POLYMERS AS STUDIED BY SOME PHYSICAL METHODS

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INTRODUCTION

THAT high polymers are composed of large structures built up by the successive repetition of small units was first pointed out by Staudinger[1] in 1920. This simple hypothesis has, during the last three decades, stimulated a large amount of both experimental and theoretical work. The high polymer molecule may thus be looked upon as just a long chain endowed with the ability to assume all sorts of configurations through rotations about its valence bonds. Under such circumstances, we have to speak of average size, average shape and so on.

In addition to developing theoretical concepts based on statistical methods of dealing with such problems, diverse experimental investigations such as determinations of turbidity, osmotic pressure, acoustic absorption and viscosity of these polymers in solution, have been undertaken with a view to estimate their effective sizes, shapes and molecular weights. In the glassy or solid state too, they exhibit other characteristic and easily measurable physical properties such as rubber elasticity and photoelasticity. Experimental techniques involving both static and dynamic methods, the frequencies used in the latter ranging from sonic to the ultrasonic, have been pressed into service in recent times to study such interesting mechanical properties.

RELAXATION EFFECTS IN HIGH POLYMERS

It follows that in such long chain polymer molecules, because they are flexible and can take up many different shapes, certain shapes are sometimes more probable than others and if a molecule is distorted from a more probable shape, it tends to return to it in a very short time when the distorting stress is removed. The rapidity with which the more probable shape is regained determines the relaxation time for such a configurational elasticity. The measurement of the propagation constants of acoustic waves is a well-known means for studying such mechanical relaxation effects.

The dispersion in solid samples of several polymers of ultrasonic velocity and of absorption of longitudinal and torsional waves was observed by earlier workers.[2-4] Work on concentrated polymer solutions in the audio-frequency range by Ferry and his co-workers,[5,6] has revealed that there is a dispersion of dynamic rigidity and the dynamic viscosity. These studies have established a strong correlation in the distribution of the relaxation times of such solutions with those of the corresponding solid polymers. Mason and co-workers[7] found from measurements with longitudinal ultrasonic waves, a dispersion of velocity and an associated dispersion of attenuation in polyisobutylene liquids. Direct measurements of shear viscosity and shear elasticity of these liquids by the torsional crystal method developed by Mason[8] showed that a relaxation occurs in the shear modulus and that the dispersion of the longitudinal velocity in these liquids is due to the dispersion of their shear elasticity.

The mechanical properties of solids, pure liquids and concentrated solutions of high polymers appear to be affected by interchain reactions arising from the close proximity of the polymer molecules to one another as well as by intrachain reactions pertaining to the chain of a given molecule itself. In studying the possible motions occurring within the chains, it is desirable to isolate the two effects. This is accomplished by taking such dilute solutions of the polymer that the molecules do not touch each other on the average (about 1 g./100 c.c.). In such solutions, the thermal motions of the segments in the polymer molecule co-ordinate with one another to produce changes in the configuration of the molecules and the configurational changes are associated with a series of relaxation times. Baker and his co-workers[9] employing the torsional crystal method showed the existence of three relaxation frequencies for dilute solutions of polyisobutylene in cyclohexane. Similar results were obtained by Rouse and Sittel[10] for polyisobutylene dissolved in different solvents like cyclohexane, benzene and toluene and for polystyrene dissolved in toluene. These relaxation frequencies characterising the configurational relaxation between different members of the chain, range from audiofrequency to the megacycle region.

With a view to study such relaxation effects in the megacycle region, measurements of velocity and absorption in dilute solutions of some vinyl polymers have been undertaken by the present writer and his co-workers and some very interesting results obtained. The method adopted is similar to that described by Pellam

and Galt.[11] A second crystal was used instead of a reflector and the ultrasonic velocity and absorption have been measured. The two crystals employed have identical fundamental frequencies, namely, 1·18 mc./s. and were worked at their 3rd, 5th and 7th harmonics. The temperature was controlled to within ± 0·5° C. The alignment of the crystals as well as the accuracy of the method as a whole was tested by making measurements on standard liquids like benzene and CCl_4, at all the frequencies. For absorption measurements, the height of the received pulse was adjusted to be constant by using a calibrated decade attenuator with a bandwidth of 0 to 30 mc./s. and capable of reading correct to 0·1 db. The absorption measurements are accurate to within 3 to 6%, the lower limit applying to higher frequencies.

to 600,000 have been studied by way of confirmation.

The variation of velocity and of $(a/f z)$ where a is the absorption coefficient, with concentration is plotted for one fractionated polyvinyl acetate sample in Fig. 1. The "wobbling" of these factors with concentration is most striking and appears to result from the presence of a number of relaxation frequencies characteristic of the polymer molecule.

Fig. 2 shows the plot of $a\lambda$ (absorption per wavelength) against the frequency, for one fraction of polyvinyl acetate as an illustration. Each curve in the graph represents the values for a particular concentration of the solution mentioned alongside the curve. In the range of frequencies studied, there is a frequency at which the maximum for $a\lambda$ is occurring for
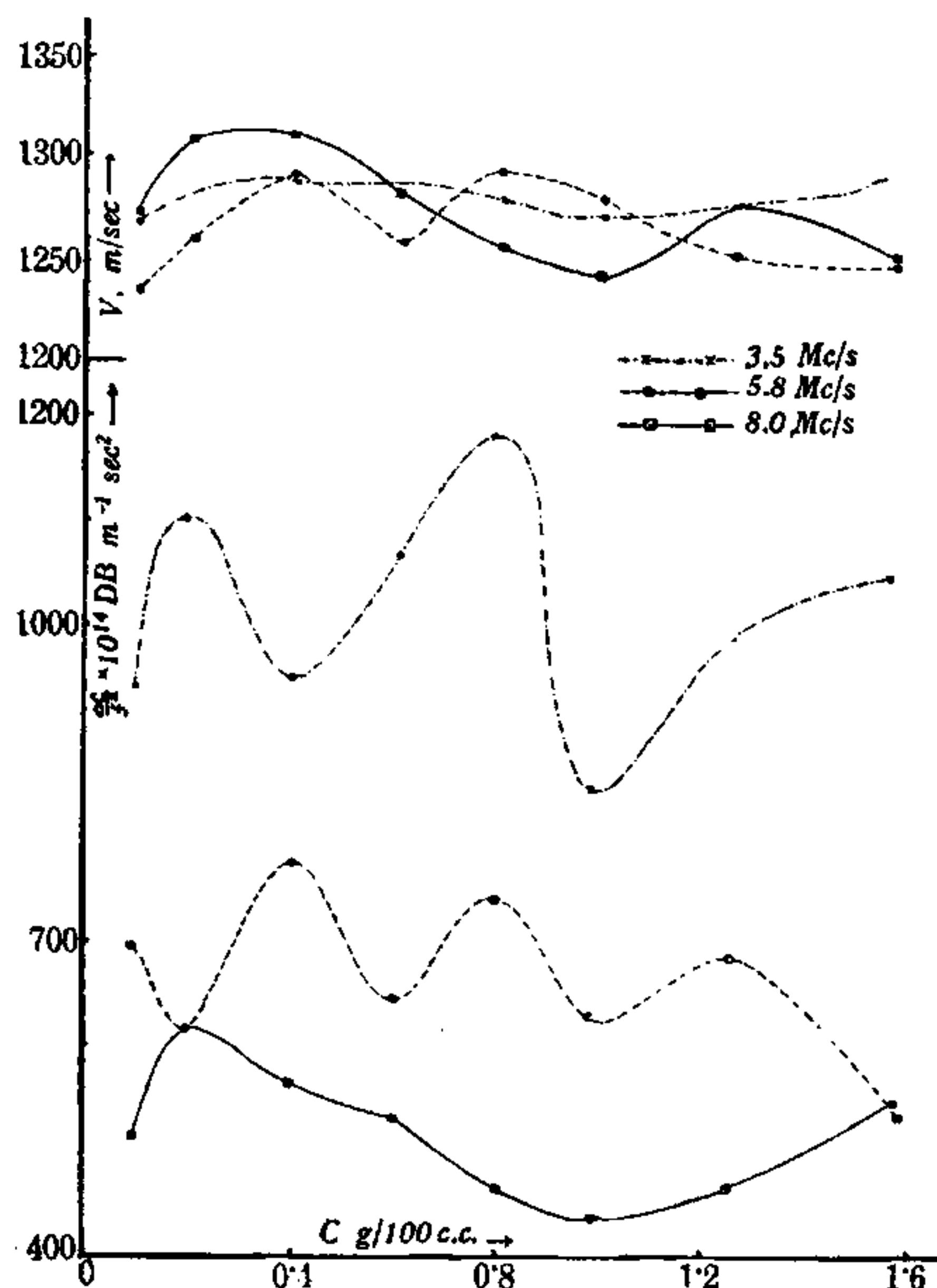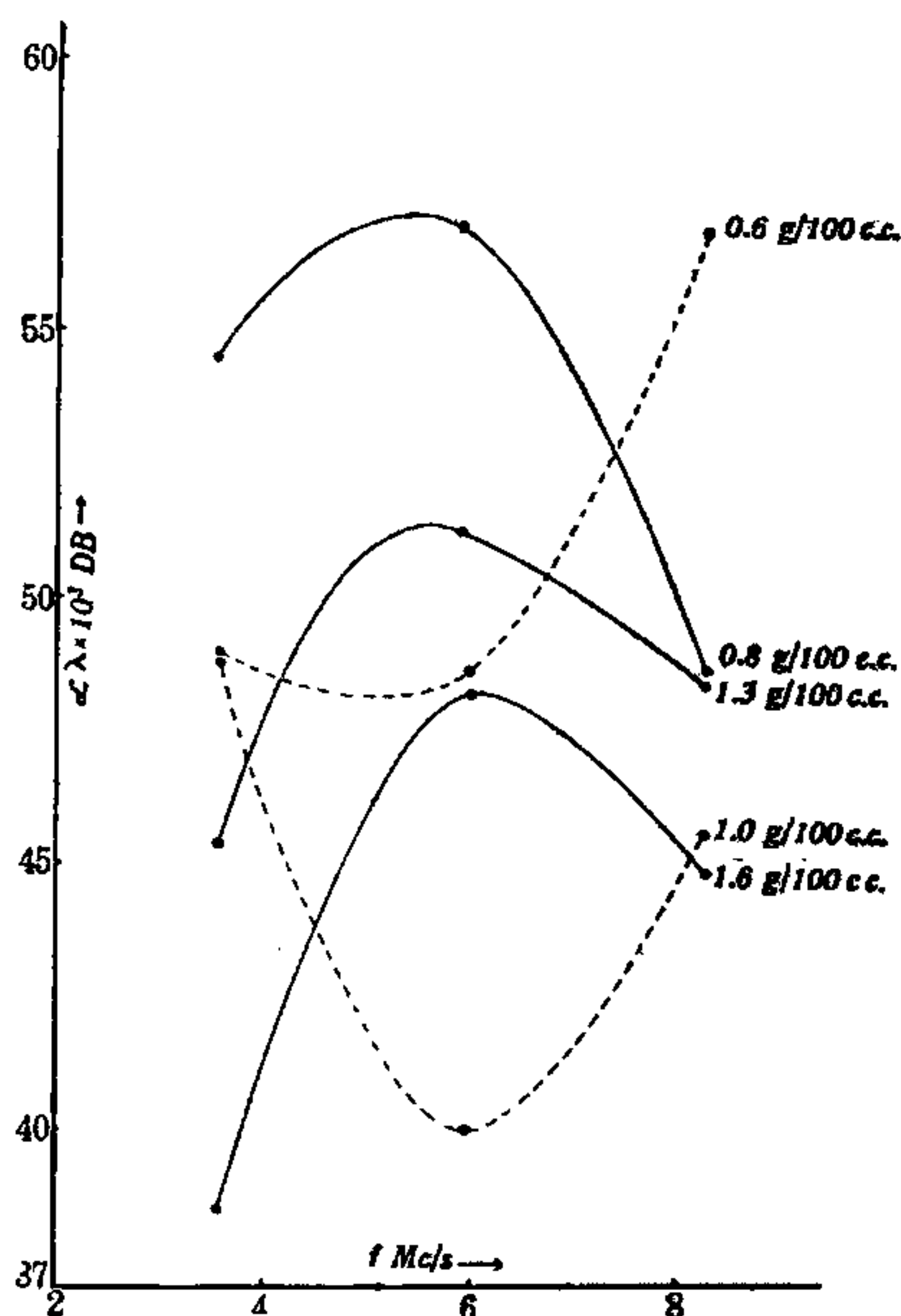

FIG. 1

FIG. 2

Solutions in benzene of fractionated polymers exhibit a peculiar and hitherto undiscovered phenomenon consisting of rapid fluctuations both of velocity and of absorption from the values appropriate to pure benzene, as the concentration is varied. This new result, first observed in polyvinyl acetate is found to exist in the cases of polymethyl methacrylate and polystyrene also. Several fractions of the same polymer with different molecular weights ranging from 20,000

some concentrations of the solution, while for some others a minimum absorption is observed. The frequency showing the maximum absorption is not the same for all concentrations and is found to vary in an irregular fashion. Further extensive results have been obtained which show that the velocity is not constant with frequency and also that its variation is erratic. The above results observed in the case of all the different polymer fractions, indicate the

presence of multiple relaxation frequencies. The minima observed for some concentrations in Fig. 2 can only be explained as due to the presence of at least two relaxation frequencies situated very close to each other and on either side of the minimum.

The above phenomena are however altogether absent when unfractionated commercial samples of polystyrene and polymethyl methacrylate are dissolved in benzene. That the peaks and depressions occur in such a closely spaced manner for the different fractions of the same polymer whereas they are not found at all before the fractions are separated can only be understood by presuming that they are apparently cancelled out by superposition in an unfractionated sample.

Moreover, it has been observed that unlike benzene which is a good solvent, in a poor solvent like ethyl methyl ketone, if measurements are made on a fraction of each of the above polymers, these phenomena are not exhibited. This has to be attributed to the lack of freedom to the polymer molecule in a poor solvent to assume different configurations as it is then known to be in a completely coiled state, all the relaxation effects being thereby suppressed.

SECOND ORDER TRANSITIONS IN HIGH POLYMERS

Another important feature of high polymers is that they generally exhibit a discontinuity in thermal expansion at a characteristic temperature. This temperature also marks a relatively abrupt change in other thermal, mechanical, electrical and optical properties. These discontinuities are termed as second order transitions because as the temperature is raised through this point, there appears to be a change of state without latent heat. In many of these substances, the sound velocity varies with frequency, showing characteristic relaxation frequencies. Thus a study of physical properties of high polymers as affected by temperature and frequency is of considerable importance.

The experiments of Protzman[12] were the first to disclose the existence of a discontinuity in the slope of the velocity-temperature curves for ultrasonic waves in polymer materials. Working on methyl methacrylate polymers by the optical diffraction method, he found a transition temperature which decreased linearly with frequency; in the range of 3 to 11 mc./s., covered by his experiments. As pointed out by him, the observed frequency dependence would have the opposite sign if a relaxation mechanism were responsible for the discontinuity. This created a difficulty. Later, Melchor and

Petrauskas,[13] working on the same polymer, did not find an appreciable dependence of the transition temperature on frequency, in the range 0·5 to 10 mc./s. They also noted that the transition occurred near a temperature T_g the glass transition temperature, which was obtained from the length-temperature measurements using the same specimen of material. We have also determined the transition temperatures in a few polymers over a wide frequency range in order to arrive at a possible mechanism responsible for them and two different experimental techniques were employed. We covered the frequency range of 0·1 to 6 mc./s.

The two experimental methods used are the ultrasonic pulse method involving the principle of total internal reflection and the composite oscillator method for working in the low frequency region. A brief description of the two methods has already been given in earlier publications.[14] The variation of ultrasonic velocities with temperature has been determined in the case of polymethyl methacrylate and polystyrene. The specimens used in both experiments have been taken from the same sheet of the materials. Using the pulse method, Krishnamurthi and Sivarama Sastry[15] determined the velocities at four different frequencies, namely, 1·15, 2·30, 3·45 and 5·75 mc./s. The transition temperatures observed in both the polymers were found to be the same at all the four frequencies. Their results show the transition temperatures at 61° C. for polystyrene. Subrahmanyam,[16] employing the composite oscillator method, determined the same for both the polymers round about 0·1 mc. The transition temperatures obtained by him agree with the above values.

Thus in the frequency region of 0·1 to 6 mc./s. covered by the two experiments, the discontinuities in the V-T curves are found to be independent of frequency, in both polystyrene and polymethyl methacrylate. The exact value for the transition temperature in polymethyl methacrylate is a little smaller than that observed by Melchor and Petrauskas but the effect of plasticizer content, molecular weight, etc., in polymers can account for the substantial differences in the transition temperatures, as observed by different workers.

Supporting evidence to the above observation has since come from other workers.[17] Recent work of Wada and Yamamoto[18] has in fact shown that the transition temperatures, determined in the case of eight polymers, are independent of frequency. Using the two experimental methods described above, they covered

the same frequency region. Another result of their observations is that these transition temperatures occur very near those for thermal expansion (T_g).

A different line of work on polymers is the measurement of birefringence produced in samples of polymethyl methacrylate and polystyrene when subjected to stress. A detailed description of the experimental set-up and the results obtained have been given by Bhagavantam and Krishnamurty.[19] Transition points have again been observed in the birefringence temperature graphs, and they occur at the same temperatures as were found in the ultrasonic experiments. This result is in conformity with similar observations made on the widths of nuclear magnetic resonance absorption lines[20] and the dielectric constants of polymethyl methacrylate and polystyrene respectively, where discontinuities in the above quantities were again observed near the glass-transition temperature.

Viscometric and Light Scattering Studies of High Polymers

Viscosity and light scattering methods are now widely used to determine the molecular weights and the root mean square end to end distances for different high polymer molecules. The intermolecular interactions of such a polymer dissolved in a solvent can be characterised by a few thermodynamic parameters, and their evaluation for various solvent systems becomes important. For instance, the single polymer molecule dissolved in a solvent is subject to the osmotic action of the surrounding molecules which tends to swell it to a larger average size than it would otherwise assume, and can be represented by an average expansion factor of the unperturbed mean square end to end distance of the molecule. From measurements on the variation of intrinsic viscosity with temperature, it is possible to evaluate these parameters for the particular polymer-solvent system as well as the unperturbed dimensions of the molecule.

Light scattering photoelectric photometers have been built in various laboratories. They are usually calibrated by a narrow fraction of polystyrene or other standard polymers for which the molecular weight is arrived at independently, say by the viscosity method. The description of one such arrangement has been given by Varadaiah[21] in a paper which has been published recently in the *Journal of Polymer Science*. Molecular weights are obtained from light scattering data employing Debye equation.[22]

$$\frac{Hc}{\tau} = \frac{1}{M} + \frac{2Bc}{RT}$$

where $H = 32\pi^3 n_0^2 (n_0 - n_c)^2 / 3C^2 N\lambda^4$, and other letters have the usual significance. τ stands for the turbidity of the polymer solution for incident polarised light. $(n_c - n_0)/c$ or dn/dc is determined with a differential refractometer for different polymer solvent systems. The molecular weights are obtained from the Hc/τ vs. c graphs. By finding the symmetry of scattered light at $45°$ and $135°$, appropriate corrections are applied to molecular weights and the length of the polymer molecule is calculated, assuming a tangled coil model, by the usual procedure as explained by Oster.[23]

Conclusion

Many other tools of the physicist, such as the infra-red spectrometer, the X-ray diffraction camera and so on are finding their applications in the solution of intricate problems in polymer chemistry but, for want of space, these have not been dealt with in the foregoing. There is, however, no doubt that this is a field where much remains to be done by the experimenter as well as the theorist.

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