Dielectric Properties of Poly(methyl Methacrylates)

G. A. JOHNSON and AURORA DOREN
Escuela de Quimica y Farmacia, Universidad de Chile, Catedra de Fisico-Quimica, Santiago, Chile

CONSIDERABLE WORK has been done on the dielectric properties of organic solvents and of dilute solutions of fairly large organic molecules (*11*), but there is a lack of data for polymer solutions. One of the systems which has been studied is that of dilute solutions of poly(methyl methacrylates) and the present work was done to clarify apparent discrepancies between the results of Pohl, Bacskai, and Purcell (*9*) and de Broukère, Buess, Bock, and Versluys (*2*). Pohl obtained very broad distributions of relaxation times, and showed that the dielectric properties were dependent on the structure of the polymer chain, i.e.—isotactic, atactic, or sindiotactic. Their measurements were in the microwave region. De Brouckère showed that the critical frequency was independent of molecular weight, was also independent of concentration, and fell with decreasing temperature. All measurements were at 0° C. or below and all critical frequencies were below 30 Mc. per second. They also found a considerable distribution of relaxation times and the apparent random behavior of the critical frequency may be due to this. The experimental results of the two articles mentioned are compared with the data presented in this work.

EXPERIMENTAL

The apparatus (Test Set for Dielectrics, H. Tinsley and Co. Ltd., London, designed by Hartshorn and Ward (*6*)) measured dielectric constants and loss factors in the frequency range of 0 to 100 Mc. per second. The apparatus utilizes the resonance method for the measurement of the electrical quantities. It was calibrated by taking toluene as the standard and assuming zero loss for it. In certain cases this necessitated repeated distillations of the toluene until this zero loss was obtained. With these precautions the error in the loss factor was $\pm 16 \times 10^{-4}$.

The molecular weights of the polymer samples were obtained from viscosity measurements in a capillary viscometer using the following equation (*1*):

$$M_v = 2.811 \times 10^5 [\eta]^{1.32}$$

where M_v is the viscosity average molecular weight and $[\eta]$ is the intrinsic viscosity. For these measurements dilute solutions of maximum concentration 0.5 gram per 100 ml. were used.

The polymers were prepared by Kirkman (*8*) by the method of emulsion polymerization.

The solutions were made by dissolving known weights of the polymer in analytical reagent grade toluene. In general the concentrations 1, 0.5, 0.25, and 0.125 gram per 100 ml. were used. The results are expressed by the method used by Pohl (*9*) and in all cases the quantities a′ and a′′ are plotted on the graphs or are in the table where:

$$a' = \partial\epsilon'/\partial C \qquad a'' = \partial\epsilon''/\partial C$$

The results are given in Table I and Figures 1 and 2. In Figure 1 the factor $a''_{\max}$ is plotted against the molecular weight and in Figure 2 the Cole-Cole arc plots (*3*) are shown for three values of α: 0.11, 0.56, and 0.65. In this case the curve is the plot of a'' *vs.* a'. On the same graph are the results of Pohl and others for atactic poly(methyl methacrylates).

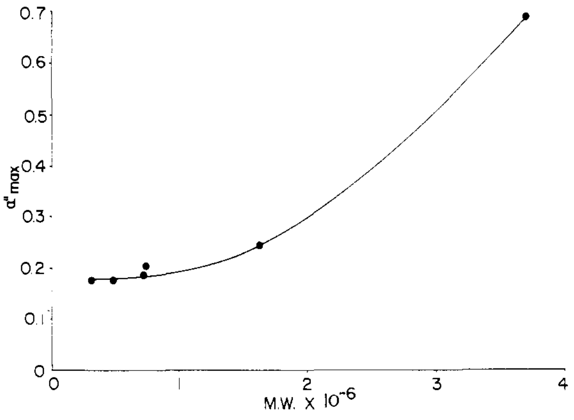

Figure 1. The parameter $a''_{\max}$ vs. molecular weight

The value of the critical frequency, f_c, was obtained from a plot of the dielectric loss factor against the logarithm of the frequency, the maximum of this curve corresponding to this value of the frequency.

The values of a' and a'' were calculated from the dielectric data at four different concentrations using the equations quoted above. The mean of these values was then calculated and the best curves were drawn through the points. From the loss curves thus obtained the value of $a''_{\max}$ was read from the curve.

The static dielectric constant was measured and is quoted in Table I (ϵ_s), and the value of a'_∞ at infinite frequency was obtained from the Cole-Cole plot.

The value of the parameter, α, was calculated by the usual methods as the radius of the circle drawn through the center of the circle from the a'_∞ point makes an angle $\alpha\pi/2$ with the abscissa.

The relaxation time, θ_o was calculated directly from the critical frequency assuming $\theta_o = \frac{1}{2}\pi f_c$. The relaxation times θ_1 and θ_2 define the limits of the distribution of relaxation times and were calculated from an equation developed by Higasi, Bergmann and Smyth (*7*). In this

$$\theta_1 = \theta_o \exp. - A/2$$

and

$$\theta_2 = \theta_o \exp. + A/2$$

where A is related to α in the following way

$$\alpha = 1 - 4/\pi \tan^{-1}[2/A \tan^{-1} \sinh A/2]$$

Unfortunately this applies only when $\alpha < 0.3$ and thus can be used in only one case.

DISCUSSION

The effects are more or less identical with those observed by de Brouckère and others, in that the critical frequency is independent of the molecular weight and the concentration; the static dielectric constant, the dielectric constant measured at the critical frequency, and the dielectric constants at infinite frequency are independent of molecular

Table I. Dielectric Data for Poly(methyl Methacrylates)

Sample	M.W. × 10^{-5}	f_c Mc./secs.	$a''_{\max}$	θ_0	θ_1 × 10^9 secs.	θ_2	α	ϵ_s	a'_∞
R29	7.2	20	0.20	79.7			0.63	2.53	0.89
R30	7.02	20	0.18	79.7			0.65	2.51	0.87
R34	36.8	28	0.70	56.8	18.9	170.4	0.11	2.49	0.85
R36	3.0	21	0.18	75.8			0.65	2.50	0.86
R38	4.61	20	0.17	79.7			0.68	2.49	0.85
R40	16.0	21	0.24	75.8			0.56	2.49	0.85

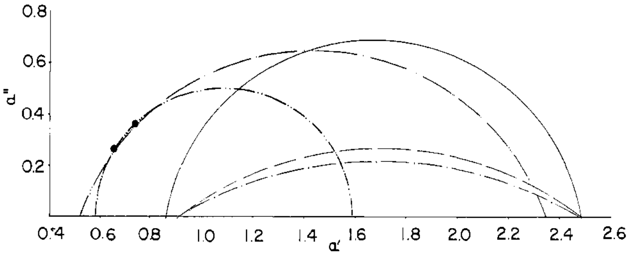

Figure 2. Cole-Cole arc plots: a'' vs. a' for the data

This work α 0.11 ——
0.56 – –
0.65 –·–
Phol ond others 0.21 –····–
Theoretical 0.0 –···–

weight; and finally, the Cole parameter α decreases as the molecular weight increases. The last effect is far more marked in this work than in the work of de Brouckère and others. This could be due to the difference in temperature. If one extrapolates the critical frequencies obtained by de Brouckère at the different temperatures to 25° C., the result is a critical frequency of the same magnitude. This seems to suggest that the same absorption band is being measured in the two works. The only exception is that in the present work the parameter $a''_{\max}$ increases with molecular weight, the variation being between 0.17 and 0.70; whereas de Brouckère showed that $\epsilon''_{\max}/C$, where C is the concentration, was independent of molecular weight, at least within experimental error, the variation being between 75×10^{-4} and 87×10^{-4}.

From the data presented here it appears that the absorption band under consideration will terminate at a frequency somewhere above 100 Mc. per second, overlapping at the highest frequencies with the band found by Pohl and others. In the magnitude of the absorption, however, there appears to be a marked difference between the results of this work (and those of Pohl and others) and the results of de Brouckère and others. The simplest explanation could be the temperature difference. This seems unreasonable, as de Brouckère measures between −30° and 0° C. and obtains the same effect at all frequencies; in this work the temperature is 25° C. Because of the high frequency a second absorption band might overlap the first, with a large maximum value for the loss factor. This does not appear reasonable, as a smooth curve is found for the three curves: dielectric constant and loss factor *vs.* log frequency and dielectric constant *vs.* loss factor. In Figure 2, the points are omitted from the curve for the sake of clarity; measurements were made at twelve frequencies in the range of 1 to 100 Mc. per second. The accuracy was high; hence the semicircles of the Cole arc plot are accurate and because of this, the values of the parameter α. Therefore, a definite explanation of the differences between the results of de Brouckère and this work is not possible; agreement is possible only in the general picture of the effect.

Pohl and others obtained values of the dielectric constant and loss factor at three frequencies in the microwave region (corresponding to wavelengths of 10, 25, and 50 cm.) and the static dielectric constant at 1000 cycles per second. They drew Cole Arc plots passing through the four points. The result for the atactic polymer is given in Figure 2. In the light of the results presented here this does not appear reasonable and the absorptions may be characterised as shown in Figure 2: a pure Debye absorption at high frequencies overlapping the wide dispersion low frequency band. The overlapping of bands has been observed before (*10*). In fact, this is a well recorded phenomenon when more than one group in the molecule can be oriented in the alternating field (*4*).

The explanation which can therefore be offered for the observed dependence of the dielectric properties of poly(-methyl methacrylates) on the frequency of the applied field is that at low frequencies the band observed is due to oscillations of part of the polymer chain. This part of the chain is of constant length and independent of the molecular weight of the polymer and of the concentration. This probably means that the degree of coiling of the chain is independent of the concentration at least within the range of concentrations studied. At some frequency above 100 megacycles per second this band overlaps a further high frequency band.

This second band has been interpreted as a pure Debye type and appears to be due to oscillations of the smallest segmental modes. At these frequencies the solvent also shows relaxation and the final value of the dielectric constant is exceedingly low, 0.6 for a' according to the results of Pohl and others.

A reasonable picture seems therefore to have been offered and the experimental data available appears to support it.

ACKNOWLEDGMENT

The authors thank K. Kirkman of the Manchester College of Science and Technology, England, for kindly supplying the samples of polymers used in this work.

LITERATURE CITED

(1) Baxendale, J.H., Bywater, S., Evans, M.C., *J. Poly. Sci.* **1**, 237 (1946).
(2) Brouckère L. de, Buess D., Bock J. de, Versluys, *J. Bull. Soc. Chim. Belg.* **64**, 669 (1955).
(3) Cole, K.S., Cole, R.H., *J. Chem. Phys.* **9**, 341 (1941).
(4) Davidson, D.W., Cole, R.H., *J. Chem. Phys.* **19**, 1484 (1951); **20**, 1389 (1952).
(5) Franklin, A.D., Heston, W.M., Hennelly, E.J., Smyth, C.P., *J. Am. Chem. Soc.* **72**, 3447 (1950).
(6) Hartshorn, A.J., Ward, W.H., *J. Inst. Elec. Eng.* **79**, 597 (1936).
(7) Higasi, K., Bergmann, K., Smyth, C.P., *J. Phys. Chem.* **64**, 880 (1960).
(8) Kirkman, K., M. Sc. Tech. thesis, Manchester, England, (1960).
(9) Pohl, H.A., Bacskai, R., Purcell, W.P., *J. Phys. Chem.* **64**, 1701 (1960).
(10) Roberti, D.M., Smyth, C.P., *J. Am. Chem. Soc.* **82**, 2106 (1960).
(11) Smyth, C.P., "Dielectric Behavior and Structure," McGraw-Hill, New York, 1955.

RECEIVED for review December 21, 1961. Accepted April 16, 1962.