the restrictions of motion imposed by the chain configurations.

Substituting a methyl group for a chain hydrogen of I gives II ("Lucite"), polymethyl methacrylate, which is markedly different in its electrical behavior from the simple acrylate. Apparently the methyl group on the same carbon which carries the polar group stiffens the chain

so that free rotation[4] is very much reduced. Consequently we find here a low static dielectric constant and a very broad distribution of relaxation times. Furthermore, the low temperature maximum in loss factor which has appeared for the other polar polymers which we have investigated fails to appear. Replacing the ester methyl group by a chloroethyl group again raises the dielectric constant, as expected. The chloracrylate is quite similar to the methacrylate, when allowance is made for the dielectric contribution of the halogen. Like Lucite, it also does not have a secondary low temperature maximum in loss factor, which confirms the idea that steric hindrance due to two groups on a chain carbon prevents crystallization.

2. **Experimental Details.**—Cells, electrical apparatus and general procedure were much the same as those used in previous papers of this series.

Polymethyl acrylate was otained from a commercial sample. It was freed from monomer and some material of low molecular weight by dissolving in acetone (17 g. to 800 cc.) and precipitating by adding an excess of cold methyl alcohol slowly to the chilled acetone solution. The original polymer was rather soft and the precipitate coagulated, instead of remaining flocculent. It was vacuum dried and stored over phosphorus pentoxide in an evacuated desiccator for a week before use. Discs were made by pressing for five minutes in a closed mold at 145°. Aquadag electrodes were painted on the discs, after which they were dried in a desiccator over phosphorus pentoxide. The index of refraction, measured on a Benford refractometer,[5] was 1.48.

The viscosities at 25° in cyclohexanone were measured for solutions containing 0.0288, 0.0528 and 0.0784 monomoles per liter of polymethyl acrylate. The measurements at each concentration were made at a series of pressures, and extrapolated to zero pressure.[6] The pressure dependence was about four times as large as for polyvinyl chloride. The three data give a straight line when $\lambda = (\ln \eta_r)/c$, the equivalent viscosity, is plotted against concentration. The corresponding equation is

$$\lambda = 12.38 (1 - 1.92 c) \qquad (1)$$

No estimate of molecular weight can be made because no absolute determination for polymethyl acrylate is available.

(1) Paper XII. THIS JOURNAL. 64, 283 (1942).

(2) Mead and Fuoss. ibid., 63, 2832 (1941).

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

(4) Bunn. Proc. Roy. Soc. (London), 180, 67, 82 (1942).

(5) Benford. J. Optical Soc. Am.. 29, 352 (1939).

(6) Mead and Fuoss, THIS JOURNAL, 64, 277 (1942).

Polymethyl methacrylate was obtained in powder form by pouring a dilute (25 g./1300 cc.) dioxane solution of a commercial polymer into water. After digesting to degelatinize the precipitate, it was thoroughly washed with water and vacuum dried. Discs for measurements were hot pressed, five minutes at 170°. Aquadag would not wet the polymer satisfactorily, so thin tin-foil electrodes[7] rubbed on with a little vaseline were used to eliminate the air film. The index of refraction was 1.47.

Several plasticized samples were made, by dissolving diphenylmethane in petroleum ether and mixing the solution with the powdered polymer.[8] After evaporation of the ether, discs were hot pressed: five minutes at 155° for the 20% sample, and five minutes at 150° for the 30% sample. The indices of refraction were 1.53 and 1.68.

Viscosities of solutions of the polymethyl methacrylate in cyclohexanone at 25° were determined. Concentrations were 0.0232, 0.0502 and 0.0760 monomole per liter; the data, after extrapolation to zero pressure, gave a straight line when λ was plotted against c

$$\lambda = 5.29(1 - 0.44 c) \qquad (2)$$

Although the methyl methacrylate probably has a higher molecular weight than the acrylate, the constant λ_0 is smaller for the former; this may mean that the methyl groups on the chain carbon inhibit curling of the chain in the methacrylate.

Polymethyl-α-chloracrylate was used without any fractionation. A piece of resin was crushed cold, and then hot pressed for five minutes at 155°, to form a test disc. The d. c. conductance was rather high, either due to pyrolysis or to impurities in the sample. The conductance, however, was not high enough to interfere with the low temperature measurements, which were the main point of interest for this polymer.

Chloroethyl methacrylate was prepared by ester interchange between methyl acrylate and ethylene chlorohydrin: 200 g. (2 moles) of monomethyl methacrylate, 241 g. (3 moles) of ethylene chlorohydrin, 6 g. of concd. sulfuric acid in 40 cc. of water and 4 g. of pyrogallol were refluxed for two hours, and then distillation of methyl alcohol was started. After the expected amount of alcohol was removed, the contents of the flask were washed several times with water containing 2.5% pyrogallol (to inhibit polymerization), in order to remove sulfuric acid and excess chlorohydrin, and then the chloroethyl methacrylate was distilled; it came over at 78° at about 18 mm. The normal boiling point was found to be 170°, by the usual micromethod. (By using the micro-method, a boiling point determination could be made before appreciable polymerization took place.) The ester was then polymerized by heating for five days at 40–45°. A hard, transparent solid was obtained. Chlorine analyses gave 20.87, 20.80% Cl, as compared with 23.8% theoretical. Apparently, some hydrogen chloride split out during the heating, giving a small amount of vinyl methacrylate. This was confirmed by the behavior of the polymer toward solvents: it swelled in ketones and ethylene chloride, but would not dissolve. Vinyl methacrylate is a bifunctional polymerant, and hence could give cross bonds in the final product, which would account for the insolublity. For electrical

measurements, discs were pressed (ten minutes at 150°) from a coarse powder made by crushing a piece of the polymer. The samples were not quite smooth, so they were polished flat before painting on the aquadag electrodes. The index of refraction was 1.51.

3. Experimental Results and Discussion.— A summary of the 60-cycle data for the four polymers is given in Table I; data at other frequencies are summarized in tabular form[9] as American Documentation Institute Document No. 1642.

TABLE I

ELECTRICAL PROPERTIES AT 60 CYCLES OF POLYMETHYL ACRYLATE (I), POLYMETHYL METHACRYLATE (II), POLYMETHYL-α-CHLORACRYLATE (III) AND POLYCHLOROETHYL METHACRYLATE (IV)

t, °C.	I ϵ'	ϵ''	II ϵ'	ϵ''	III ϵ'	ϵ''	IV ϵ'	ϵ''
-70	3.942	0.045	2.850	0.035	3.264	0.055	4.01	0.032
-60	3.990	.040	2.882	.040	3.330	.062	4.08	.034
-50	4.04	.036	2.916	.045	3.394	.067	4.14	.035
-40	4.09	.034	2.952	.053	3.473	.075	4.21	.037
-30	4.13	.032	2.998	.066	3.559	.087	4.28	.041
-20	4.19	.035	3.057	.085	3.650	.102	4.36	.049
-10	4.26	.041	3.130	.111	3.764	.123	4.44	.059
0	4.36	.053	3.206	.137	3.885	.151	4.50	.069
5	4.44	.068	...	...	...	...	..	...
10	4.64	.119	3.322	.177	4.01	.176	4.59	.083
15	4.96	.236	...	...	...	...	..	...
20	5.42	.424	3.453	.217	4.14	.209	4.69	.099
24	6.12	.620	...	...	...	...	..	...
30	6.98	.541	3.590	.251	4.37	.278	4.78	.116
35	7.33	.299	...	...	...	...	..	...
40	7.21	.083	3.79	.283	4.56	.343	4.95	.138
45	7.13	.032	...	...	...	...	..	...
50	7.05	.014	4.00	.298	4.83	.443	5.19	.179
55	6.89	...	..	...	...	...	..	...
60	6.84	...	4.20	.283	5.12	.554	5.46	.244
70	6.61	...	4.40	.250	5.42	.591	5.78	.347
80	6.53	...	4.61	.218	5.77	.622	6.23	.444
90	6.28	...	4.82	...	...	...	6.62	.421
100	6.13	...	...	...	...	...	6.79	.402

The results for several frequencies in the dispersion range for the polymers are shown in Figs. 1, 2, and 3. A definite similarity between the behavior of polymethyl acrylate (I) and that of its isomer, polyvinyl acetate (PViAc),[10] will be noticed, as well as some marked differences. Both show a dispersion and absorption which is describable in terms of a distribution of relaxation times, as indicated by the fact that the maximum loss

(9) For a copy of these tables, order Document 1642 from the American Documentation Institute, Offices of Science Service, 2101 Constitution Ave., Washington, D. C., remitting 25 cents for microfilm or 60 cents for photocopies readable without optical aid. The tables give dielectric constants and loss factors for the following: Table S-I, polymethyl acrylate at 60, 600, 6000 cps. 0 to −70°; S-II, polymethyl acrylate at 60, 120, 240, 480, 1000, 2000, 4000 and 8000 cps., 5 to 100°; S-III, polymethyl methacrylate at 1000 cps., −20 to −70° and at 60, 600 and 6000 cps., 40 to 90°; S-IV, polymethyl methacrylate–diphenylmethane, 80:20 at 60–8000 cps., 20 to 90°; S-V, polymethyl methacrylate–diphenylmethane, 70:30 at 60–8000 cps., 20 to 70°; S-VI, polychloroethyl methacrylate at 60, 600 and 6000 cps., −70 to +100°; and S-VII, polychloroethyl methacrylate at 60–8000 cps. and −73°.

(10) Ref. 2, Fig. 2.

(7) Fuoss, THIS JOURNAL, **59**, 1703 (1937).
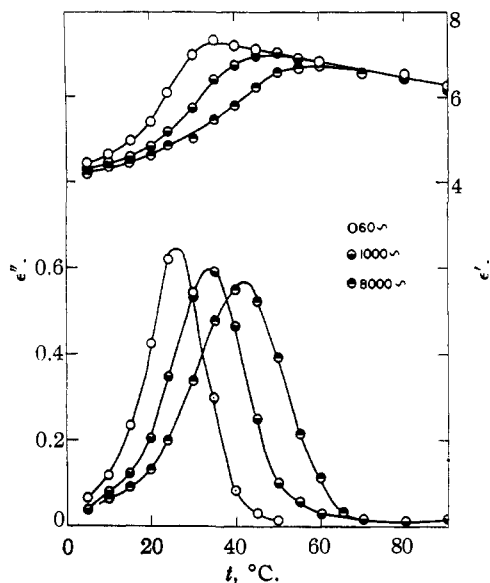
(8) Fuoss, *ibid.*, **63**, 369 (1941).
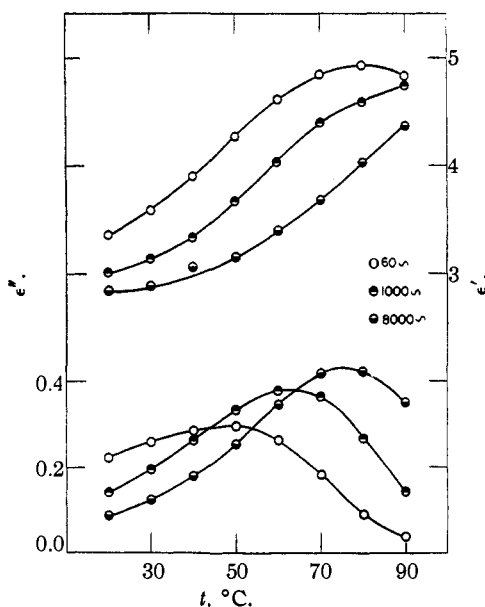
Fig. 1.—Electrical properties of polymethylacrylate.

Fig. 2.—Electrical properties of polymethylmethacrylate-diphenylmethane, 80:20.

Fig. 3.—Electrical properties of polychloroethylmethacrylate.

loss factor maxima.[2]) For a system describable by a single relaxation time, this ratio is unity, of course. It is interesting to note that the spatial reversal of the —CO·O— ester group from PViAc to I broadens the distribution considerably; in the former, the strongly polar carbonyl is attached to the chain by a flexible oxygen hinge and hence is relatively free to move, while in the latter it is directly attached to the chain carbon (like the halogen in PViCl) and its orientation is controlled by the configurations of the polymeric chain. The moment per monomer unit[11] of polymethyl acrylate is 2.0×10^{-18}, as compared with 2.3×10^{-18} for polyvinyl acetate.

The mechanical properties of polymethyl acrylate are also quite different from those of polyvinyl acetate. The former was soft and flexible at room temperatures, while both Gelva 15 and 60 were hard. The corresponding limiting viscosities in cyclohexanone were: I, 12.38; Gelva 15, 4.25 and Gelva 60, 9.25. If we assume that the loss factor maximum at a given frequency comes at lower temperatures for compounds of lower molecular weight,[12] then the acrylate had the lower molecular weight, because its 60-cycle maximum is at 27°, while those for the Gelvas are at nearly 60°. If it is argued, however, that the acrylate is soft, because it has a low molecular weight, then it must have a very much larger Staudinger constant than the acetate; ultracentrifuge or os-

factor is considerably less than half the difference between the square of the index of refraction and the static dielectric constant.[11] For I, the ratio $2\epsilon''_m/(\epsilon_0 - \epsilon_\infty) = 0.245$ while for PViAc, it is 0.536, nearly twice as large. (These figures are calculated from the 60 cycle data; $\epsilon'' = 0.645$ at 27° for I and 1.78 at 57° for PViAc. The static dielectric constants were determined by extrapolating the asymptotic envelopes of the corresponding $\epsilon' - T$ curves to the temperatures of the
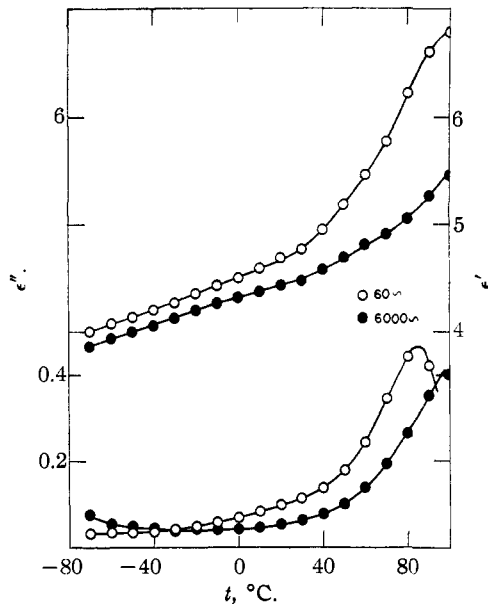
(11) Fuoss and Kirkwood, THIS JOURNAL, 63, 385 (1941).

(12) Fuoss, ibid., 63, 2401 (1941).

mometer data on these compounds would be very valuable aids in clearing up this point.

The only structural difference between the acrylate and methacrylate (aside from differences in molecular weight and distribution) is that, in the latter, the hydrogen atom on the carbon carrying the polar group has been replaced by a methyl group. This substitution has a far-reaching effect on the properties of the polymer. The 60-cycle loss factor maximum is shifted up to 50° from 27°, which indicates a very considerable increase in internal viscosity. At the same time, the static dielectric constant is reduced from 7+ to 5+, showing that internal rotations are very much hindered, even at low frequencies.

The most striking difference between polymethyl methacrylate and the other polymers so far studied, however, appears in the low temperature properties. Instead of showing a secondary loss factor maximum at low temperatures, polymethyl methacrylate has a single absorption peak in the high temperature range, from which it drops uniformly with decreasing temperature.
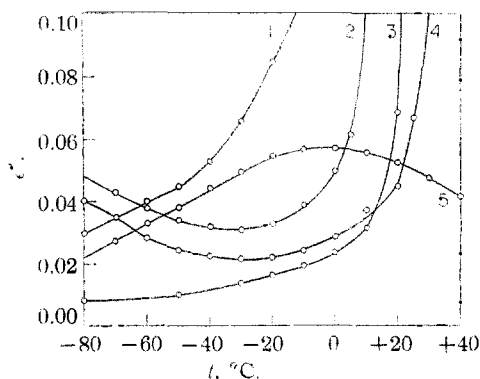

Fig. 4.—Comparison of polymers at low temperatures: 1, p-methyl-methacrylate; 2, p-methyl acrylate; 3, 20% plasticized p-vinyl chloride; 4. p-vinyl chloroacetate: 5, p-vinyl chloride.

As is shown in Fig. 4, the shape of the curve resembles most closely that of a plasticized polymer, which contains enough plasticizer to eliminate the low temperature maximum. It is not likely that polymethyl methacrylate exhibits a secondary maximum at temperatures below −70°, the lower limit of our experimental range, because the Cole plots[13] are symmetrical and, as was shown in the case of polyvinyl chloride and acetate, they are necessarily unsymmetrical when a low temperature maximum appears. Data for polymethyl methacrylate in the dispersion range

(13) Cole and Cole. *J. Chem. Phys.*, **9**, 341 (1941).

are given in Table II. A circular arc through these points extrapolates at $\epsilon'' = 0$ ($f = \infty$) very closely to 2.16, the square of the index of refraction, n. In all cases where a low temperature maximum appeared, a circular arc through the $\epsilon' - \epsilon''$ points in the dispersion range terminated at a point on the ϵ'-axis much larger than n^2.

TABLE II

ELECTRICAL PROPERTIES OF POLYMETHYL METHACRYLATE: DISPERSION CURVES

f	$t = 60°$		$t = 70°$		$t = 80°$	
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
60	4.16	0.282	4.36	0.252	4.56	0.216
120	4.03	.305	4.24	.289	4.46	.259
240	3.88	.311	4.09	.316	4.33	.294
480	3.72	.309	3.93	.330	4.18	.333
1 kc.	3.55	.297	3.75	.335	4.00	.348
2	3.42	.258	3.58	.318	3.80	.358
4	3.28	.227	3.42	.291	3.62	.343
8	3.17	.207	3.26	.255	3.43	.311

It has been argued[2] that the secondary maximum was characteristic of a polymer which was largely crystalline, while the high temperature maximum was due to dipole orientation in the liquid-like disordered or amorphous state. If this hypothesis is correct, then we assume that the methyl groups on the chain carbon interfere with close packing of the polymeric chains, and thus prevent crystallization, much as does the addition of a plasticizer of low molecular weight to a polymer of the $(-CH_2 \cdot CHX-)_n$ type. The addition of plasticizer[9] to polymethyl methacrylate affects the electrical properties in the expected way: it shifts the loss factor peak for a given frequency to lower temperatures.

Polymethyl-α-chloracrylate resembles polymethyl methacrylate in its mechanical and electrical properties. Data through the dispersion range were not obtained, on account of difficulties due to warping, and to the high d. c. conductance ($\kappa_0 = 0.078 \times 10^{-10}$ at 90°). Enough of the curve was obtained, however, to show that the 60-cycle maximum in absorption comes at about 90°, and an estimate of 9.2 as the lower limit for the static dielectric constant at 90° can be made. The chlorine atom on the chain raises the dielectric constant by about the expected amount, and, like the methyl group in Lucite, gives a uniformly decreasing loss factor with decreasing temperature (Table I).

Polychloroethyl methacrylate (IV) has a higher static dielectric constant than II, on account of the halogen, and the relatively free rotation of the

latter at the end of the —CH$_2$·CH$_2$Cl group. It is, however, much lower than the static dielectric constant of polyvinyl chloroacetate,[2] although it contains the same kind and number of polar groups. Two reasons for this difference may be advanced: (1) the methyl group in IV inhibits the rotation of the polar ester group, as shown by the comparison of I and II, and (2) the carbonyl group is attached directly to the chain, instead of through an oxygen. There is also a possibility that the side-chain carrying the chlorine is long enough to permit some intramolecular association of dipoles, which reduces the polarization much as intermolecular dipole interaction decreases the polarization of ordinary polar liquids.

A detailed discussion of IV is not possible, because the chlorine analysis and the insolubility suggest that it is somewhat cross-linked, instead of being a simple linear polymer. Other preparations, made under milder conditions, gave higher chlorine analyses, but the polymers were also insoluble in solvents which might be expected to dissolve polymers of the structure IV. However, only a few hundredths of a per cent. of bifunctional polymerant is enough to produce an insoluble polymer. It will be noted that IV, in con-tradistinction to II, shows the presence of a secondary maximum at low temperatures. Probably the replacement of a methyl hydrogen of II by the —CH$_2$Cl group changes the spatial relationships so that crystallization becomes possible again; this is indicated by some simple experiments with models. But considerable work remains to be done on the (—CH$_2$·CXY)$_n$ polymers before a detailed correlation between structure and mechanical and electrical properties can be made.

Summary

1. The dielectric constants and loss factors of polymethyl acrylate, polymethyl methacrylate (alone and plasticized with 20 and 30% diphenylmethane), polymethyl-α-chloracrylate and polychloroethyl methacrylate at temperatures in the range −70° to +100° and at frequencies from 60 to 8000 cycles have been determined.

2. The preparation of chloroethyl methacrylate (b. p. 170°) is described.

3. Some preliminary results on a correlation between structure and electrical properties for polymers of the type (—CH$_2$·CXY—)$_n$ are given.

The Hydration of β-Lactoglobulin Crystals*

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Knowledge of the composition of protein crystals is of importance in the interpretation of solubility, precipitation and X-ray data on proteins.

Several methods have been utilized in calculating hydration of protein crystals. Sørensen and Høyrup[1] developed the "Method of Proportionality" for evaluating the water content of protein crystals. Adair and Adair[2] applied density determinations to the measurement of hydration. A further method was devised by Crowfoot and Riley,[3] which is based on X-ray measurements of wet and dry crystals. The present report deals with the direct measurement of hydration by the loss in weight of a single protein crystal as well as hydration deduced from density determinations.

β-Lactoglobulin crystals as described by Palmer[4] are particularly valuable for direct study of hydration, since the crystals are quite large and may be prepared in the absence of salt or in the presence of high concentrations of salt.

Materials and Methods

β-Lactoglobulin was prepared from skim milk by the method of Palmer.[4] After several recrystallizations by dialysis, a further crystallization was made by adding concentrated ammonium sulfate solution to the protein solution through a rotating cellophane membrane. When the concentration of ammonium sulfate reached 2.66 molar, needle-shaped crystals appeared. The crystals were separated from the supernatant liquid and dissolved in a small volume of water. Salt was then removed by dia-

* Not copyrighted.

(1) S. P. L. Sørensen and Høyrup, Compt. rend. trav. lab. Carlsberg, 12, 169 (1917).

(2) Adair and Adair, Proc. Roy. Soc. (London), B120, 422 (1936).

(3) Crowfoot and Riley, Nature, 141, 521 (1938).

(4) Palmer, J. Biol. Chem., 104, 859 (1934).