

181

THE VELOCITY OF PROPAGATION OF ULTRASONIC WAVES AND THE FORM OF THE MOLECULES OF HIGH POLYMERS *

GIULIO NATTA AND MARIO BACCAREDDA

ISTITUTO DI CHIMICA INDUSTRIALE DEL POLITECNICO AND THE CENTRO DI STUDIO PER LA CHIMICA INDUSTRIALE DEL C. N. R., MILANO, ITALY

In earlier and what was preliminary work¹, the present authors observed that the velocity of propagation of ultrasonic waves in liquids of high molecular weight or in solutions depends on the form of the molecule and particularly on the frequency and length of side chains. It was also observed, in a study of a series of hydrocarbons and of certain polyethers, that the ratio of the velocity of propagation and the density of homologous polymers increases with increase in the molecular weight of chain compounds with no side chains or with but few side chains, that the ratio remains practically constant for compounds containing closely spaced side methyl or ethyl groups, and that it decreases with increase in the molecular weight of compounds containing closely spaced side groups of larger size.

In addition it was found in the earlier work that, in the case of substances of low molecular weight, the adiabatic compressibility depends on the form of the molecule.

The velocity of propagation u of ultrasonic waves in a liquid is related to the adiabatic compressibility β and to the density ρ by the known equation:

$$u = \sqrt{\frac{1}{\rho\beta}}$$

As has been shown by one of the present authors², the adiabatic compressibility for various series of liquid isomers of low molecular weight is related directly to the molecular structure, provided that the isomers are at the particular temperatures at which their densities are the same. Under such conditions, for example, the greater the number of side chains in the molecules of the nine isomeric heptanes, the greater is their adiabatic compressibility, and various isomeric ethylenes are more compressible in the *cis*-form than in the *trans*-form.

Other authors, for example, Frenkel³, had assumed previously from other considerations that the molecules of a liquid are not to be regarded as "rigid" but rather as appreciably compressible. Furthermore, the variations in the molecular refraction observed in some gases at high pressures, *e.g.*, carbon dioxide, have been explained by De Groot and Seldam⁴ as the effect of variations in the molecular radius as a function of the pressure. In view of these hypotheses we could only conclude that the spatial structure influences the compressibility.

We have now extended the study to numerous substances of high molecular weight.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Gazzetta Chimica Italiana*, Vol. 79, No. 5, pages 364-368, May 1949.

weight, and have been able to establish a clearer dependence between the velocity of the propagation of ultrasonic waves on the form of the molecule by comparing experimental velocities with those which can be theoretically predicted by empirical formulas already known and fairly well verified for compounds of low molecular weight.

As we shall see later, we have defined as the *form factor* the ratio between the experimental velocity and the calculated velocity, because this ratio has been found to be related to the form of the molecule.

Let us examine how this definition of the form factor was derived.

According to Rao⁵, the velocity of propagation of ultrasonic waves in an unassociated liquid can be calculated on the basis of the nature of the atoms which make up the molecule by means of the empirical relation which he established between the cube root of this velocity u and the molecular volume:

$$\sqrt[3]{u \cdot \frac{M}{\rho}} = R = \sum m_i R_i$$

where M is the molecular weight and ρ is the density. R is independent of the temperature for every unassociated liquid, and appears as an additive constant. It can, in fact, be calculated as the sum of the partial constants R_i , each one relating to every atom contained m_i times in the molecule, or better, can be referred to the different valence bonds present in the molecule. Obtaining thus the value of R , the value of u at any temperature can be calculated from the above equation by introducing for ρ the value of the density at the same temperature. If the law of additivity assumed by Rao for the R constants, based on the partial R_i values relative to the individual atoms composing the molecule, were strictly valid, it would obviously be incompatible with the dependence, already demonstrated by us, of the velocity of propagation of ultrasonic waves on the structure of the molecule of various series of isomers. In fact, on the basis of the formula of Rao, the velocities of propagation in various isomers at the same temperature would have to be proportional to the third power of the density, and this does not agree with facts, as is evident when one considers, for example, such a case as the isomeric heptanes mentioned above.

Lagemann and Corry⁶ have proposed to calculate the R constants, not as the sum of the constants relating to the single atoms, but rather as the sum of the values corresponding to the various bonds contained in the molecule, and have thus introduced the concept of "bond velocity".

The values proposed by Lagemann and Corry for the bonds which are involved in the products studied in the present work are given below:

C—H	95.2	O—H	99.0
C—C	4.25	C—C	129
C—O	34.5	C—O	186

Such a method of calculation should give, according to the authors, results which would appear to be in better accord with experimental data than were those of Rao. Nevertheless, even this method necessarily disregards the influence on the velocity of propagation of the form of the molecule when isomers containing the same chemical bonds or *cis*- and *trans*-isomers are involved.

We propose, therefore, to introduce a definite form factor for every liquid compound as the ratio of the velocity of propagation found experimentally at

a definite temperature to the calculated velocity of propagation at the same temperature, based on the atoms or on the component chemical bonds and on the relation:

$$u = \left(\frac{R_p}{M} \right)^3$$

The form factor is found to be independent of the temperature.

The velocity of propagation of the ultrasonic waves was measured by the method of Hiedemann, which is applicable only to transparent substances and to the liquid state. The same method was also used for substances which are solid at ordinary temperature. When the substances melted at temperatures below 100°, the measurements were made at different temperatures above those of the melting points. On the other hand, in the case of substances fusible with difficulty or which were extremely viscous even at a high temperature (the coefficient of absorption of the ultrasonic waves is proportional to the coefficient of viscosity), various measurements were made on solutions close to the point of saturation and also on solutions of lower concentration. In such a case the velocity of propagation as determined experimentally was assumed to be that obtained by extrapolation of the velocities of propagation of solutions of increasing concentrations to a concentration of solute of 100 per cent, and introducing, to calculate the velocity of propagation by the formula of Rao, the density for the hypothetical superfused liquid state deduced in a similar way from the densities of the solutions.

Such extrapolations give values which are in satisfactory agreement, even in the case of limited solubility, only when the solutions conform approximately to the laws of additivity of specific volumes, or when ideal solutions are involved; in such a case, in fact, while the density ρ_c of the mixture appears to be a linear function of the concentration by volume c , the velocity of propagation u_c , as has been already shown by the present authors⁷, can be expressed by the formula:

$$u_c = \frac{1}{\frac{c}{u_1} + \frac{1-c}{u_2}}$$

where u_1 and u_2 are the velocities of propagation in the two pure components, or rather if it is desired to refer to the concentration by weight x , by the formula:

$$u_x = \frac{1}{\left(\frac{x}{u_1 \rho_1} + \frac{1-x}{u_2 \rho_2} \right) \rho_x}$$

where u_1 and u_2 are the densities of the pure components in the liquid state; u_x and ρ_x are the velocities of propagation and density of the mixture of concentration x , respectively.

Either of these two equations can be solved with respect to the unknown u_1 (velocity of propagation determined experimentally in the solid considered as in the superfused liquid state) when the values of all the other factors contained in the equation are known.

$$u_1 = \frac{c}{\frac{1}{u_1} - \frac{1-c}{u_2}} = \frac{x}{\left(\frac{1}{u_x \rho_x} - \frac{1-x}{u_2 \rho_2} \right) \rho_1}$$

The value of $\rho_1 = \frac{\rho_c - \rho_2(1 - c)}{c}$ is also introduced into the formula of Rao for the calculation of the theoretical velocity of propagation expressed as $u = \left(\frac{R}{M \rho_1}\right)^{\frac{1}{2}}$ in all those cases in which direct measurement of the density of the polymer in the liquid state is not possible. The values of the densities of the products calculated in this way are affected by errors the magnitudes of which are greater the less the concentration of the solute and the greater the deviation of the solution from the ideal.

As far as substances of low molecular weight are concerned, the influence of the molecular structure on the form factor is evident by an examination of Table I, which gives the velocities of propagation of the nine isomeric heptanes

TABLE I

Hydrocarbon	Experimental u at 20° C (Freyer, Hubbard and Andrews) (m. sec. ⁻¹)	Calculated u at 20° C (Rao) (m. sec. ⁻¹)	Form factor
n-Heptane	1154	1170	0.985
2-Methylhexane	1120	1158	0.965
3-Methylhexane	1135	1205	0.940
3-Ethylpentane	1169	1260	0.925
2,2-Dimethylpentane	1080	1123	0.960
2,3-Dimethylpentane	1148	1238	0.931
2,4-Dimethylpentane	1083	1143	0.947
3,3-Dimethylpentane	1129	1234	0.913
2,2,3-Trimethylbutane	1101	1225	0.900

already determined at 20° C by Freyer, Hubbard and Andrews³, the velocities calculated by the equation of Rao, on the basis of the values of the bond velocities of Lagemann and Corry, and finally the form factors derived from them.

An examination of Table I makes it evident that the form factor decreases with increase in the length and number of side chains and with increase in the symmetry of the molecule.

A detailed examination of these factors for substances of low molecular weight will be the object of a further paper. In the present work we wish to refer to the results already obtained in the determination of the form factor of substances of high molecular weight.

It should be noted in the first place that, if the law of Rao holds true, the velocity of propagation of the ultrasonic waves for members of a series of homologous polymers ought to be proportional to the cube of the density and be independent of the molecular weight.

In fact, if n is the degree of polymerization, m is the weight of the base molecule, and r the relative constant of Rao, then for degrees of polymerization which are sufficiently high to reduce the influence of the terminal groups:

$$M = n \cdot m \quad R = n \cdot r \quad u = \frac{R^{\frac{1}{2}}}{M^{\frac{1}{2}} \rho^{\frac{1}{2}}} = \left(\frac{r}{m}\right)^{\frac{1}{2}} \rho^{\frac{1}{2}} = K \rho^{\frac{1}{2}}$$

For very high molecular weights, ρ also tends toward a constant limiting value, and the same should be true for the velocity of propagation.

Consequently, the form factor, which is the ratio of the two velocities of propagation, also should tend, at sufficiently high molecular weights, toward a

limiting value which is independent of the molecular weight and therefore is dependent only on the form of the molecule. The experimental results which the present authors have already obtained confirm these deductions, as will be seen later.

The method proposed, notwithstanding the low stability of the large molecules with respect to ultrasonic waves recently pointed out by Mark², can be applied to the study of substances of high molecular weight because it is possible to avoid practically any appreciable depolymerization by using an apparatus of small power and reducing the time necessary for carrying out the measurements.

EXPERIMENTAL PART

The results so far obtained in determining the velocity of propagation of ultrasonic waves in different series of high polymers, both in the fused state and in solution, and in the calculation of their respective form factors, will now be explained.

The experimental determination of the velocity of propagation was carried out with the method of Bache, Heidemann and Asbach¹⁰, as modified by Giacomini, and described in an earlier work¹¹.

The high-frequency oscillator (4MHz) was designed and constructed at the National Institute of Electro-Acoustics of the National Council of Research (l'Istituto Nazionale di Elettroacustica del Consiglio Nazionale delle Ricerche).

For the products in the liquid state which were examined at temperatures other than room temperature and for solutions, the approximation of the measurements can be controlled within ± 2 meters per second; the values of the extrapolated velocities for the solutes are, on the other hand, subject to greater errors, particularly in cases where it is necessary to carry out measurements on solutions of low concentration and on solutions which are extremely viscous or are not transparent.

The experimental velocities were compared with the calculated velocities, using the values of the "bond velocity" proposed by Lagemann and Corry; for the bonds C—N and N—H, which were not studied by Lagemann and Corry, we carried out corresponding determinations with carefully chosen compounds.

The densities of the solutions and of the fused products which were not very viscous were determined by means of a Westphal balance with a cylinder, heat-controlled to within $\pm 0.1^\circ$ C; the densities of the highly viscous products were determined by means of a volumometer.

HYDROCARBONS OF HIGH MOLECULAR WEIGHT

In this group three hydrocarbons were examined: an ordinary grade of paraffin with a melting point of 60° C, a paraffin obtained with the Fischer-Tropsch process having a melting point of 90° C, and polyethylene from the Imperial Chemical Industries.

The first two products were examined in the fused state, the third was examined in a hot xylene solution and in a solution in paraffin having a melting point of 60° C, likewise at elevated temperature.

In Table II are reported the velocities of propagation of the ultrasonic waves and the experimental densities at various temperatures of the liquids examined, as well as the velocities of propagation that were calculated for polyethylene in the superfused state by extrapolating the values of the solutions

in xylene or in paraffin, on the assumption that these solutions are ideal. The densities of the solutions of polyethylene in xylene are obviously equal to those of the pure solvent, which shows that, at the temperatures at which the experiments were carried out, the polyethylene in solution had practically the same density as the solvent.

In the same table are also recorded, for the three products examined, the velocities of propagation, calculated by the method described, which is based on the equation of Rao and the relative form factors: $f = \frac{u_{\text{exptl.}}}{u_{\text{calcd.}}}$.

For all three of the products examined, these latter are close to unity, and, as was foreseen, do not vary appreciably with changes in temperature.

TABLE II

Substance	°C (±0.1°)	Experi- mental u (m. sec. ⁻¹)	ρ (g. per cc.)	Calcu- lated u (m. sec. ⁻¹)	$f = \frac{\text{experimental } u}{\text{calculated } u}$
Paraffin with melting point	60.0	1293	0.781 ± 0.001	1278	1.01
	70.0	1261	0.776 ± 0.001	1250	1.01
	95.0	1179	0.763 ± 0.001	1193	0.99
	99.0	1165	0.761 ± 0.001	1179	0.99
Paraffin (Fischer) (m.p. 90° C)	98.0	1224	0.764 ± 0.001	1196	1.01
	100.3	1217	0.763 ± 0.001	1190	1.01
Solutions of polyethylene:					
(1) Xylene solutions (5.52% by wt.)	75.0	1129	0.819 ± 0.001	—	—
	80.0	1107	0.815 ± 0.001	—	—
(2) Xylene	20.0	1340	0.865 ± 0.0002	—	—
	75.0	1107	0.819 ± 0.001	—	—
	80.0	1087	0.815 ± 0.001	—	—
(3) Solution in paraffin (m.p. 60° C) (5.87% by wt.)	95.0	1189	0.765 ± 0.001	—	—
	99.0	1175	0.763 ± 0.001	—	—
(4) Polyethylene in xylene in paraffin	75.0	1480	0.819 ± 0.010*	1472	1.00
	80.0	1450	0.815 ± 0.010*	1750	1.00
	95.0	1420	0.804 ± 0.010*	1395	1.02
	99.0	1380	0.800 ± 0.010*	1372	1.01

* Values of the density in the superfused state calculated from the density of the solutions in xylene assumed to be ideal.

In addition, there were examined not only a triisobutylene which the present authors prepared, but also a series of polyisobutylenes (Oppanol-B of the I-G. Farbenindustrie) of different molecular weights (3000, 6000, 15,000 and 200,000), a sample of Butyl rubber (isobutylene copolymerized with 1-2 per cent of isoprene), a polymer of α -butylene prepared in the laboratory of the present authors, and a copolymer obtained from a mixture of 79 per cent of α -butylene and 21 per cent of butadiene by the action of aluminum chloride. The relative results are reported in Table III.

Of these products we were able to examine directly the first and the last two at more or less elevated temperatures; the polyisobutylenes with higher degrees of polymerization were examined in a solution in normal heptane at 20° C, and the Butyl rubber was examined in solution in cyclohexane.

The form factors of the polyisobutylenes were practically independent of the molecular weight, and equal to 0.80; the form factor of Butyl rubber (dissolved in cyclohexane) was 0.65. The polymer of α -butylene showed a form

TABLE III

Substance	Temp. °C (±0.1°)	Experi- mental u (m. sec. ⁻¹)	ρ (g. per cc.)	Calcu- lated u (m. sec. ⁻¹)	$f = \frac{\text{experimental } u}{\text{calculated } u}$
Triisobutylene	20	1237 ± 1	0.759 ± 0.001	1360	0.91
Polyisobutylene (mol. wt. 3000)	65	1350 ± 2	0.860 ± 0.001	1700	0.80
Polyisobutylene (mol. wt. 6000) in heptane (10.80% by wt.)	20	1173 ± 2	0.704 ± 0.001	—	—
Heptane	20	1153 ± 1	0.6834 ± 0.0002	1170	0.985
Polyisobutylene (mol. wt. 6000)	20	1460 ± 10	0.884 ± 0.002	1853	0.79
Polyisobutylene (mol. wt. 15000) in heptane (14.0% by wt.)	20	1180 ± 2	0.709 ± 0.001	—	—
Polyisobutylene (mol. wt. 15000)	20	1485 ± 10	0.892 ± 0.002	1900	0.79
Polyisobutylene (mol. wt. 200,000) in heptane (5.10% by wt.)	20	1171 ± 2	0.693 ± 0.001	—	—
Polyisobutylene (mol. wt. 200,000)	20	1848 ± 25	0.953 ± 0.010*	2318	0.80
Butyl rubber in cyclo- hexane (5.57% by wt.)	20	1286 ± 2	0.784 ± 0.001	—	—
Cyclohexane	20	1281 ± 1	0.777 ± 0.0002	1259	0.01
Butyl rubber	20	1395 ± 10	0.930 ± 0.005*	2152	0.65
Poly- α -butylene	45	1320 ± 2	0.842 ± 0.001	1620	0.82
	50	1306 ± 2	0.840 ± 0.001	1600	0.82
	55	1291 ± 2	0.837 ± 0.001	1575	0.82
Copolymer of 79% α -butylene and 21% butadiene	80	1238 ± 2	0.846 ± 0.001	1630	0.76
Polystyrene in styrene (6.50% by wt.)	20	1364 ± 2	0.898 ± 0.001	—	—
Styrene (monomer)	20	1354 ± 1	0.887 ± 0.001	1360	1.00
Polystyrene in benzene (19.88% by wt.)	20	1346 ± 2	0.913 ± 0.001	—	—
	20	1323 ± 1	0.879 ± 0.001	1310	1.01
Benzene	30	1275 ± 1	0.869 ± 0.001	1265	1.01
Polystyrene in styrene	20	1524 ± 25	1.093 ± 0.020*	1832	0.83
Polystyrene in benzene	20	1470 ± 10	1.093 ± 0.005*	1790	0.82

* Values of the density in the superfused state calculated from assumed ideal solutions.

factor of 0.82, and the form factor of the copolymer with butadiene was lower, viz., 0.76.

Table III also gives data on solutions of a polystyrene obtained by spontaneous polymerization of the monomer in styrene and in benzene at ordinary temperature, and the corresponding form factor, which was calculated as 0.82-0.83.

In further experiments, samples of natural rubber and masticated rubber, a sample of Buna-32, and another sample of Buna-32 completely hydrogenated in our laboratory, were examined. All the products were examined in normal heptane solutions at 20° C except the natural rubber, which was examined at elevated temperature in solution in paraffin having a melting point of 60° C. The results are reported in Table IV.

The value of the form factor is 0.89-0.90 for natural rubber; 0.80 for rubber masticated 10 minutes, and 0.82-0.94 for Buna-32, whether hydrogenated or not.

TABLE IV

Substance	Temp. °C ($\pm 0.1^\circ$)	Experi- mental η (m. sec. ⁻¹)	ρ (g. per cc.)	Calcu- lated η (m. sec. ⁻¹)	$f = \frac{\text{experimental } \eta}{\text{calculated } \eta}$
Natural rubber in paraffin (melting point 60° C) (see Table II) (7.43% by wt.)	70	1273 \pm 2	0.783 \pm 0.001	—	—
	75	1256 \pm 2	0.780 \pm 0.001	—	—
Natural rubber	70	1465 \pm 20	0.880 \pm 0.010*	1635	0.90
	75	1435 \pm 20	0.876 \pm 0.010*	1610	0.89
Masticated rubber in heptane (see Table III) (6.64% by wt.)	20	1166 \pm 2	0.696 \pm 0.001	—	—
Rubber masticated 10 minutes	20	1387 \pm 20	0.904 \pm 0.010*	1730	0.80
Buna-32 in heptane (11.45% by wt.)	20	1170 \pm 2	0.708 \pm 0.001	—	—
Buna-32	20	1435 \pm 10	0.906 \pm 0.002**	1710	0.84
Hydrogenated Buna-32 in heptane (20.60% by wt.)	20	1200 \pm 2	0.717 \pm 0.001*	—	—
Hydrogenated Buna-32	20	1530 \pm 10	0.885 \pm 0.002**	1870	0.82

* Density values in the superfluid state calculated from the density of assumed ideal solutions.
 ** Values calculated by extrapolations from determinations at higher temperatures.

The comparison between the form factors of the hydrocarbons of high molecular weight with those of hydrocarbons of analogous constitution but of low molecular weight is of particular interest:

In this connection Table V shows, both for compounds of low molecular weight and for those of high molecular weight which were examined, the form factors in relation to the ratio ψ between the number of side chains and the number of atoms in the principal chain.

An examination of Table V shows that, both with products of high molecular weight and with those of low molecular weight, the more frequent and the

TABLE V

Hydrocarbons of low molecular weight				Hydrocarbons of high molecular weight			
Substance	ψ	Type of side chains	f	Substance	ψ	Type of side chains	f
Normal heptane	0	—	0.985	Normal paraffins and polyethylene	0	—	1.00
Methylhexanes (2- and 3-)	0.167	CH ₃	0.952	Natural rubber	0.25	CH ₂	0.90
Ethylpentane	0.2	C ₂ H ₅	0.925	Poly- α -butylenes	0.5	C ₂ H ₅	0.82
Dimethylpentanes (2,2-; 2,3-; 2,4-; 3,3-)	0.4	CH ₃	0.937	Polystyrenes	0.5	C ₆ H ₅	0.82
Trimethylbutane	0.75	CH ₃	0.900	Polyisobutylenes	1	CH ₃	0.80

more extensive are the side chains, the smaller is the form factor; and furthermore that, for products of high molecular weight, the influence of the side chains of the molecules is somewhat more sensitive than in products of low molecular weight.

The effect of the side chains of the molecule on the form factor is evident also from conclusions which can be drawn from the results in the preceding tables. Thus the lowest value of f (0.76) shown by the copolymer obtained from a mixture of 79 per cent of α -butylene and 21 per cent of butadiene, both in comparison with the polymer of α -butylene (see Table III) and in com-

parison with Buna (see Table IV), is explained by the formation of bridges and consequent increase in the degree of branching of the molecules. It should be noted also that this effect is even more marked in Butyl rubber (copolymer of isobutylene with 1-2 per cent of isoprene), which has a form factor of 0.65 (see Table III).

The lowest form factor of rubber masticated for 10 minutes (0.80) in comparison with that of natural rubber (see Table IV) can be explained on the basis of the hypothesis advanced by Staudinger¹², according to which not only does depolymerization occur during mastication, but the form of the molecules changes in the sense of more extensive branching by formation of oxygen bridges.

The data in Table IV also give further confirmation that the polymerization of butadiene to Buna does not take place, at least not mainly, in the 1,4-position; in fact the values of f for Buna and for the product obtained by the hydrogenation of this same Buna are equal to 0.82-0.84, i.e., equal to the form factor found for the polymers of α -butylene, which is but slightly different from the form factors of polyisobutylene; this polymerization must, therefore, take place for the most part either in 1,2-position or in 2,3-position. This is in agreement also with the recent results of Homson and Halverson¹³, which are derived from the roentgenographic examination of samples of Buna stretched at a low temperature.

POLYVINYL ESTERS AND POLYVINYL ETHERS

With a view to a more thorough study of chain compounds with branchings and in some cases where these side chains in turn contain branchings, a sample of polymethyl acrylate, a sample of polymethyl methacrylate, and a sample of polyvinyl isobutylene ether (Oppanol-C of the I.-G. Farbenindustrie) were examined. These products were examined in solutions of methylene chloride, of benzene, and of carbon disulfide at room temperature. The results are summarized in Table VI, which also contains data on monomeric methyl methacrylate.

The form factor, which is close to 1 for the monomers, is 0.89 for polymethyl

TABLE VI

Substance	Temp. °C ($\pm 0.1^\circ$)	Experi- mental η (m. sec. ⁻¹)	ρ (g. per cc.)	Calcu- lated η (m. sec. ⁻¹)	$f = \frac{\text{experimental } \eta}{\text{calculated } \eta}$
Polymethacrylate in methylene chloride (5.20% by wt.)	30	1058 \pm 2	1.305 \pm 0.001	—	—
Methylene chloride	30	1050 \pm 2	1.312 \pm 0.001	—	—
Polymethacrylate	20	1257 \pm 20	1.150 \pm 0.010*	1408	0.89
Methyl methacrylate (monomer)	30	1175 \pm 2	0.929 \pm 0.001	1227	0.96
	40	1132 \pm 2	0.918 \pm 0.001	1184	0.96
Polymethyl methacrylate in acetone (5.13% by wt.)	20	1197 \pm 2	0.820 \pm 0.001	—	—
Acetone	20	1192 \pm 1	0.7927 \pm 0.0002	1158	1.03
Polymethyl methacrylate	20	1265 \pm 20	1.220 \pm 0.010*	2008	0.62
Polyisobutyl ether in carbon disulfide (4.01% by wt.)	20	1157 \pm 2	1.246 \pm 0.001	—	—
Carbon disulfide	20	1157 \pm 1	1.264 \pm 0.001	—	—
Polyvinylisobutyl ether	20	1160 \pm 20	0.925 \pm 0.010*	1470	0.78

* Data obtained from solutions assumed to be ideal.

do not deviate more than a few per cent from unity, whereas products of high molecular weight show f values which are lower than those of compounds with branched chains. A comparison of these values themselves with those given in Table V confirms the dependence of the form factors of the high polymers on the frequency of the branchings, on the length of the latter, and, finally, on the secondary branchings.

In conclusion, the results of the determinations of ultrasonic wave velocities in substances of high molecular weight, where the concept of the form factor, defined as the ratio between the experimental velocity and the calculated velocity, is introduced, make it possible to draw important deductions concerning the degree of branching of the molecules of high polymers. It appears, therefore, that this method can be applied, in addition to the other methods previously mentioned, to the study of natural and synthetic products of high molecular weight.

SUMMARY

The velocity of propagation of ultrasonic waves in numerous substances of high molecular weight was determined. For substances not fusible at temperatures below 100° C, this velocity was determined by extrapolation from solutions considered ideal.

For linear macromolecules without side chains, the ultrasonic velocity appears to be practically equal, within the limits of experimental error, to that calculated by the formula of Rao and on a basis of the additive values of the bond velocity of Lagemann and Corry.

For molecules which have many side chains, the velocity is lower than the calculated value, whereas for compounds of low molecular weight this deviation is relatively small, viz., less than 10 per cent; it becomes much higher, viz., almost up to 40 per cent, for macromolecules.

The form factor is defined as the ratio of the velocity determined experimentally to the velocity calculated by the formula of Rao. This form factor is equal to 1 for polymers without side chains or with very few side chains, such as paraffins, polyethylenes, Nylon, polyethylene oxides, and polyoxymethylenes; is only 0.89–0.90 for natural rubber; only 0.82–0.84 for Buna and for hydrogenated Buna, poly- α -butylenes, and polystyrenes; only 0.79–0.80 for polyisobutylenes; only 0.89 for polymethacrylates; only 0.78 for polyvinylisobutyl ethers; only 0.65 for Butyl rubber; and only 0.63 for polymethyl methacrylates.

The form factor is thus affected by the frequency and length of the side chains, and by any secondary side chains which may be present.

REFERENCES

- Natta and Baccaredda, *J. Polymer Sci.* 3, 829 (1948).
- Baccaredda, *Ricerca sci.* 17, 1108 (1947).
- Frankel, "Kinetic Theory of Liquids", Clarendon Press, Oxford, 1946, p. 125.
- De Groot and Seldam, *Physica* 13, 47 (1947).
- Rao, *J. Chem. Physics* 9, 682 (1941).
- Lagemann and Corry, *J. Chem. Physics* 10, 759 (1942).
- Natta and Baccaredda, *Rend. accad. Lincei* [8] 4, 300 (1948).
- Freyer, Hubbard, and Andrews, *J. Am. Chem. Soc.* 51, 759 (1929).
- Mark, *J. Acoustical Soc. America* 16, 183 (1945).
- Buche, Hiedemann, and Asbach, *Z. Physik* 87, 734 (1934).
- Baccaredda and Giacomini, *Rend. accad. Lincei* [8] 1, 401 (1946).
- Staudinger, "Die hochmolekularen organischen Verbindungen", Berlin, 1932, p. 442.
- Holmes and Halverson, *J. Am. Chem. Soc.* 70, 779 (1948).
- The following values were obtained at 20.0° \pm 0.1° C. Methyl acetate: $u = 1183 \pm 1$ m. per sec.; $\rho = 0.937 \pm 0.001$ g. per cc. Methyl propionate: $u = 1173 \pm 1$ m. per sec.; $\rho = 0.909$. Isobutyl acetate: $u = 1178$ m. per sec.; $\rho = 0.870$. Methyl isobutyrate: $u = 1163$ m. per sec.; $\rho = 0.890$. For ethyl ether, the values of Freyer, Hubbard, and Andrews (*J. Am. Chem. Soc.* 51, 759 (1929)) and reported by Hiedemann ("Ultraschallforschung", de Gryter, Berlin, 1939, p. 227) were accepted.

PROPAGATION OF AUDIOFREQUENCY SOUND IN HIGH POLYMERS*

R. S. WITTE, B. A. MROWCA, AND E. GUTH

POLYMER PHYSICS LABORATORY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA

INTRODUCTION

The evaluation of the dynamic viscoelastic properties of a material can be made from measurements of the velocity of transmission and the attenuation of sound in the material. Such methods have been applied chiefly to "low loss" materials, such as metals, and to some plastics by Mason, McSkimin, *et al.* A standing wave method for measurement of the dynamic modulus in thin strips was suggested by Bridgeman and Trueblood, and was applied by Ballou and Silverman¹ to the measurement of Young's modulus in low-loss materials. A modification of this technique can be extended to measure also the viscoelastic constants of some high polymers. By this method, Nolle² obtained the internal friction of high-loss materials. Independently, a method similar to that employed by Nolle has been used in the present work³.

The experimental procedure may be best understood by reference to the block diagram shown in Figure 1. The signal generator drives a crystal,

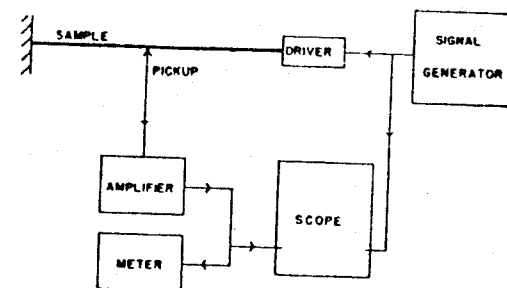


FIG. 1.—Schematic diagram of experimental method.

setting up longitudinal waves which are transmitted through the sample and picked up by a reluctance or crystal receiving element. The received signal is amplified and fed to one set of oscilloscope plates; the other set is connected directly to the driving oscillator. Thus, the phase difference between the driven end and the pick-up can be ascertained for any point along the sample. By moving the pick-up along the sample, the distance between two adjacent points in the same phase of motion can be measured, and thus the wave length of the sonic wave in the sample can be determined. Knowing the frequency of the driving oscillator, the velocity can be directly obtained.

* Reprinted from the *Journal of Applied Physics*, Vol. 20, No. 6, pages 481–485, June 1949. This paper was presented at the sixth meeting of the Division of High Polymer Physics of the American Physical Society, New York, January 27–29, 1949.