

First experiments on electro-optics properties of polymers

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Being only able to speak in this contribution about what did happen 50 years ago my lecture will be more an historical lecture than a scientific one. My thesis⁽¹⁾ project was devoted to electrical birefringence of classical organic polymer solutions. Prof. C. Sadron told me that, since one obtains orientation of polymer solutions in flow fields, one should obtain also some similar effects on polymers in electrical fields and this became my thesis project. Unfortunately I did realize very fast that the effect on polymer solutions was practically the same one observes on monomeric units and needed very high voltage. This led me to the idea of looking at rigid molecules like D.N.A and tobacco mosaic virus. Since it was impossible to apply a constant field, due to the conductivity of solutions, I decided to use pulses and, to my surprise, the optical signal observed during the pulse was asymmetric and deformed by the non-negligible value of the rotary diffusion constant D . Moreover the curves for the apparition and the disparition of the effects were different and this could not be explained by a simple theory neglecting the presence of permanent dipole. This led me to propose a theory of this effect. It was shown that, regardless of the mechanism of orientation, the decay of the signal is proportional to \exp^{-6Dt} calling D the rotary diffusion constant and t the time. Very high values of D were found for tobacco mosaic virus (which was to be expected) and also for D.N.A . This result was difficult to explain since, at this time, the double helix of Crick and Watson was not yet known. Now, looking in the book of S. Stoylov⁽³⁾ I realize that from this time (1948) a lot of results have been obtain in this field and that all what I will tell you here is more history of science than new results.

Before entering into the subject I want to give you a brief survey of the situation in our University after the liberation from the Germans in 1945 in order to explain the curious situation in which we were in an University almost completely ruined.

After studying in Paris during the war I did arrive in Strasbourg beginning of October 1945, having obtained a position of assistant lecturer at the Physics department of the Strasbourg University. This department had a good reputation since it use to be, before the second word war, special-

ized in the physics of magnetic properties of metals and was directed by Prof Pierre Weiss, a well known specialist of this field.

Perhaps you remember that, at the beginning of the war (1939) Strasbourg was completely evacuated because, being at the border between France and Germany, the risk of bombing was serious. It stayed empty until the arrival of the Germans (in 1940). So during approximately one year the city was almost dead under the supervision of the French army. The Germans came at this time and tried to build a modern university to show to the French that they were devoted to Sciences. When Strasbourg was liberated (fall 1944) the University was left open and was used by the American and the French soldier. Later the Americans and the French used it as barracks and when they went away they left the building of the University empty with all the doors open. You can imagine the condition of it. It was practically impossible to make any experimental work in these buildings which were half destroyed. Anyway, full of enthusiasm I wanted to make a thesis in order to obtain a PhD. degree but the problem of finding a domain of Science and a laboratory where I could make some experimental work was a difficult choice. I had discussion with the different professors asking for suggestions. The head of the institute told me that magnetic properties of metals and alloys was a dead subject. I was not particularly interested in nuclear physics. Eventually I met Prof. C. Sadron who had spend one part of the war in a concentration camp in Germany and was full of projects. His idea was that the field of Macromolecules was a new one and that there were a lot of problem to be solved. He was also thinking that natural and synthetic polymers could be studied by similar methods and wanted to obtain from the authorities enough money to build a new laboratory devoted to this field.

So I decided to work with him and I did participate in the birth of the “Centre de Recherches sur les Macromolecules” being assistant director in 1954 and director from 1967 to 78. I shall not describe the history of the laboratory and will limit myself to my thesis project.

Prof. C. Sadron had made his thesis on the comparison of the magnetic properties of different metals and went, as a post-doc to the laboratory of Prof. von Karman in Pasadena where he studied the flow of a fluid along a surface by measuring its birefringence. These experiments were difficult and, in order to increase the sensitivity he did use, first classical solutions and later more efficiently macromolecular solutions. Back in Strasbourg he decided to build a laboratory on the physical chemistry of biopolymers and classical polymers. He therefore proposed me to study electrical birefringence of polymer solutions, thinking that, since macromolecules are oriented by a

flow field, they should also be oriented by an electrical field. This idea was reasonable and I began to study the literature on the subject and tried to make classical experiments to get acquainted with the subject. It was not easy. I remember that, in order to have a slit, I stuck two razor blades on a piece of cork. It was perfect but unfortunately impossible to change its width. With this material I began to make experiments on CS_2 (having it burning quite often), and did realize that the effect was small and difficult to observe (at least with the material I was using). After that I did try on classical polymer solutions in organic solvents. Usually the monomers (or their analogous molecules with no double bond) have a very small Kerr effect. My hope was to find that, even in these conditions, the polymers could have a measurable Kerr effect. So I spent a lot of time trying to measure different polymers in different solvents and concentration without any success.

This made me very unhappy and this was amplified by the remark of a professor in rheology which, once, visiting the laboratory, told me that in his lab people were finding a large Kerr effect on the most classical homopolymer: Polystyrene. I tried many time changing the sensitivity of my machine without any success. I was ashamed not to be able to reproduce his results. Meeting him later in a colloquium I asked him precisely about his experimental method and he told me that it was a mistake from his collaborators and that Kerr effect on Polystyrene did not exist. Morality: be very cautious about oral results and believe (never completely) only what has been published. This absence of electrical birefringence on flexible polymers is now easy to understand. The Kerr effect is due to the influence of the electrical field on the dipoles. These dipoles are essentially distributed on the side groups of the molecules and can move in the field without changing the conformation of the polymer, i.e., they do not introduce birefringence. The only polymers which could be interesting are polymers with dipoles in the backbone, all oriented in the same direction like polypeptides.

Seeing the difficulties of the project Prof. Sadron suggested me to change the subject and courageously I did refuse. The situation was that, in order to observe large effects, one has to deal with large molecules very anisodiametric with strong electrical moments. Since I had colleagues working on Tobacco Mosaic Virus and D.N.A., I tried these substances and after some negative results I found conditions which where allowing to see the electrical birefringence. But, in order to see an effect one had to use large electrical fields and due to the conductivity of the solvent it begins to boil rapidly. The only way to eliminate this effect was to use a single pulse, long enough to reach the permanent state but short enough to be able to neglect the production of heat.

This did oblige me to learn a lot of electronics. Due to the absence of equipment at this time I was obliged to build myself all what I needed. I had to make a generator for a single pulse and a double beam oscilloscope to study the signal. It took me a lot of time but it was fun to build entirely a new instrument. When the equipment did begin to work I did put a water solution of Tobacco Mosaic Virus in the cell and to my surprise I did obtain an image showing a large deformation of the pulse (see fig. 1). I was very happy since, from what I knew, this was the first time an effect of this type was observed.

I have to say a few words about the equipment necessary to make the observation. I was using a classical automobile light source alimented on batteries in order to have a reasonably stable light source. The polymer solution was immersed in the cell. The electrodes were 10 cm long and separated by a distance of the order of 1 mm or less. The applied voltage was of the order of 100 volts giving a field of 10^3 V/cm. The photo multiplier was branched at the exit of a D.C. amplifier to the double beam oscilloscope, one showing the birefringence, the other the electrical pulse. A camera in front of the double beam oscilloscope allowed me to take a picture of a single pulse.

The first thing which did surprise me was that the pulse was not symmetrical. The establishment of the signal and its disappearance where not similar. This effect was observed on P.M.Ma (Poly-Methyl-Methacrylate) at very high fields⁽⁴⁾. Dissymmetry of the peak was observed but no explanation of this phenomenon could be provided.

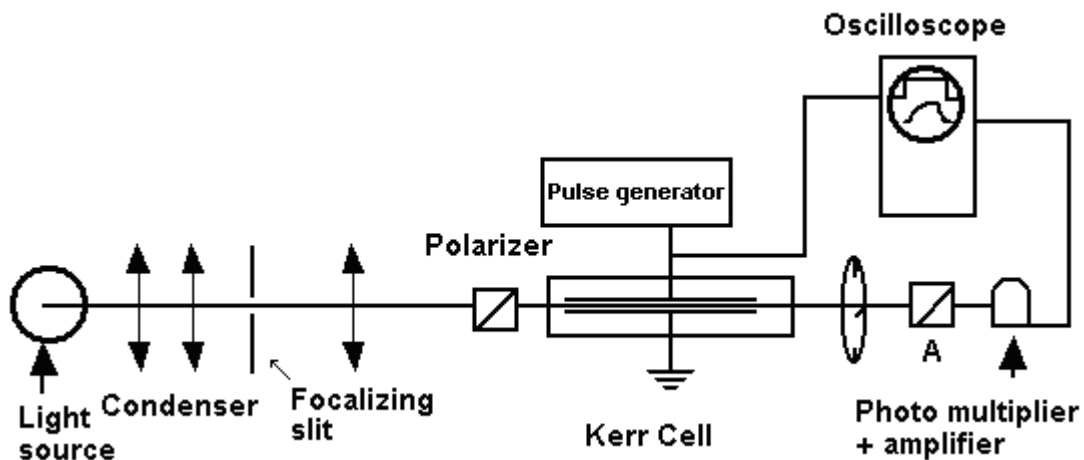


Fig. 1 The apparatus used to study the time effect on electrical birefringence.

The optical part is very classical. Linearly polarized light is used in order to avoid stray light, the two polarizers are crossed at an angle of 45° from the electrical field. This gives a signal which is proportional to Δn^2 , calling Δn the difference between the index of refraction of the activated cell and the normal index due to the anisotropy of the dissolved molecules. Theoretically one knows that if one places a quarter-wavelength plate on the beam one obtains a signal which is proportional to Δn and is therefore more sensitive but perhaps, due to the failure of the equipment, we were unable to use this method. This last method allows to measure the sign of the birefringence but on all the systems we did study it was positive, meaning that the index of refraction along the axis of the particle is larger than in the perpendicular direction. A rotating disk was used to measure the velocity of the time base of the oscilloscope. This quantity is needed when one wants to make absolute values of the rotary diffusion constant.

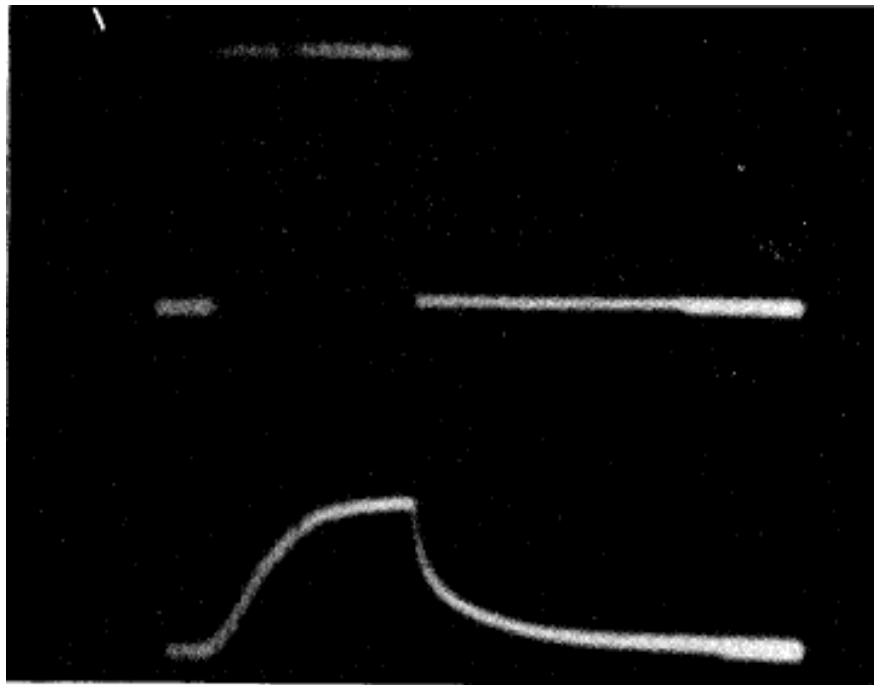


Fig.(2) Typical signal obtained on Tobacco Mosaic Virus in water.

Theoretical part

This is a classical problem in the diffusion theory and it was resolved by Prof. A. Peterlin⁽⁵⁾ in the case of flow birefringence. We therefore had just to adapt this method to the problem of electrical birefringence.

If one calls D the rotary diffusion constant which, for the sake of simplicity, we assume to have the symmetry of an ellipsoid of revolution and if one introduces at time t the function $f(\theta, \phi, t)$ where θ and ϕ are the polar angles one defines the normalized probability for the particle to have at time t the orientation characterized by θ and ϕ of the particle at time t by this probability. This function obeys the equation

$$\int_0^\pi \int_0^{2\pi} f(\theta, \phi, t) \sin \theta d\theta d\phi = 1 \quad (1)$$

The laws of Brownian motion require to satisfy the general equation

$$D\Delta^2 f + \text{div} f \vec{c} = \frac{\partial f}{\partial t} \quad (2)$$

The rotary diffusion constant D has been evaluated by J. Perrin⁽⁶⁾ for ellipsoids. The vector \vec{c} is defined as the velocity of the molecules in the absence of Brownian motion.

This quantity can be written as:

$$\vec{c} = \frac{\vec{\gamma}}{\zeta} \quad (3) \text{ where}$$

$\vec{\gamma}$ is the orientation couple and ζ the frictional coefficient.

The rotary diffusion constant D is bound to ζ by the relation : $D = \frac{kT}{\zeta}$. This allows to write the

differential equation (2) as :

$$\nabla^2(f) + \frac{1}{k_B T} \text{div} f \vec{\gamma} = \frac{1}{D} \frac{\partial f}{\partial t} \quad (4)$$

If $\vec{\gamma}$ depends on a potential w ($\vec{\gamma} = -\overrightarrow{\text{grad}} w$), the preceding equation becomes:

$$\Delta^2 f + \frac{1}{k_B T} \text{div} f \overrightarrow{\text{grad}} w = \frac{1}{D} \frac{\partial f}{\partial t} \quad (5)$$

This equation allows the determination of the function f when one knows the value of D and the expression of the potential w .

Calculation of the orientation energy w

In the case of a particle without dipole this energy corresponds to the energy of the particle in an electrical field. It has been evaluated by J. C. Maxwell⁽⁷⁾ for ellipsoids of revolution and gives:

$$w_1 = -\frac{1}{2}v(g_1^0 \cos^2 \theta + g_2^0 \sin^2 \theta)E^2 \quad (6)$$

where g_1^0 and g_2^0 are coefficients depending on the differences of the dielectric constant between the axis and its perpendicular direction.

If the particle has also a dipole moment $\vec{\mu}$, assuming that it is in the direction of its axis an extra energy has to be added:

$$w_2 = E\mu \cos \theta \quad (7)$$

There is a final problem. It is interesting to know the orientation of the particles but the experimental property is the index of refraction. Its variation as a function of time allows the evaluation of the birefringence as a function of time. It depends on the optical anisotropy of the particles. For the sake of simplicity we have decided to study the general case where $w = w_1 + w_2$, or :

$$w = -\frac{1}{2}v(g_1^0 \cos^2 \theta + g_2^0 \sin^2 \theta)E^2 + \mu E \cos \theta \quad (8)$$

The simplest problem corresponds to the case where $w = 0$. This means that the system has been oriented by an arbitrary method at time $t = 0$. One suppresses the field and look at the return to equilibrium. In this case $w = 0$ and the differential equation is very simple.

The optical problem

Now we are able to evaluate the energy of orientation of the particles and the function f describing it. But, since we are looking at the birefringence we have to evaluate its changes as a function of time. One can replace the function $f(\theta, \phi, t)$, which describes orientations as a function of time, by

a function limited to $f(\theta, \phi, t) = \frac{1}{4\pi} \rho(u, t)$ where $u = \cos(\theta)$ for the optical and for electrical prob-

lem, and then we just have to obtain the birefringence Δn evaluating this quantity (difference between the principal indices), as a function of time.

The simplest way, for resolving this differential equation is to write it as a expansion in terms of Legendre polynomial and to evaluate successively the first terms.

This is not difficult but rather long and I do not intend to give you here the whole development. I shall just give you the result :

$$\frac{1}{c} \frac{\Delta n}{n} = \frac{2n}{15} (g_1^2 - g_2^2) \left[E^2 (P + Q - + P e^{-\tau Dt} + E^4 \dots) \right] \quad (9)$$

where :

$$P = \frac{\mu^2}{kT} \quad \text{and} \quad Q = \frac{v(g_1^0 - g_2^0)}{kT}$$

I do not give here the higher terms since the final result does not depend on their value.

What is comforting is that if we put $t = \infty$ in this equation one recovers the classical result of the Kerr effect in the steady state.

Having now a method to describe the results it is interesting to show what one could get experimentally:

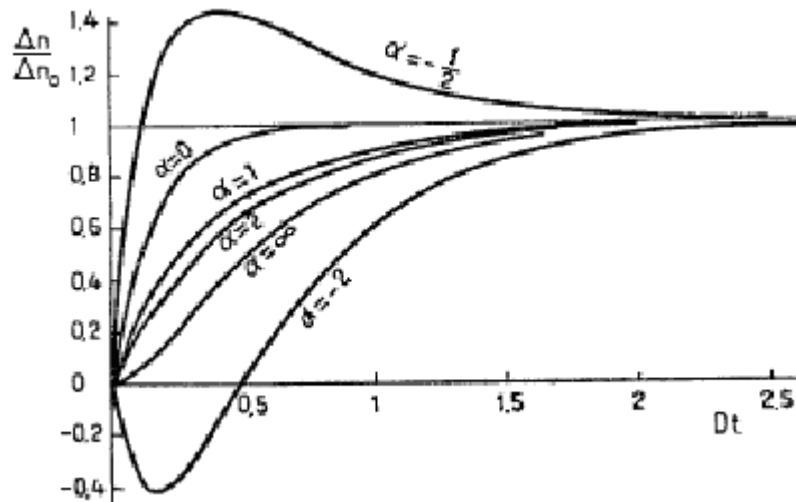


Fig. 3 Evolution of the birefringence when a square pulse is applied to the solution. The quantity α is the ratio of the effect of the anisotropy to the energy of the permanent dipole.

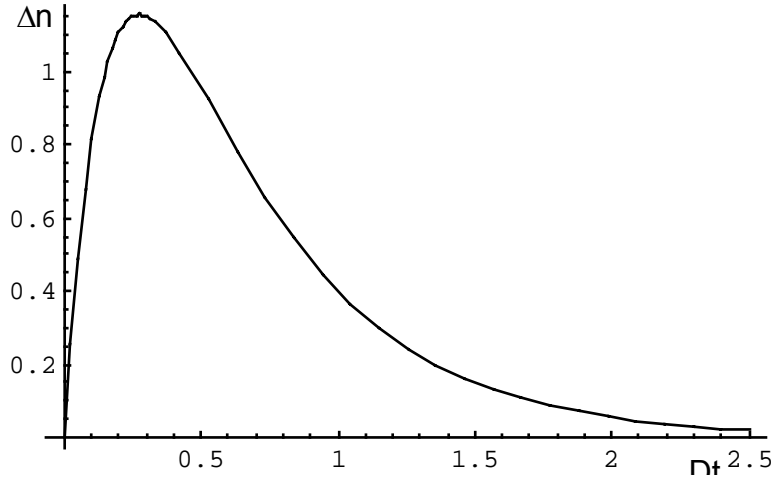


Figure 4. Theoretical value of the birefringence of an hypothetical object for which the polar orientation and the orientation due to anisotropy in a permanent field have the same absolute anisotropy, equal in absolute values but with different signs.

Fig. 4 gives the change of birefringence as a function of time for different relative values of the dipole term and the anisotropy.. They correspond to what is seen on the oscilloscope. More precisely :

$$\alpha = \frac{\frac{\mu^2}{kT}}{g_2^0 - g_2^1} \quad (10)$$

the numerator corresponds to the dipole moment and the denominator to the induced dipole.

When α goes to infinity one has a pure permanent dipole effect and course of the establishment of the pulse and its disappearance are identical. On the other case when $\alpha = 0$ the effect is only due to the anisotropy of the particles.

The curves have very different aspects when α varies. They can go through a maximum or a minimum. The reason for this result is due to the fact that anisotropic polarizability can be positive or negative. Since both effects have not the same velocity of response to the field they orient the particle in a direction or another. At the beginning the orientation by anisotropy is faster which explains the form of the curves:

$$\frac{\Delta n}{\Delta n_0} = 1 - \frac{3\alpha}{2(\alpha+1)} \exp^{-2Dt} + \frac{\alpha-2}{2(\alpha+1)} \exp^{-6Dt} \quad (11)$$

The only approximation which has been made has been to neglect the terms corresponding to higher order of approximation. As far as I know one has never obtained results showing either a

maximum or a minimum. One of my colleagues has tried to take more terms into account but from my point of view this correction has very limited applications and, until now, the precision is not sufficient to take into account these extra terms.

An interesting case corresponds to $\alpha = -1$. It gives the paradoxical curve of the figure 3. Since the sign and the amplitude of both effects are not the same and their absolute value identical. There is no signal in the steady state but, since both effects have not the same time constant one can detect them only at very short times. In fact I do not know anyone having obtained results justifying the theoretical predictions of fig. (4).

As an example of results we give in fig. 4 the result obtained with the equipment just described: a picture of the screen of the oscilloscope for a solution of Tobacco Mosaic Virus obtained on the machine.

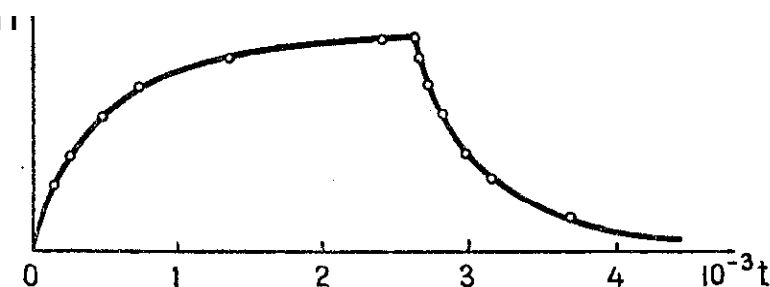


Fig. 5 Version on paper of results obtained as in fig. 4

Comparison with results one obtains with A.C. electrical voltage

Tinoco and Yakaoma⁽⁸⁾ have proposed to use a series of pulses of opposite sign. This is, from a theoretical point of view more difficult, since a square pulse has to be described by a Fourier series needing not just one term. So it seems interesting to try the effect of an alternating field applied for a sufficient short time to prevent overheating. The theory is easy and one has just to use the relations established by P. Debye.

The theory of Tinoco and Yakaoma is interesting but, from my point of view it is rather difficult to obtain clear information from the experimental results.

It has been tried to use alternating field⁽⁹⁾ and to look at the change of the signal as a function of its frequency. I do not write the equations and I shall just show the result in two cases. (a) the orientation is only due to a dipole moment and (b) it is due to an induced moment (Fig. 6). In

abscissa one plots the frequency of the field and in ordinate the birefringence. This diagram is very rich since it can give precise information about the properties of the solute. Unfortunately one has the problem of the heating of the solution. It has the advantage of allowing a precise determination of the relaxation term D just changing the frequency and observing the change in shape of the Lissajous curves obtained by plotting the field on the x axis and the birefringence on the y axis.

The two following figures give the value of the maximum and the minimum values of the birefringence as a function of frequency.

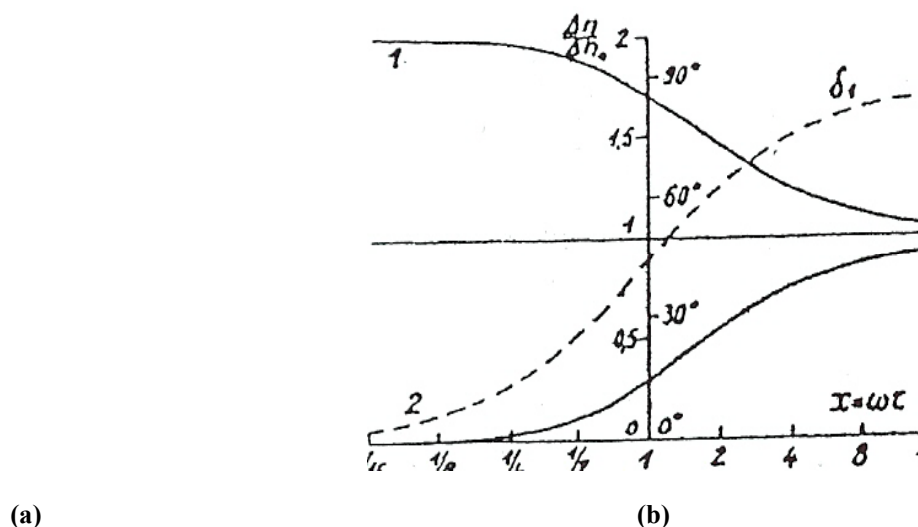


Fig. 6. The graphs (a) and (b) present the theoretical result of the influence of frequency on the orientation of the particles. (a) corresponds to a permanent dipole, (b) to an induced dipole on the effect of anisotropy. The full lines represent the maximum, the minimum and the average value of $\Delta n/\Delta n_0$ as a function of frequency. The dotted line shows the phase difference between the applied voltage and the optical signal.

Experimental results

A lot of time was used to build the machine and no time was left to make an exhaustive experimental work. Moreover the precision was far from being satisfactory so it was just checked that the machine could give correct results.

Another difficulty was to obtain good sample. At this time the preparation of pure sample was a problem which was not entirely resolved so depending on the sample we had very different results. This means that not too much time was devoted to the experiments. They were developed just to show the possibilities of this type of equipment and did not try to bring definitive answers to the problems of characterization. The first system which was studied was Tobacco Mosaic Virus solutions. From electron microscopy studies it was known that it is a rod-like particle: its

rotary diffusion constant is well known and the comparison of its theoretical results with the results of pulsed electrical birefringence was satisfactory and this reinforced the statement that this kind of technique could be used for more sophisticated systems. One interesting problem everybody was studying at this time was the conformation of nucleic acid in solution. This was before the discovery of the double helix by Crick and Watson and it was interesting to see if the D.N.A. was having an elongated structure. Since we did observe large Kerr effects I was convinced that this molecule was very elongated and rather rigid but this was just a qualitative result which was confirming what people were supposing without real proofs.

Finally another system was studied by my colleagues J. B. Donnet et al. It was the suspensions of vanadium pentoxide (V_2O_5) which are making interesting colloidal solutions. From the electron microscopy studies the particles were looking monodisperse and their length was measured. Applying different techniques in solution all the result were in agreement with the known dimensions, in particular electric birefringence, confirming the validity of the method.

Conclusion

In this paper I gave a summary of the work I did on electrical birefringence in the early fifties. Since the laboratory became more and more devoted to classical properties of organic polymers I left the field and I never did work again on this topic. I am sure that, due to the progress of industry in the building of scientific instruments, one should arrive to a much better precision and obtain results which should help our understanding of the properties of colloids. I excuse myself for proposing to you attention to something which is more history than Science and I thank the organizers of this meeting to have invited me to speak about a subject I have abandoned for more than fifty years.

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