RELATION BETWEEN PHOTOELASTIC PROPERTIES AND MOLECULAR BEHAVIOR IN CERTAIN PLASTICS

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Tamma Venkata Kameswara Rao

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THESIS

This is to certify that the

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TAMMA VENKATA KAMESWARA RAO

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Abstract

The object of the present investigation was to find why materials are birefringent under stress. Polystyrene which has a very low photoelastic effect, and Columbia Resin which has a high photoelastic effect were chosen as the experimental materials. These materials were rendered into thin films by machining and polishing techniques and were later stressed using a specially designed and constructed straining unit. The changes in the absorptions of an infrared beam by individual atomic groups were computed by first obtaining the infrared absorptionespectra of Polystyrene and CR - 39 under stress using a Perkin-Elmer Infrared Spectro-Photometer. It was found that the C - H aromatic does not contribute appreciably towards the change in absorption in Polystyrene and CR - 39; also there is a somewhat greater absorption in Polystyrene due to C - H aliphatic group than in CR - 39, thus leading to the surmise that stress birefringence in Polystyrene might be due to the presence of a vibrating group like C - H aliphatic. Further, the change in the absorption due to C - H wagging in the case of CR - 39 is remarkably high compared with that due to the same group in Polystyrene. It seemed probable that the C - H aliphatic influences the behavior of Polystyrene under stress and the C - H wagging is a deciding factor in CR - 39. The high photoelastic behavior of CR - 39 compared with Polystyrene could be due to 1) lack of the presence of heavy groups like benzene rather too close to other relatively small groups like C - H and 2) the presence of additional groups like C = O, C = C, C - O, C - C.

Charles O. Harris

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Statement of the problem

The object of the present investigation is to find why materials are birefringent under stress; in other words to find a relation between the behavior of the molecules under stress and mechanical birefringence.

Historical Sketch

An experimental investigation of the optical properties of certain transparent solids in 1816 led David Brewster[1] to the discovery that the forced deformation of a transparent solid alters its optical properties. He found that an optically isotropic transparent solid becomes optically anisotropic when subjected to external loads, and the degree of optical anisotropy is proportional to the deformation of the material. Polarized light transmitted through a piece of glass under stress exhibits a brilliant color pattern. Brewster suggested that these color patterns might serve for the measurement of stresses in engineering structures such as masonry bridges, a glass model being examined in polarized light under various loading conditions. This suggestion went unheaded by engineers at the time. Comparisons of the color patterns with analytical solutions were made by the physicist Maxwell[2]. The suggestion was adopted much later by C. Wilson[3] in a study of the stresses in a beam with a concentrated load and by A. Mesnager[4] in an investigation of arch bridges. The method was developed and extensively applied by E. G. Coker[5] who introduced celluloid as the model material

Brewster's discovery became one of the useful subjects for investigation and development during the present century. The application of this optical property of transparent solids to experimental stress analysis has been given the name of Photoelasticity. Today photoelasticity has grown to the full stature of a powerful technical instrument for quantitative stress analysis which for two dimensions, at

least, exceeds many other methods in reliability, scope and practicability. There is hardly any method by which the complete exploration of principal stresses, let alone the stresses on free boundaries, can be determined with the same speed and accuracy and at such a surprisingly small cost as the photoelastic method. Nor is there a method which has the same visual appeal and covers the whole stress field with one pattern.

A critical observation shows that the materials which exhibit photoelastic effect are essentially high polymers and are sometimes called plastics. We know, that there are a number of plastics in the market today e.g. Bakelite, CR - 39, Catalin, Fosterite, Polystyrene, Cellulose acetate, Polymethyl methacrylate and so on; but only a few of them satisfy the requirements of a good photoelastic material and hence could be used in the preparation of the models for stress analysis. The characteristics of an ideal photoelastic material could be summarized as follows;

a) Optical transparency

b) Optical sensitivity to deformation

c) Strict adherence to Hooke's law

d) Freedom from aging effects

e) Freedom from initial internal stress

f) Elastic and optical isotropy and homogeneity

g) Machinibility

h) Constancy of properties during moderate changes in temperature and treatment

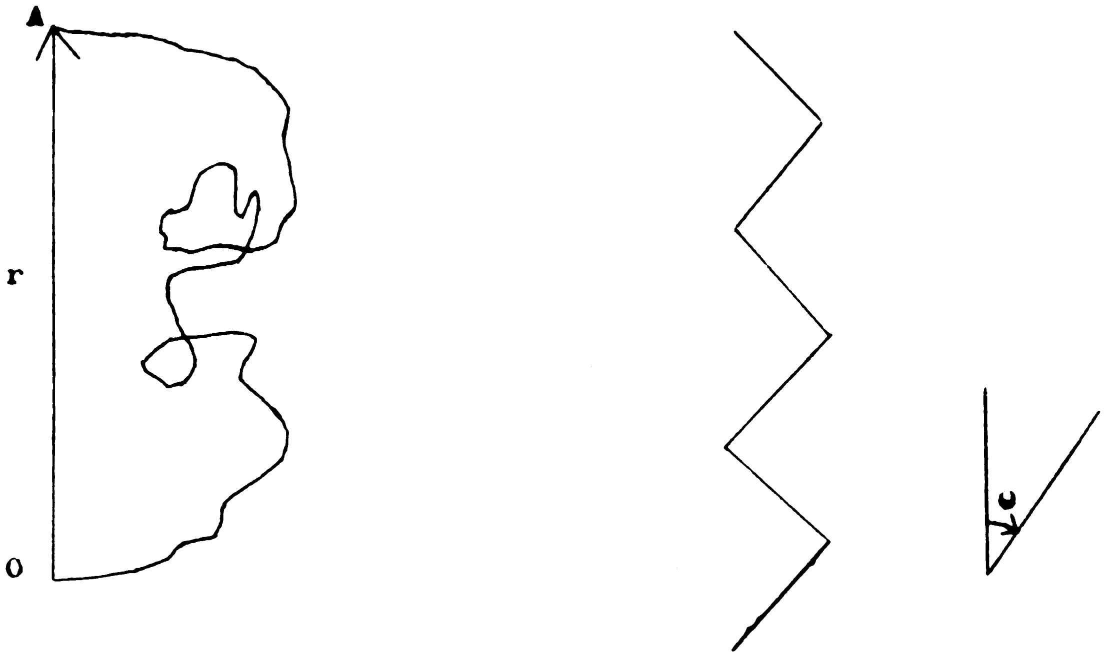
i) Reasonable price

Needless to say none of the materials thus far investigated meets all these requirements. In fact very few of the materials that are available for the construction of photoelastic model are more than partially satisfactory. Two of the most satisfactory are 1) a special type of Bakelite, designated by the number BT - 61 - 893 and 2) the Pittsburgh Plate Glass company product CR - 39, now produced by the Homalite Company of Wilmington, Del. There are several other materials of a similar nature that are fairly satisfactory. Celluloid has been an old standby for years.

In the following pages an attempt has been made to explain why materials are birefringent under stress; or, in other words, what is the mechanism of artificial double refraction in materials under stress? Directly or indirectly this problem has been under investigation since about 1920, some of the research workers in the field being Kuhn and Grun[6], Treloar[7], Rudd[8], Gurnee[9], and Andrews[10], who tried to answer the why of artificial double refraction in materials under stress. The optical anisotropy of a randomly linked chain, Fig. 1, has been theoretically worked out by Kuhn and Grun. They arrived at the equation

$$\left(\alpha_z - \alpha_x\right) = n\left(\alpha_1 - \alpha_2\right)\left[1 - \frac{3\left(r/nL\right)}{\mathcal{L}^{-1}\left(r/nL\right)}\right] \qquad (1)$$

where α_1 and α_2 are the electronic polarizabilities, parallel and perpendicular, respectively, to the individual links; α_z and α_x are the total electronic polarizabilities parallel and perpendicular,



(a) Random Chain

(b) Zig-Zag Chain

Fig. 1. The Random and Zig-zag Chains.

respectively, to the vector 'r' Fig. 1 (a); 'n' is the number of links in the chain; 'r' is the straight line distance between the ends of the chain; 'L' is the length of each link; and $\mathcal{L}^{-1}$ is the inverse Langevin function.

For a zigzag chain of 'n' links, a portion of which is shown in Fig. 1 (b), it can be shown from standard optical theory that

$$\left(\alpha_z - \alpha_x\right) = n\left(\alpha_1 - \alpha_2\right)\left[1 - \frac{3}{2}\sin^2\theta\right] \tag{2}$$

In the derivation of this equation, the zigzag chain is assumed to have free rotation about the 'r' vecter. This introduction of three-dimensional character is necessary in order to make a comparison between eqs. (1) and (2). It is also assumed that in any extension of this zigzag chain the bond angles all change in the same manner; eq. (2) may also be written as

$$\left(\alpha_z - \alpha_x\right) = n\left(\alpha_1 - \alpha_2\right)\left[\frac{3}{2}\left(\frac{r}{nL}\right)^2 - \frac{1}{2}\right]$$

Trelear's work was an extension of Kuhn and Grun's theeretical studies. He plotted the relative polarization anisotropy referred to the completely extended chain, $\left(\alpha_z - \alpha_x\right)/n\left(\alpha_1 - \alpha_2\right)$ against the extension (r/nL) for the random coil and the zigzag chain. Gurnee attempted to put orientation on a quantitative basis. He started with the Lorenz-Lorentz equation

$$\left[\frac{n^2-1}{n^2+2}\right]\frac{M}{\rho} = \frac{4\pi}{3} N\alpha$$

where n = refractive index,

M = molecular weight,

α = electronic polarizibility,

N = Avagadro's number,

and ρ = density;

The relation between birefringence and polarization anisotropy which Gurnee arrived at is as follows:

$$(n_z - n_x) = \frac{2\pi}{9} \cdot \frac{N\rho}{M} \cdot \frac{(\bar{n}^2+2)^2}{\bar{n}} (\alpha_z - \alpha_x)$$

where $\bar{n}$ is the arithmetic average of n_z and n_x.

Rudd and Andrews probably found some difficulties to devise methods for the loading of thin filaments which they used and hence they tried to investigate the relation between birefringence and internal stress in oriented filaments during retraction. They found in their experiments that a fairly linear relation existed between internal stress and birefringence.

It has been observed that the previous workers in this line, who derived some relations between optical anisotropy and stress and have developed some experimental techniques towards the finding of optical anisotropy with change in the magnitude of stress really did not explain the mechanism of birefringence in the so called photoelastic materials; i.e., having been given a certain photoelastic material how can one relate the optical anisotropy with the molecular deformation? Further, what is this deformation made up of? Is it a change in the bond angle?

or, is it a change in bond length? or, could it be a change in the amplitude of vibration of a pair of atoms inside the molecule? The object of the present investigation is to solve the above questions.

Background Theory

The application of photoelasticity requires some familiarity with not only the fundamental concepts of mechanics of solids but also some optical theory as it is related to stress analysis. In both areas the theory has been well developed. The following two sections give some of the fundamental concepts of the optical theory in photoelastic research and the theory of orientation and double refraction in polymers.

Optical theory as applied to stress analysis

A material is said to be double refracting if an incident plane polarized light ray is broken up into two component rays as it passes through the material. The resolution of the light ray is illustrated in Fig. 2, where OC is the incident ray and OA and OB are the component rays.

If a polarizing element called the analyzer is placed with its axis perpendicular to the original axis of polarization the light ray passing through the analyzer will have a magnitude represented by the difference of the two vectors OA'and OB'. The displacement of the component OA in the OA direction at any time t can be written as

$$OA = OC \sin \beta \sin (wt + \epsilon) \qquad (1)$$

and the displacement of OB in the OB direction as

$$OB = OC \cos \beta \sin (wt + \epsilon) \qquad (2)$$

where w is the angular velocity and ϵ is the phase angle.

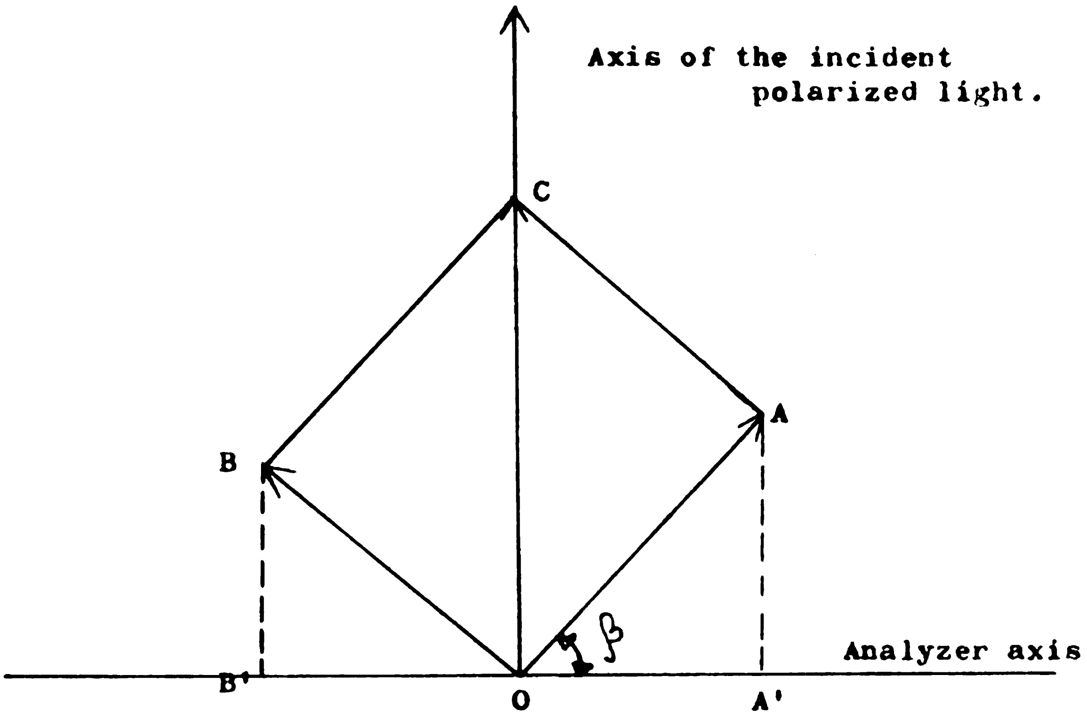


Fig. 2. Resolution of plane polarized light ray.

The magnitude of the resultant light ray emerging from the analyzer is

$$R = OC \sin\beta \sin(wt_1 + \epsilon) \cos\beta - OC \cos\beta \sin(wt_2 + \epsilon) \sin\beta$$

or,

$$R = (OC/2) \sin 2\beta \left[\sin(wt_1 + \epsilon) - \sin(wt_2 + \epsilon) \right] \qquad (3a)$$

where the times t_1 and t_2 are the times taken by the components of the resultant light ray in passing through the material. In solids the velocity is dependent on the magnitude of the principal stresses.

Equation (3a) indicates that there will be no light transmitted under the following two conditions:

(1) When $\sin 2\beta = 0$. This condition is satisfied if the plane of polarization coincides with either of the planes containing the OA or OB vectors. A dark spot will appear in the material wherever this condition is satisfied and the locus of these points is called an "isoclinic". For solids it has been well established that the incident light ray is resolved into components the principal stress directions and therefore the directions of the principal stresses can be determined from the isoclinics.

(2) When $\sin(wt_1 + \epsilon) = \sin(wt_2 + \epsilon)$ (4)

This condition is satisfied if

$$(wt_1 + \epsilon) = (wt_2 + \epsilon + 2n\pi) \qquad (5)$$

where n is an integer. The relationship between t_1 and t_2 can be written as

$$t_1 = t_2 + \Delta t \qquad (6)$$

and equation (5) reduces to

$$w \Delta t = 2n\pi \qquad (7)$$

as the necessary condition for extinction. Since

$$T = 2\pi/w = \lambda/c \qquad (8)$$

Equation (7) can also be written as

$$c\,\Delta t = n\,\lambda \qquad (9)$$

The term $c\,\Delta t$ is the relative retardation between the component rays as they pass through the body. One of the fundamental theorems in solid photoelasticity is the relationship between the retardation and the principal stresses

$$c\,\Delta t = K\,d\,(S_1 - S_2) \qquad (10)$$

Substitution of equation (10) into equation (9) gives

$$K\,d\,(S_1 - S_2) = n\,\lambda \qquad (11)$$

Therefore when the difference in the principal stresses is such that equation (11) is satisfied extinction of the emergent light ray will be accomplished. If the incident light ray is monochromatic i.e. the wave-length is a constant for each integral value of n, a series of black spots will be formed in the image of the specimen wherever equation (11) is satisfied. The loci of these points are called "fringes". If the incident light ray is white light the stressed areas in the specimen, as viewed through the analyzer, will appear in colors as certain components of the white light are extinguished. Upon proper calibration the colors can be related to the difference of the principal stresses. Each line of a single color is called an "isochromatic"

It is apparent that a doubly refracting material when subjected to a stress will produce both isoclinics and isochromatics. However, the isoclinics can be removed by using circularly polarized light.

Strains in the case of a Linear Chain molecule subjected to external load

Let a tensile force P be applied to a chain molecule parallel to its axis (Fig. 3). There will result an elongation of the chain due to both stretch of the valence bonds and the opening of the valence angles. These separate effects as they pertain to a single repeating unit are:

a) Elongation of the Repeating Unit due to Stretching of valence Bonds: Let the bond length be L_i and the bond angle be α_i as shown in Fig. 3. Let ΔL_i be the elongation in the bond length due to a load P acting in the direction of the arrow shown in the figure. If we denote the interatomic force constant for the bond under consideration by k_i, then

$$\Delta L_i = \left[P \cos \theta_i\right] / k_i$$

Now the contribution of each ΔL_i to the elongation along the axis of the chain will be

$$(\Delta L_i)' = P \cos \theta_i \cdot \frac{1}{K_i} \cdot \cos \theta_i$$

In order to facilitate the analysis a little bit let us treat the repeating distance along the chain as consisting of a number of segments in series, each of the segments in turn consisting of a few valence bonds. Then the elongation of the j^{th} segment will be given by

$$(\Delta L)'_j = \sum_i (\Delta L_i)' = P \sum_i \frac{1}{K_i} \cos^2 \theta_i$$

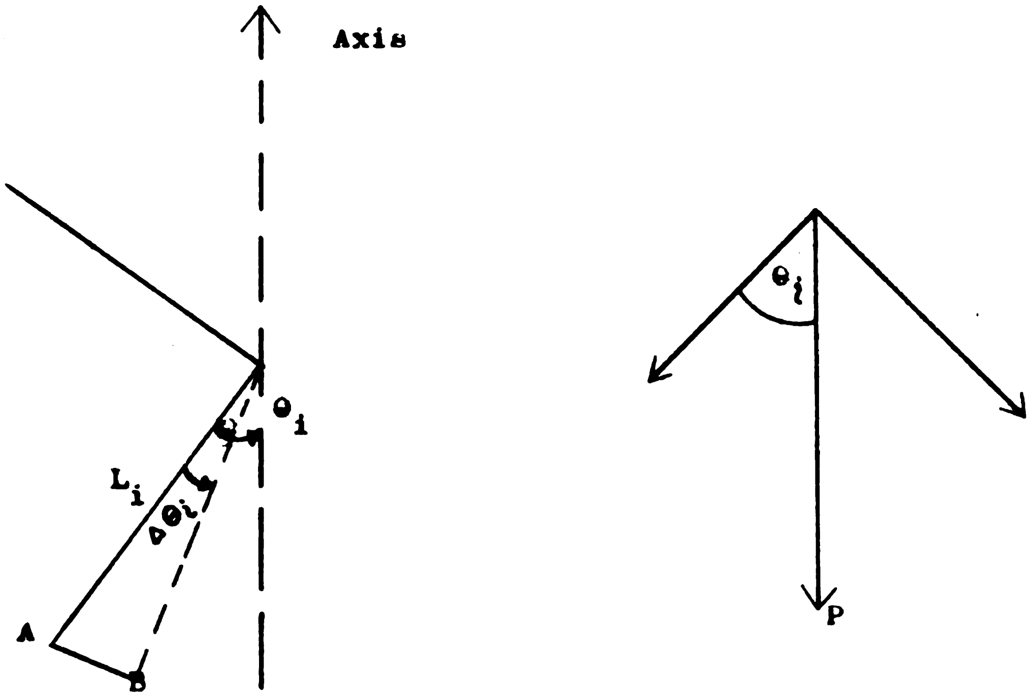


Fig. 3. Definition of valence and axial angles.

and finally for the total elongation along the chain axis due to stretching only we have the expression

$$(\Delta L)_s = \sum_j (\Delta L)'_j$$

b) Elongation of the Repeating Unit due to Opening of Valence Angles: The Fig. 4 represents the geometry of the opening of the valence angles. As is apparent in the figure the opening of the valence angles may be accomplished by the application of torques to the valence bonds in such a way as to decrease the angles α_i. Such torques are supplied by the components of P perpendicular to the particular valence bonds. The value of each such component is P sin θ_i.

Let d_i be the "angular" force constant, i.e., the force per cm required to move a mobile atom in a direction perpendicular to the bond direction, as from A to B in Fig. 4. It can be seen from Fig. 5 that $AB = L_i \Delta \theta_i$ and $d_i\, AB = d_i L_i \Delta \theta_i$, where L_i is the internuclear bond distance, and $\Delta \theta_i$ is the change in the angle θ_i. In equilibrium the resisting force for the atom in position B is

$$d_i L_i \Delta \theta_i = P \sin \theta_i$$

or,

$$L_i \Delta \theta_i = (P \sin \theta_i)/d_i$$

Referring to Figs. 4 and 5 the contribution of each displacement to elongation along the chain axis will be

$$(\Delta L_i)'' = AB \sin \theta_i = (P \sin^2 \theta_i)/d_i$$

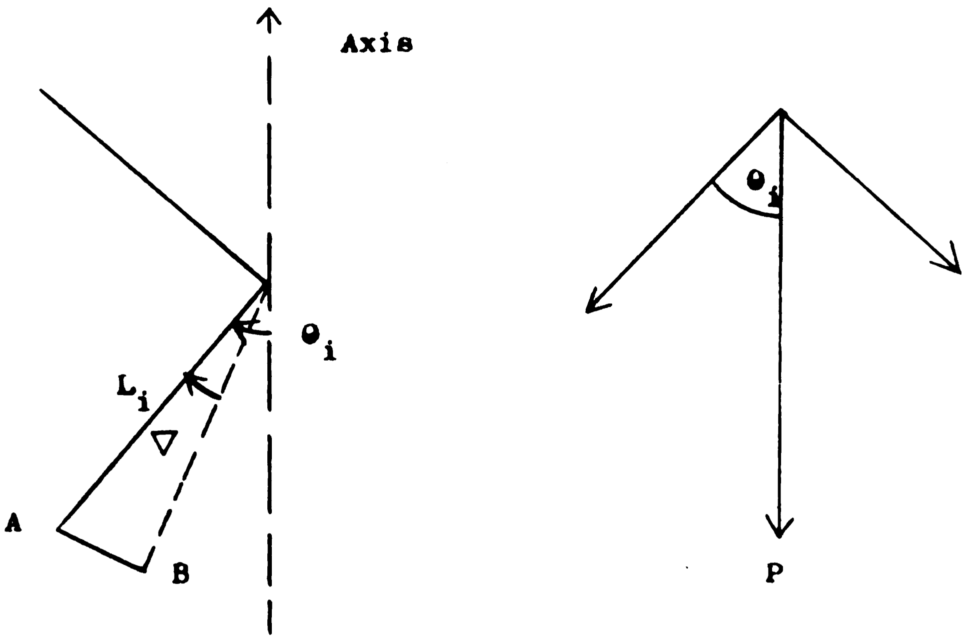


Fig. 4. Geometry of opening of valence angles.

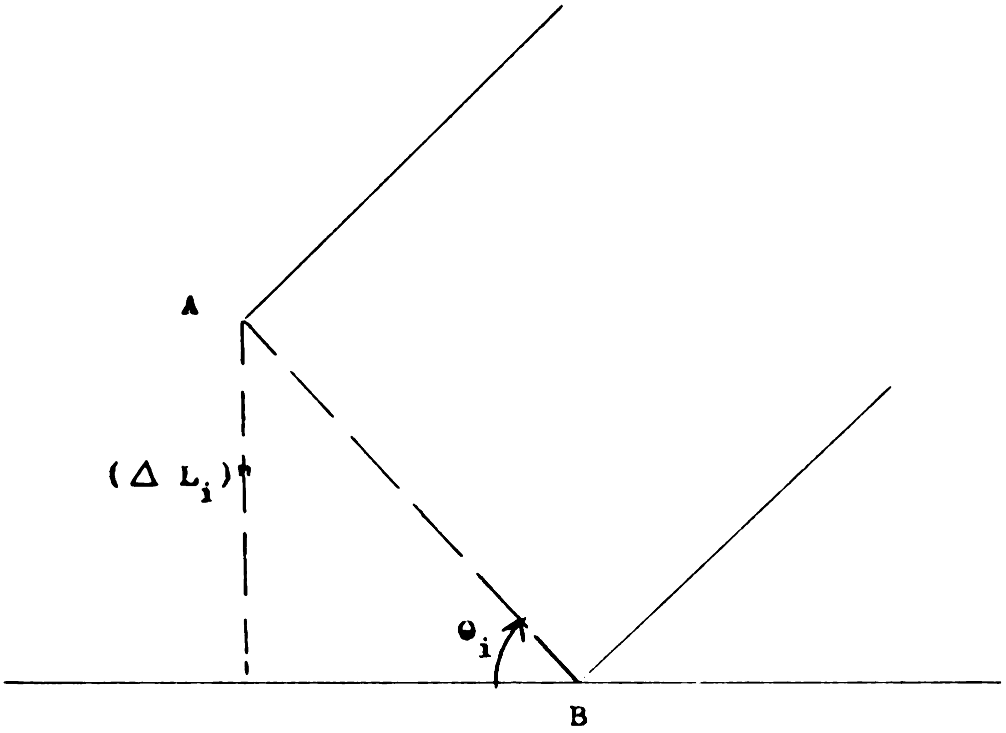


Fig. 5. Contribution of angular displacement of an atom from A to B to the elongation along the chain axis.

Then for the j^{th} segment the elongation will be

$$(\Delta L)_j'' = \sum_i (\Delta L_i)'' = P \sum_i \frac{1}{d_i} \sin^2 \theta_i$$

and finally, for the total elongation along the chain axis due to opening of valence angles we can write the following equation:

$$(\Delta L)_\theta = \sum_j (\Delta L)_j''$$

c) Total elongation of the repeating unit will be given by summing the elongations due to stretching of the bonds and opening of the valence angles. Thus the expression for the total elongation ΔL is

$$(\Delta L) = (\Delta L)_s + (\Delta L)_\theta$$

$$= P\left[\sum_i \frac{1}{k_i} \cos^2 \theta_i + \sum_i \frac{1}{d_i} \sin^2 \theta_i\right]$$

The Theory of Infra-red Spectra

The atoms of any molecule, when they are not at the absolute zero temperature, are in a state of constant oscillation about their equilibrium positions; and the amplitudes of these oscillations are of the order of 10^{-9} to 10^{-10} cm. Their frequencies are high and are of the order of 10^{+13} to 10^{+14} cycles per second. One could expect a direct relationship to exist between the vibrations of the atoms within a molecule and their effects on infrared beam incident upon them on account of the reason that these frequencies are of the same order of magnitude as those of infrared radiations. Actually those molecular vibrations which are accompanied by a change of dipole moment, so-called "infrared active" vibrations, absorb, by resonance, all or part of the incident radiation, provided the frequencies of the latter coincide exactly with those of the intramolecular vibrations.

A concept of the dipole moment is given in the following lines. If a neutral molecule or atom is placed in an electric field, the charged particles in the molecule or atom are affected by the field. The electrons are attracted to the positive side, and the positive particles are attracted to the negative side of the field. If the charge centers can be displaced, then a dipole has been induced and the atom or molecule is said to have been polarized. In general, the degree of polarization is proportional to the strength of the applied field and proportionality factor is dependent on the structure of the molecule.

Some molecules, by virtue of their structure, have a built-in displacement of charge, whereas some other molecules do not have their positive and negative charges displaced unless the molecules are subjected to an external electric field. The charge displacement that occurs without an external field is termed a permanent dipole.

A molecule containing a permanent dipole is termed a polar molecule. The product of the displaced charge and the distance of displacement is termed the dipole moment and is a vector quantity. Permanent dipole molecules, when subjected to an electric field, attempt to align themselves parallel to the field, and the degree of alignment is a function of the field strength and the temperature. Temperature acts to prevent alignment by producing thermal motion. Permanent dipoles can be additionally polarized by the applied field, but the extent is small compared to the permanent displacement.

If a sample of molecules of a single kind is irradiated in succession by a series of monochromatic bands of infrared beam, and the percentage of light transmitted is plotted as a function of either wave length or frequency, the resulting graph may be interpreted in terms of intramolecular vibrations. At the outset these atomic vibrations seem to be very complicated, but by detailed analysis it is possible to show that these motions happen to be the summations of a number of simple oscillations. Each of these simple vibrations is referred to as a "fundamental" or "normal" mode of vibration. One could prove mathematically that a nonlinear molecule containing 'n' atoms possesses

3n - 6 such normal modes, whereas a linear molecule possesses 3n - 5. Carbon dioxide, CO_2, is an example of a linear molecule. On the other hand methane CH_4 is a non-linear molecule. CO_2 and formaldehyde can be schematically represented as in Figs. 6(a) and 6(b).

A normal mode of vibration is defined as a mode in which the center of gravity of the molecule does not move, and in which all of the atoms move with the same frequency and in phase. Each normal mode can occur without affecting the others. It is possible for all of the vibrations 3n - 6, or 3n - 5, as the case may be, to occur simultaneously and yet for each one to retain its characteristic frequency. Infrared spectral studies therefore, constitute an analysis of the mechanics of the molecule.

In order to get a picture of a normal vibration let us take the case of a mechanical model. A benzene molecule is conventionally represented as in Fig. 7. It can be constructed to bring out the mechanical analogy by using weights in the ratio of 12 to 1 for the Carbon and Hydrogen atoms, respectively, these weights held in proper orientation by suitable springs. Suppose further that the carbon-hydrogen springs are now stretched slightly by moving each of the six pairs of weights so that the hydrogens are moved 12 times as far from the equilibrium positions as the carbons and in opposite directions. If, now, the weights are released simultaneously, a vibration will occur in which the weights move back and forth along the connecting springs or bonds. The center of gravity of the whole model remains at rest and the weights move only along the line of the connecting

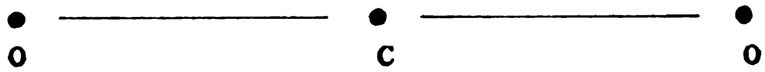
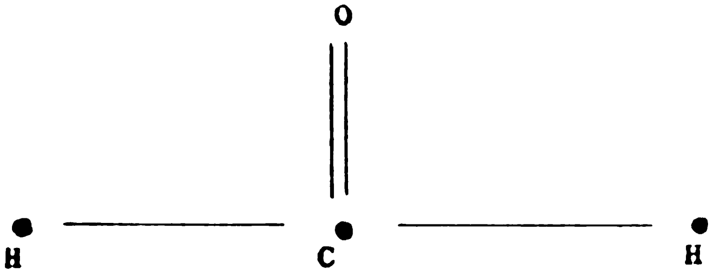
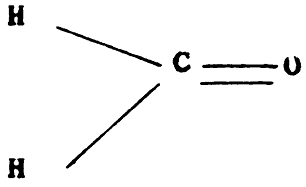


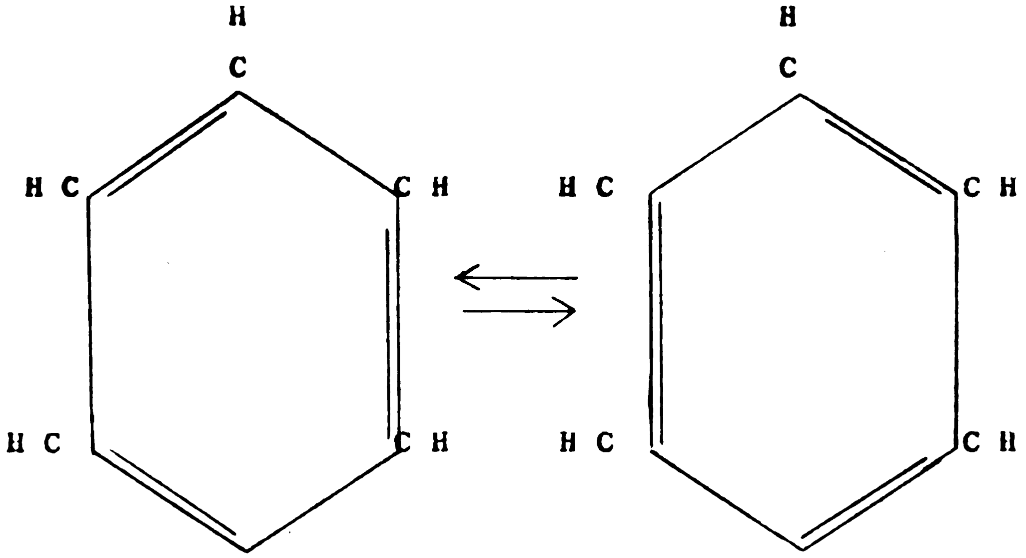
Fig. 6 (a) Linear molecule of CO_2 (carbon dioxide).



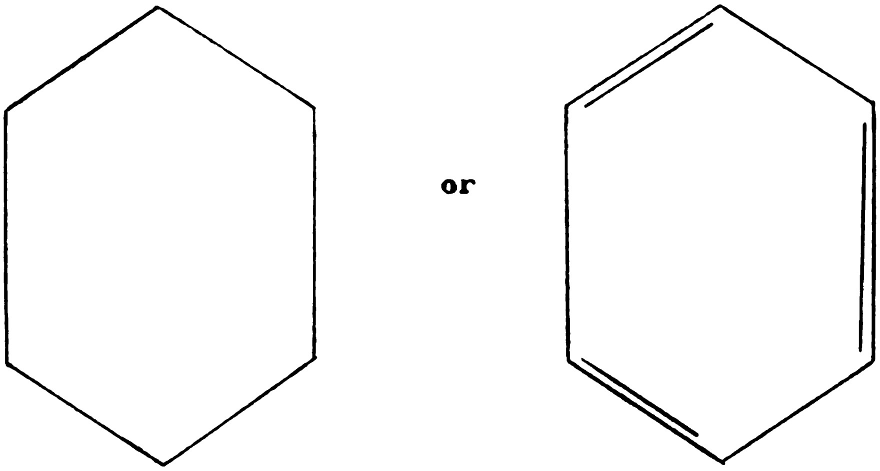
formaldehyde
(as in bakelite, for example)

Fig. 6 (b) non-linear molecule of





Conventional



Schematic

Fig. 7. Benzene molecule ($C_6 H_6$).

springs, since no original impetus was given to the weights in any other direction. This is a characteristic vibration of the model and it does not excite any other vibration in the model. Further, the stretching motion is quite analogous to one of the 3n - 6, or, 30 normal modes of the benzene molecule. Another benzene vibration can be visualized readily by pulling the six carbon weights slightly above the plane of the model while the hydrogen weights are pulled twelve times as far below and then releasing all twelve weights simultaneously. It is possible to demonstrate several other characteristic vibrations of the benzene molecule proceeding on similar lines.

Let us imagine, for example, that the mechanical model is given a blow with a hammer. At first sight the weights seem to be performing a complicated motion having no apparent relation to the individual modes of vibration referred to above. However, if this apparently random motion is photographed with a stroboscopic camera adjusted successively for each of the frequencies of the normal modes, each of these modes will be found to be faithfully performed by the weights.

An infrared spectrometer plays the same role with respect to the actual benzene molecule as the stroboscope does to the model. Thus, by measuring the frequencies of the infrared radiation absorbed by a substance the spectrometer determines the characteristic mechanical frequencies of its molecules. Since these molecular frequencies are functions of the atoms themselves, that is, the masses, the spatial arrangement, the valence forces, and to some extent the intermolecular

forces, the value of the infrared spectroscopic information is obvious.

A pertinent question that comes to one's mind, at this stage, is whether there is any possibility of a mathematical calculation of the normal modes of vibration. Such a calculation, if successfully completed, should make possible a unique determination of the structrure of the molecule in question. The correct structure of the molecule would obviously be that whose calculated frequencies correspond exactly to those observed in the experimental spectrum. From a theoretical stand-point of view the expected frequencies can be calculated, provided the strengths of the individual interatomic forces are known; but, the complexity of such calculations would be augmented with increase in the number of atoms and their geometrical arrangement.

When there is an increase in the complexity of the structure of a molecule a mathematical calculation might be considered to be almost an impossibility till recently. With the help of the electronic digital computers it might be possible today to handle such mathematical calculations. There are also other methods that are used when the molecules are quite complex, in order to correlate the characteristics of an observed spectrum with the structure of the molecule. Considerable success in this direction has been achieved by a purely empirical approach.

For the purpose of understanding the basis for such an empirical method, let us resort again to a discussion of mechanical molecular

models. Let the model of the molecules contain only one C - H bond as in the case of chloroform, Cl_3CH (Fig. 8). If the C - H spring is stretched and released, the carbon and hydrogen weights vibrate rapidly with a characteristic frequency. The chlorine weights, on the other hand, are so heavy they are almost totally unable to follow the vibrations. It is true, at least to a first approximation, that the observed stretching is a characteristic of the C - H spring (or bond) and the masses of these two atoms, and is practically independent of the rest of the molecules. Similarly, a bending or deformation can be studied by displacing the hydrogen weight in a direction normal to the axis of molecular symmetry and then releasing it. Again the carbon and hydrogen weights will move characteristically with the remaining weights practically at rest. From the above observations we arrive at the idea, that to the extent that atomic forces between a carbon and hydrogen atom are a function of these two atoms alone, the presence of C - H linkages in a molecule will cause at least two infrared absorptions which are practically independent of the atomic constitution of the rest of the molecule. The truth of this has been well established experimentally.. A study of hundreds of molecules containing C - H linkages has shown an absorption at a frequency around 2900 cm^{-1} (C - H stretching) and another around 1450 cm^{-1} (C - H bending). One could find out with the help of a high resolution spectrometer that these C - H frequencies are influenced slightly by the relation of the C - H linkage to the molecules as a whole. Also the exact frequency value of these absorp-

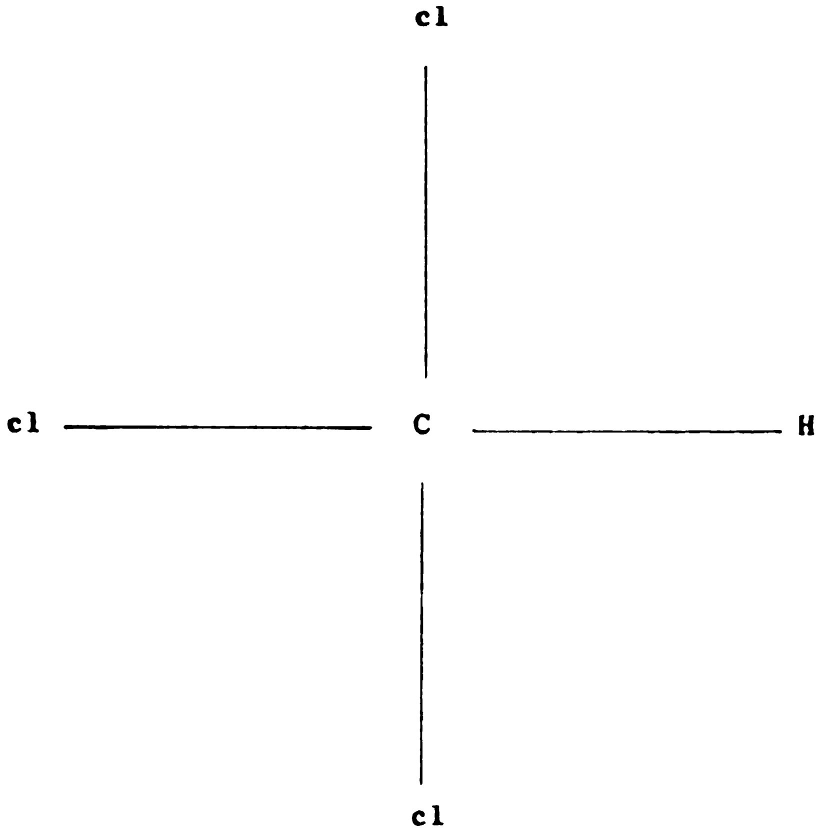


Fig. 8. Chloroform - (Cl_3CH).

tion bands may be used to indicate the degree of saturation of the carbon atom to which the H is attached or whether the C - H occurs in a CH, CH_2, or CH_3 group.

Although the mathematical approach has been of great value when applied to simple or highly symmetrical molecules, most of the information derived from infrared spectra is obtained by the application of the empirical method. It consists of comparing the spectrum of an unknown molecule with the spectra of several other molecules having a common atomic group. By a process of elimination it is often possible to find an absorption band whose frequency remains constant throughout the series. The presence of an absorption band, in an unknown molecule, at this frequency may reasonably form the basis for a guess that the particular atomic group is present. In this type of an empirical approach for identification from the spectral distribution curve, success is guaranteed only with constant application.

It must not be assumed from this discussion that it is, or will be, possible to ascribe every observed absorption to a specific group of atoms. Indeed, if this were true it would make more difficult the possibility of differentiating clearly between isomeric compounds. In fact, one could correlate in this manner very few of the observed bands. Most of the observed bands arise from normal modes of vibration which are characteristic of the molecule as a whole. However, these general absorption bands are highly sensitive to structural changes, and hence furnish us with a "finger

print" of the molecule. Only on account of this it is possible to carry on the analysis of isomeric mixtures and other closely related compounds.

It is very important to remember, at this stage, that the normal modes of a molecule do not account for all of the absorption bands observed in its infrared spectrum. For example, in the far infrared there are absorptions caused by the slower rotations of the molecules or the massive lattice vibrations of crystals. Further, throughout the whole infrared region absorptions frequently occur at integral multiples (overtone bands) of the fundamentals, or at frequencies which are equal to the sum or difference (combination bands) of fundamentals. These bands in general absorb very much less strongly than do the fundamentals and consequently must be studied with thicker samples. Since they are so sensitive to the over-all molecular structure, they can sometimes be used more for successfully accurate fingerprinting of molecules and for the analysis of mixtures than the fundamental absorptions.

Molecular Structure and Mechanical behavior of a Polymer

Polymer is the name given to a number of monomers bound together chemically. Monomer is the basic unit representing the molecule of a hydrocarbon. The gross chemical equation for the polymerization process is the rather simple one

$$n\,(C_2\,H_4) \longrightarrow (C_2\,H_4)_n$$

where n represents the (average) degree of polymerization. The above hydrocarbon is called Polyethylene. Similarly the polymerization relation in the case of Polystyrene can be represented as follows:

$$n\,(C_8\,H_8) \longrightarrow (C_8\,H_8)_n$$

There is a large diversity in the mechanical properties of high polymers. Different polymers have different atomic arrangements in the molecule and differences in the molecular architecture. Many polymers are hard glassy solids; others are rubbery or jelly-like or fibrous. The factors that govern the mechanical properties of these polymers can be listed as follows:

1. Chemical composition of the polymer
2. Molecular architecture of the polymer chain
3. Extent of crystallization

Chemical composition refers to the monomer that repeats itself to make up the polymer. Polystyrene and polyethylene, for example, can be represented as in Figs. 9(a) and 9(b).

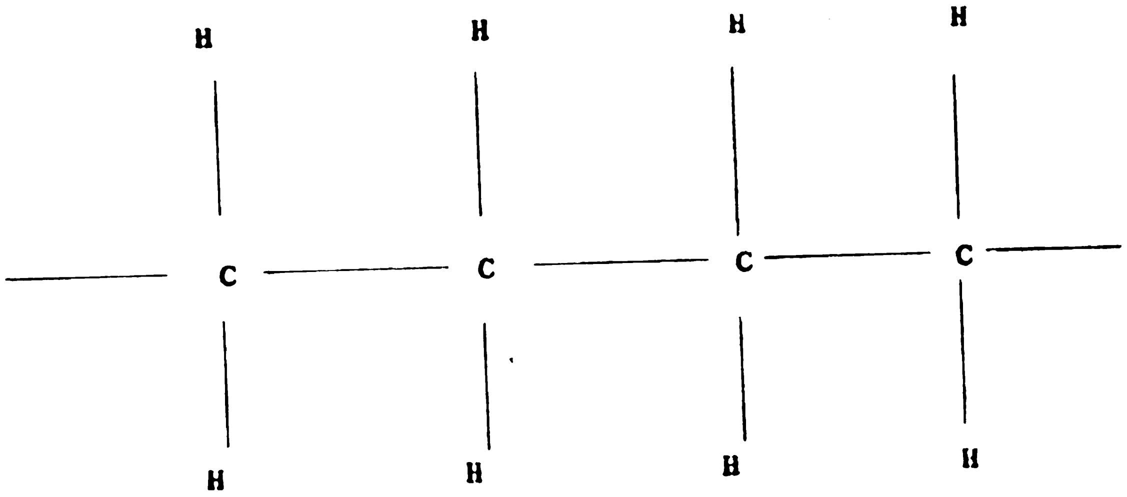


Fig. 9 (b) Polyethylene

Further the benzene ring is replaced by the chlorine atom in the case of polyvinyl chloride as shown in Fig. 10. In the case of some of the polymers like polyesters, polyamides, polysiloxanes etc., atoms other than carbon are contained in the chain itself;

The term molecular architecture refers to the molecular weight, molecular configuration, degree of cross-linking and so on. For example polystyrene of molecular weight 50,000 and polystyrene of molecular weight of 100,000 have different molecular architecture even though they have the same chemical composition.

The third structural feature refers to crystallinity; i.e. the perfect regularity of the chain structure with exact repetition of the monomer units. In high polymers the phenomenon of crystallization is somewhat different from that observed with lower molecular weight materials; the dimensions of the crystallites formed are much smaller than the chain length of the macromolecule. Thus, any one chain may thread its way through several crystallites and several intervening amorphous regions. The result is always a poly crystalline mass, with the crystallites imbedded in an amorphous matrix. The crystallites may be randomly dispersed as in Fig. 11(a) or partially oriented as in Fig. 11(b) depending on the past history of the sample.

It is also known that in the case of tissue elasticity, since most animal tissues contain a high proportion of water, the water content also plays an important part in deciding the mechanical behavior.

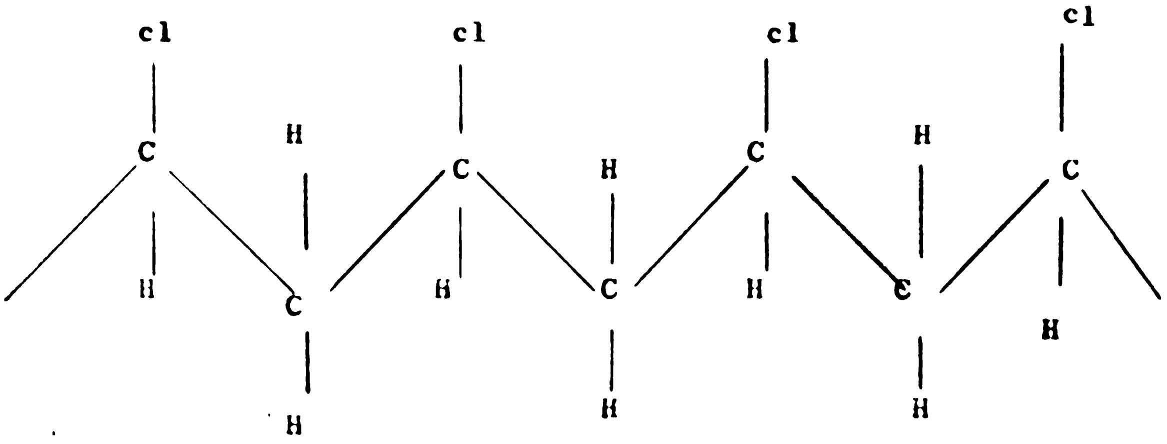


Fig. 10. Polyvinyl chloride.

Fig. 11 (a)

Fig. 11 (b)

Thus the difference in the physical properties of the polymers can be attributed to the variations in one or all or even some of the factors mentioned above. It may be worth while here to consider the variations obtainable within a single chemical composition with variation in molecular architecture and crystallinity. The molecular weight and the degree of branching can be independently controlled by the polymerization conditions. The degree of branching in turn determines the crystallinity; consequently polyethylene can be prepared with wide variations in crystallinity and molecular weight, with corresponding variations in physical properties.

It is suggested that the chemical composition, and the temperature either individually or both have a predominant effect on the resulting orientations and hence anisotropy of the molecules under stresses. Different materials under the same conditions of stress could exhibit different polarizabilities on account of their having different bond angles and bond forces. Secondly, in a particular chemical composition the flexibility of the atoms could be either increased or decreased by the introduction of an additional atom to either increase the stiffness or decrease it. Furthermore, these bond forces and bond angles are different between the different atoms of the same molecule, which would result in, under stresses, different orientations. Now in order to be able to find out the effect of these orientations on the artificial double refraction of a certain polymer under stress it would be a more thorough investigation if one

could find out to what extent each atomic group has been deformed under the particular stress than speaking of the orientation of the molecule as such. The changes in the individual atomic groups could be studied by taking an infrared absorption spectrum of the particular polymer under stress. So one could hope to get a clear picture of the changes in the constituent atomic pairs which could later be related to the stress birefringence.

Description of the Photoelastic apparatus

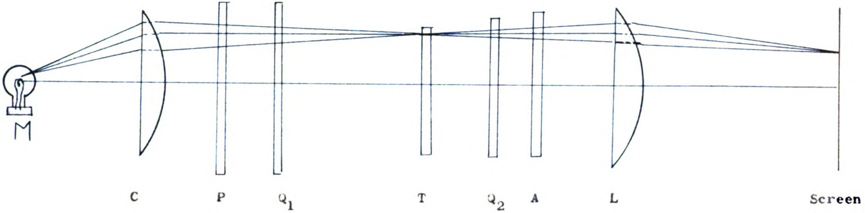
The apparatus for the Photoelastic Experiments consists essentially of the projection system, the optical alignment guides, polarizer and analyzer combination, the straining frame and accessories.

The projection system:

It consists of a double convex lens of about 3.5 ft focal length mounted on a stand [redacted], so as to enable the operator to adjust it on the guides at will. The lens projects the image on to a drawing board fixed to a wall. This would facilitate the visual observation as well as the plotting of isoclinics on a sheet of paper attached to the drawing board.

The Optical Alignment guides and Accessories:

A schematic diagram of the optical parts in the photoelastic work is given in Fig. 12. The alignment guides are a pair of mild steel rods 2½ ft long and 3/4" dia. They are set parallel on a wooden platform at a distance of 7.5". At one end of the guides there is a dual light-source enabling the operator to choose white light or mercury light at will. To protect the lamps from getting excessively hot a fan is also provided close by. The polarizer and analyzer are built in a cast iron frame in a crossed position. A condensing lens is also built into the same frame. A pair of quarter wave plates could be inserted between the polarizer and analyzer combination at will and they are held in position with the aid of flexible metal strips provided on the casting itself.



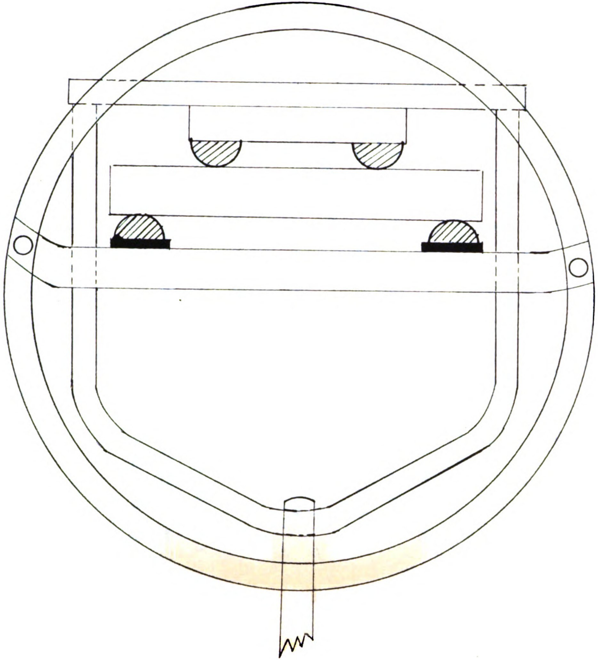
M	Light source
C	Condenser
P	Polarizer
Q_1	Quarter wave plate
T	Test specimen
Q_2	Quarter wave plate
A	Analyzer
L	Projection lens

Fig. 12.

The Straining frame:

The straining frame consists of a pair of alluminum annular rings set parallel with a separation of 3/4 inch and fixed to a steel tubing between the guides. A pair of bent alluminum plates are held in position on either side of the circular frame with the help of small pins. An alluminum frame whose shape is shown in Fig. 13 could be inserted into the space between the circular rings and held in position with the help of slotted rod and pin. A long rectangular (23" x 1" x 1") aluminum beam passes through a metal tubing held rigidly in position between the guides on to the platform by means of end flanges. One end of this beam carries a hanger and is held by means of a screw support on the other end. At about half its length the beam is supported on a pin inside the metal tubing. The screw support referred to above could be used to set the beam horizontal initially.

Fig. 13. The Straining frame.



Determination of Stress-Optic coefficient

Polystyrene

A polystyrene beam 5 (5/8)" x (5/8)" x $\frac{1}{4}$" is cut out of a $\frac{1}{4}$" thick large polystyrene sheet. It was then held in position for producing pure bending in the center portion as shown in Fig. 14. A load of 90# was added to the hanger and the appearance of a fringe on the screen was noted. We notice here that a load of as much as 90 # was necessary to produce even one fringe on the screen on account of the fact that polystyrene is a poor photoelastic material. The monochromatic light used for obtaining the isochromatic was mercury green 5461 A.

The stress-optic coefficient C is calculated from the formula

$$C = \frac{t}{2n} \cdot \frac{My}{I}$$

where n is the fringe order, t is the thickness of the specimen, and My/I is the stress on the boundary in which y is half the thickness of the beam. The stress-optic coefficient for polystyrene obtained in this experiment is 422 lbs./in.^{2}/fringe/in.

C R - 39

A C R - 39 (Columbia Resin 39) beam of the same dimensions as in the previous experiment was cut out of a large $\frac{1}{4}$" thick sheet. The experiment was repeated in this case also for the purpose of finding the stress-optic coefficient of C R - 39. A 60 # load was found to

produce as many as 4 fringes. The value for C R - 39 obtained in this experiment is 86.5 lbs./in.^{2}/fringe/in. The calculations are shown below:

Polystyrene

Test specimen	5(5/8") x (5/8") x ¼"
....	5461 A

$$My/I = \frac{90 \times 0.6 \times (5/16)}{\frac{1}{4} \times (5/8)^3 \times (1/12)}$$

(Load for one fringe was 90 #)

$$C = (t/2n).(My/I)$$

$$= 422 \quad \text{lbs/in}^2\text{/fringe/in.}$$

C R - 39

Test Specimen	5(5/8") x (5/8") x ¼"
Load	60 #
Bending moment M	60 x (3/4) lb. ins.
Fringes per ½"	4
Stress-Optic coefficient	C

$$C = (t/2n).(My/I)$$

$$= \frac{1}{4} \times (1/8) \times 60 \times (3/4) \times (5/16) \times 12 \times$$

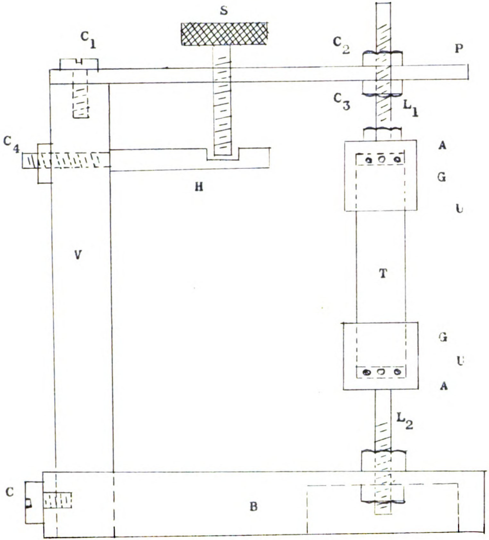
$$1\tfrac{1}{4} \times (5/8)^3$$

$$= 86.5 \text{ lbs/in}^2\text{/fringe/in.}$$

The Straining Unit for Loading the films

A special type of straining unit has been designed and constructed in order to facilitate the loading of very thin films of about five thousandths inch thickness. A sketch of the unit is shown in Fig. 14. It consists of a steel base B 6" x 2" x 1" and carries a vertical steel post V 6" long and 1" square section on one end of the base. A clamping screw C from the side of the base ensures firm positioning of the vertical post. A rectangular strip of steel P, 6" x ½" x 1/8", is fixed on to the top of the vertical post by means of a screw C_1. A thumb screw S passes through a hole in the horizontal steel plate at a distance of 1" from the center line of the vertical pillar. The bottom of the thumb screw rests on a flat bar H projecting from the vertical post and held in position by means of a clamping screw C_4 as shown in Fig. 14. A long steel bolt L_1 passes through a hole near the free end of the horizontal plate and is clamped on to it at any desired position of its length by means of clamping nuts C_2 and C_3. The steel bolt carries at one of its ends an inverted U shown in the figure. A pair of steel flats AA 1" x ¼" x 1/8", intended for the purpose of gripping the test film, are held in the inside of the U by means of a 1/8" steel pin passing through the sides. Another vertical bolt L_2 rising from the base carries a similar U at its top. A similar pair of steel grips as mentioned above are held in the inside of the U by means of a steel pin passing through the sides.

Fig. 14. The Straining Unit



Each grip has a set of three holes 1/8" diameter drilled symmetrically in it; the center hole is intended to take in the steel pin passing through the sides of the U, and the two outer holes to take in small brass screws and nuts for clamping the test film tightly in between the grips.

The load measuring device includes four SR - 4 strain gages mounted on the horizontal steel plate. They are connected to a strain indicator which is later calibrated. The four gages are intended not only to augment the output but also provide the necessary temperature compensation. The straining unit was designed to be used with a maximum load of 5 lbs.

Calibration of the Straining Unit

An SR - 4 strain indicator was connected to the strain gages. The upper portion of the gripping unit was set in position along with small steel grips AA held inside the U by means of the steel pin. The strain indicator is adjusted to zero (i.e. null deflection in the galvanometer after choosing the preper scale and gage factor). In the present experiment the gage facter of the gages was 1.97. A load of ½ lb was added to the upper gripping device and the deflection in the strain indicator was neted. The bridge was balanced for null deflection and another ½lb load was added again. This experiment was done up to a 4 lb load and each time

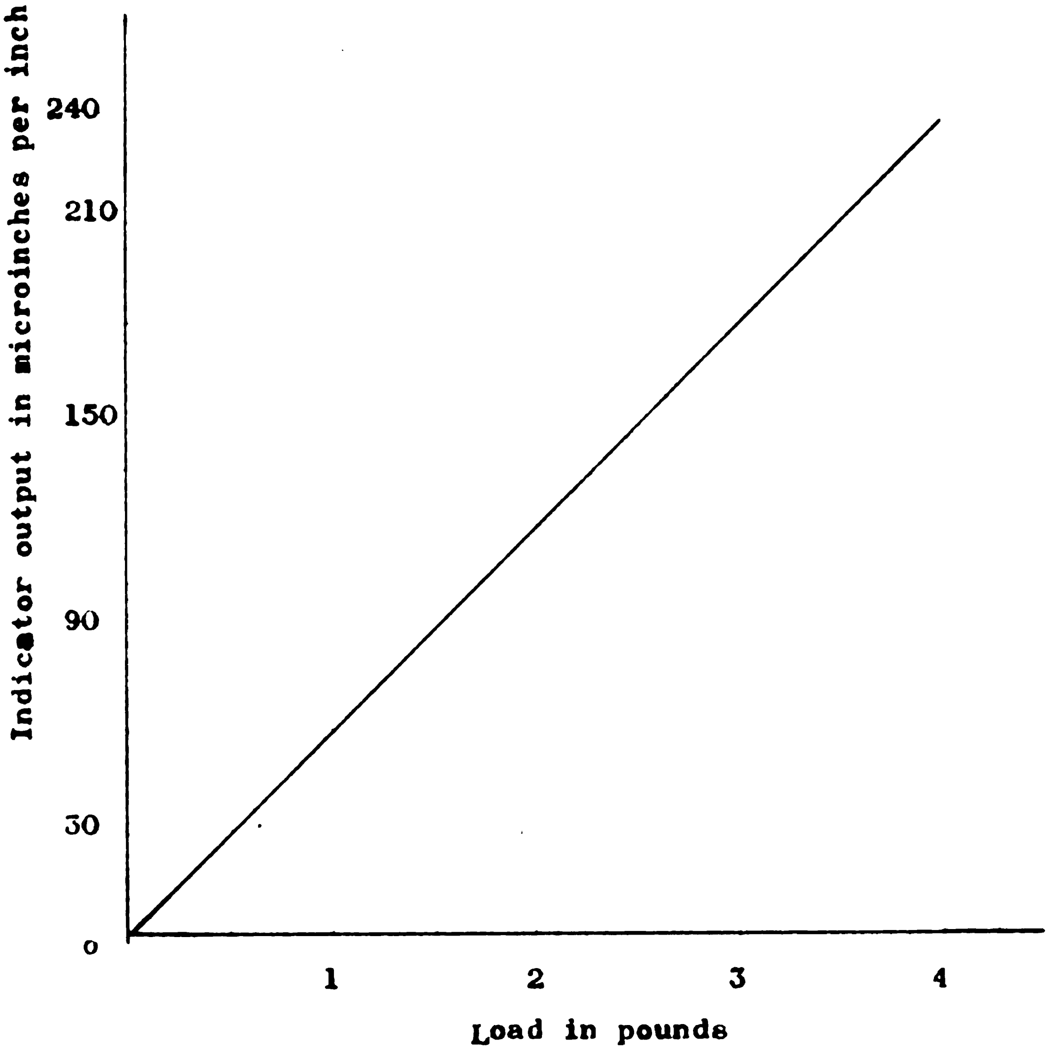
the strain indicator reading is noted. It was observed that a load of ½ lb produced an output of 30 micro-inches per inch on the strain indicator. While working with the straining unit every care was taken to see that the strain gages are protected safely. The strain indicator was calibrated for different loads and the readings are shown in table 1. A graph was drawn showing the relation between the load and the strain indicator output.

Table 1.

Strain Indicator Calibration

Load	Reading of the indicator	
	Loading	Unloading
0	1320	1320
½ lb	1290	1290
1 lb	1260	1260
1½ "	1230	1230
2 "	1200	1200
2½ "	1170	1170
3 "	1140	1140
3½ "	1110	1110
4 "	1080	1080

Strain indicator output for ½ lb = 30 micro-inches per inch


Indicator output in microinches per inch
240
210
150
90
30
0
1
2
3
4
Load in pounds

Preparation of the film

The preparation of the test film for taking the infrared absorption spectra seemed to be the most difficult part of the experiment. It has to be very thin, of the order of about 2 to 3 thousandths inch thick. There are two methods of obtaining such a thin film for infrared work. One is to dissolve the given polymer in a suitable solvent and pour it in thin layers on a flat glass piece and let the polymer dry up. But this method of preparation has the draw back that the heat of polymer (as some heat is required to melt the plastic) during the process of cooling could affect the polymerization besides inducing thermal stresses. Of course the latter can be removed by annealing but the changes in polymerization are to be guarded against. The second method of obtaining the polymer film is to take a piece of the given plastic from a thick sheet ¼" thick and attempt to thin it down to the required extent. This is not so easy as it is mentioned here; and it also makes one think if it is not ~~a~~ rather an odd procedure. It is well known to the photoelasticians in the engineering field that a ¼" thickness is good size for photoelastic work. In the present investigation as it is desired to correlate the photoelastic effect with the infrared absorptions it is but obvious that one chooses a ¼" thick piece for photoelastic studies. Further, to make sure that the directional properties of the plastic do not have any effect in the experi-

mentation one has to use a similar piece cut in the same direction from the original thick plastic sheet for the purpose of machining; and it is a successful machining that could ensure a satisfactory infrared resolution spectrum.

A piece of the plastic 3" x 1" x $\frac{1}{4}$" was cut from the large $\frac{1}{4}$" thick sheet in the same direction as the pieces for photoelastic work were cut. This piece was then fixed on the bed of the milling machine with the help of scotch tape. In using this scotch tape for fixing the specimen on the bed of the milling machine the following procedure was adopted. The adhesive side of the tape is first attached to the plastic piece and then the top layer of the non-adhesive side of the tape is carefully peeled off so that one could get another adhesive side of the tape. The bed of the machine is carefully cleaned with a piece of clean cotton cloth and then the plastic was set on it flat. The adhesive side of the tape would stick to the bed and would facilitate the firm fixing of the specimen. In the case of polystyrene a 5/16" double flute end mill driven at 2450 rpm was used and the machining job was done using the automatic drive. In the case of Columbia Resin which is a rather brittle material it was found that specially ground 1" fly cutter could yield better results. The speed was the same as before. No coolant was found to be necessary in either case but an occasional cleaning up of the surface being machined with a small paint brush using a little oil would ensure a better machined surface.

It was found that it is not a good practice to start large cuts from the begining, as it would result in excessive heat in the plastic and would melt besides sticking to the cutting edge. The following scheme was used in the process of machining. A twenty thousandths inch thick layer was removed each time for five times; then a 10 thousandths layer was removed for another 10 times; lastly a layer of 2 thousandths thick was removed each time till the desired thickness of the film was obtained. Extreme care was taken in removing the film from the bed of the machine. A blunt razor blade carefully advanced longitudinally underneath the surface of the film was found to be satisfactory for the particular job.

The specimen was then fixed on a narrow portion on all the four sides on apiece of flat of cold rolled steel using scotch tape. The surface was then polished with what is commercially known as plexi glass polish. The polishing business seemed to be a special technique in itself which should be mastered with constant practice. On the whole the preparation of the film for the infrared spectral studies seemed to be a machinist's cum artist's job. It is only with a constant practice on this job that a reasonably satisfactory film could be produced.

Description of the Infrared Spectrophotometer

A brief description of the Perkin-Elmer Infrared Spectrophotometer used in the present investigation is given below.

The basic instrument consists of a single unit, 40" long, 20" wide and 23" high. A seperate external amplifier is also provided. The main instrument consists of two separate mountings with a 6" clearance in between intended for accomodating the samples and references. The source and source focussing mirrors are under the right hand cover and the photometer unit, monochromator and detector are provided on the left hand side. The recording drum and the wavelength drive are mounted on top of the monochromator cover. The main control knobs are provided on the cover on the right hand side with additional controls on the front side of the base or chasis. The counters reading wavelength and slit width directly in microns are visible through windows in the cover on the left side. An opaque shutter for each beam is pivoted on the side of the small cover on the right.

The optical system of the Infrared Spectrophotometer is shown in Fig. 15. Two beams of light from the same source S_0 are brought to two separate foci by two pairs of mirrors, M_1 & M_3, and M_2 & M_4, one beam S, passing through the sample C, and the other R, through a reference X. These two beams are then combined by a rotating sector mirror, M_7, that transmits one beam and reflects the other into the same direction as the transmitted beam. The composite beam passes through a monochromator to a detector. If the two beams are equal in intensity no output is observed from the detector. If the beams have unequal intensities a pulsating voltage appears proportional to the difference in intensity. This off balance voltage after necessary amplification is used through an intermediate power stage to actuate a pen servo motor. Actually when the two beams are balanced, the detector sees no change in the radiation incident upon it. The moment an unbalance occurs between the sample beam and reference beam, a 13 cycle alternating voltage is developed which is amplified by the preamplifier. The first-stage transformer in the preamplifier steps up the voltage approximately 300 times and from thence the signal is amplified until a high enough voltage is attained so that the signal can be separated from its 13 cycle carrier. At this stage, the phase and amplitude of the signal are determined and this signal is filtered and fed into the 60 cycle modulator and power stage, the signal form which actuates the pen servo motor.

The Nernst Glower Source

In the Perkin-Elmer instrument a Nernst glower is used as the source ,S_0, of infrared radiation. It is mounted on an easily removable base between two ceramic posts that are wound with platinum wire for preheating and starting. The two pairs of concave mirrors, M_1 and M_3, M_2 and M_4, form two identical images, I_1 and I_2, of the

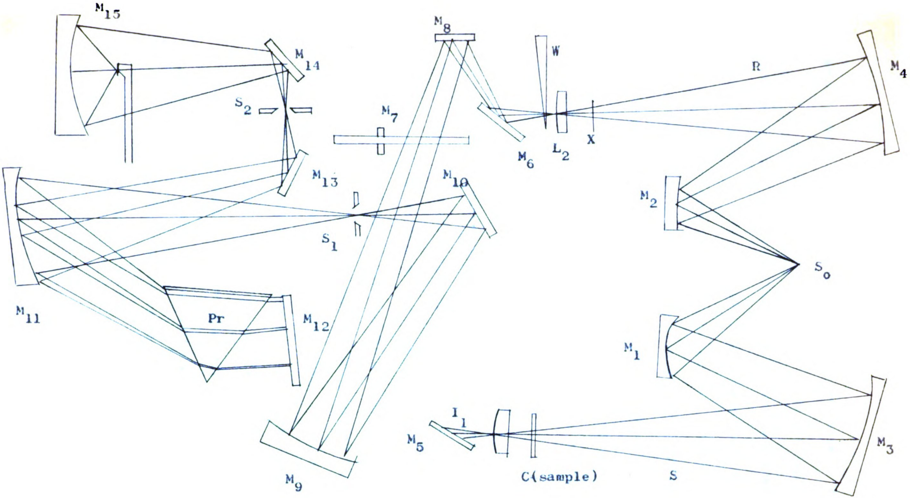


Fig. 15. The lay-out.

source, each magnified to twice its original size. The first two M_1 and M_2 are placed close together to permit taking light from the same part of the source for the reference and sample beams. They also help to make the instrument more compact and increase the amount of free space available for samples. Two solid shutters on the outside of the source housing permit closing off either or both beams independently. Nernst glower has several important properties, like long life, high operating temperature, good black body characteristics, etc., which make it useful as a source of infrared radiation.

The Photometer Section

The images formed by the first two pairs of concave mirrors are inside the main spectrometer cover. At the image I_2, in the reference beam, there is a moving multiple wedge type of diaphragm, W, that rolls in and out of the optical path to change the amount of light transmitted. A separate control provided in front of the base of the instrument would enable this wedge to be moved so as to enable the operator to adjust the percentage of light transmitted thus controlling the position of the pen on the drum. After passing through the two apertures the two divergent beams are reflected by plane mirrors, M_5, M_6, and M_8, to opposite sides of a rotating sector mirror M_7. The sample beam is reflected from the sector mirror and the reference beam transmitted by it. The concave mirror M_9 is calculated to be free from astigmatism at 8° off axis and 1:1 magnification in order to avoid blurring of the image. A flat mirror M_{10}, throws the image of I_1 and I_2 on the entrance slit S_1 of the monochromator.

The two field lenses L_1 and L_2 are made of potassium bromide. They throw images of M_3 and M_4 on M_9 and also serve as windows in the monochromator cover. Pr, (Fig. 1[illegible]) is a rock salt prism mounted on removable table. This prism serves as the monochromator. The small mirror, M_{13}, behind the prism compensates the wavelength scale for change of refractive index due to temperature variation. The collimator, M_{11}, is a concave mirror 80 mm in diameter, 27 cm in focal length, parabolized 18° off axis. It is corrected to about a quarter wavelength of sodium light, giving a visual resolving power of better than 6A at the D lines with two traversals of a light flint prism. Its mounting has screw adjustments for focus and for the horizontal and vertical angle adjustment.

The Recorder

The Recorder in the Perkin-Elmer spectrohotometer is designed to have the following properties:

1. Coupling of the scanning system and recorder such that the recorder is unaffected by changes in scanning speed,
2. High reproducibility of recording,
3. Standard size sheet charts to simplify filing procedures.
4. Allowance for wide range of scanning speeds.

5. Allowance for adjusting the abscissa to spread out spectra.

6. Compact construction.

The recording drum turns upward in front so that a good length of spectrum is clearly visible to the operator immediately after it is recorded. The recording chart is held on the drum by two pairs of spring-loaded clips which clamp the ends of the paper in position. The zero transmission point recorded by the pen may be adjusted to coincide with the zero on the recorder paper by unclamping the pen from its drive cable and moving it. On the left of the recorder are located the scanning motor, scanning pulley system, and the scale change gears. The motor speed is controlled by a knob on the main control panel. Large reductions in scanning speed can be accomplished by changing (1) the pulley belts (2) the change gear and (3) by varying the PEN SPEED control. A separate wheel provided at the left side of the recorder called as the "inching wheel " permits the operator to move the scanning system a small amount without driving the system electrically.

The observations and results for Polystyrene and Columbia Resin at zero, 2 #, and 4 # load are shown below in tables 2 to 5. The tables are computed using the infrared absorption graphs at the above mentioned loads. These graphs are obtained with a Perkin-Elmer Infrared Spectrophotometer.

Results:

Table 2

Material	....	Polystyrene
Phase	....	Solid
Sample size	....	2(5/16)" x (3/4)" x 0.008"
Reference	....	" " x 0.005"

Vibrating group	frequency in microns	percentage absorbance per 0.003" thickness		
		zero psi.	333 psi.	666 psi.
C - H aromatic	3.35	29	28.5	28
C - H aliphatic	3.5	31	29	29
C - H wagging	6.85	40	39	39
C - H aromatic out of plane vibrations	13.5	13.5	13.5	12.5

Polystyrene (contd.)

Sample .... 0.008" thick

Reference .... 0.005" "

Table 3

Vibrating group	frequency in microns	percentage absorbance per 0.001" thickness		
		zero psi.	333 psi.	666 psi.
C - H aromatic	3.35	24.4	23.9	23.5
C - H aliphatic	3.5	26	24.4	24.4
C - H wagging	6.85	33.6	32.8	32.8
C - H aromatic out of plane vibrations	13.5	11.3	11.3	10.5

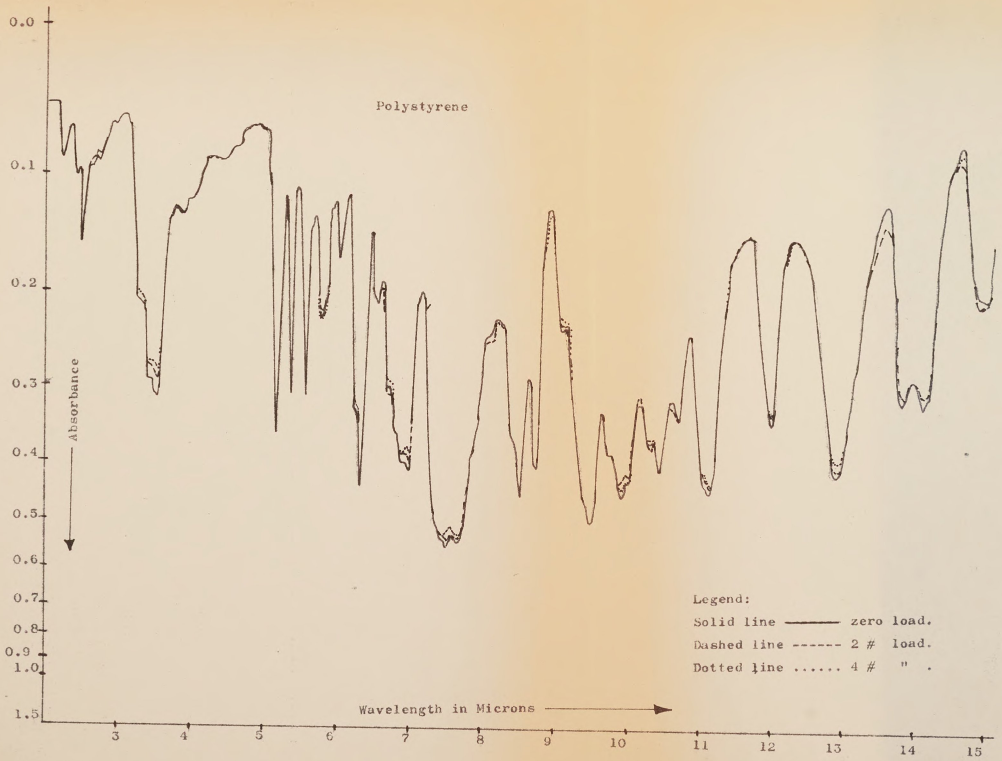

Polystyrene
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.5
Absorbance
Wavelength in Microns
3
4
5
6
7
8
9
10
11
12
13
14
15
Legend:
Solid line ——— zero load.
Dashed line ------ 2 # load.
Dotted line ...... 4 # " .

Table 4

Material	....	Columbia Resin	C R - 39.
Phase	....	Solid	
Sample	....	1(5/8)" x (3/4)" x 0.007"	
Reference	....	" " x 0.005"	

Vibrating group	frequency in microns	percentage absorbance per 0.002" thickness		
		zero psi.	380 psi.	760 psi.
O H	2.86	35	35	37
C - H aromatic	3.35	27	26	26
C - H aliphatic	3.65	30	30	30.2
C = O	5.55	43	42	42
C - O	5.9	35	39	38
C = C	6.2	45.5	45.5	48
C - C aromatic	6.4	45.5	45.5	48
C - H wagging C - C "	6.8 to 12.0	variable from 10 to 40		
C - H out of plane vibrations	12.45	27.5	30	28.5
Benzene out of plane vibrations	13.2	30	32	31.5

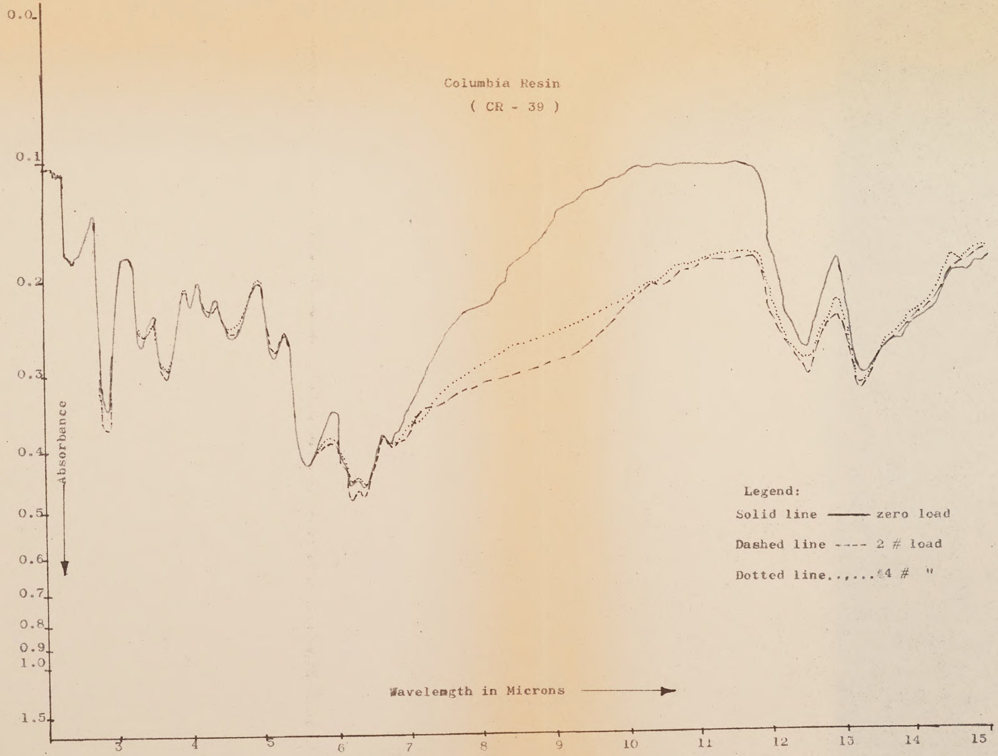
Table 5

C R - 39 (contd.)

Sample .... 0.007" thick

Reference ..... 0.005" "

Vibrating group	frequency in microns	percentage absorbance per 0.001" thickness		
		zero psi.	380 psi.	760 psi.
O H	2.86	31.5	31.5	35
C - H aromatic	3.35	24.3	23.4	23.4
C - H aliphatic	3.65	27	27	27.18
C = O	5.55	38.7	37.8	37.8
C - O	5.9	31.5	35.1	34.2
C = C	6.2	40.9	40.9	43.2
C - C aromatic	6.4	40.9	40.9	43.2
C - H wagging C - C "	6.8 to 12.0	variable from 9 to 36.		
C - H out of plane vibrations	12.45	24.8	27	25.6
Benzene out of plane vibrations	13.2	27	28.8	28.4


Columbia Resin
(CR - 39)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.5
Absorbance
Wavelength in Microns
3
4
5
6
7
8
9
10
11
12
13
14
15
Legend:
Solid line —— zero load
Dashed line ---- 2 # load
Dotted line........4 # "

Discussion of results

Polystyrene is a thermoplastic. Its chemical formula is $(C_8H_8)_n$. Fig. 16 shows a representative portion of a polystyrene chain. It consists of linear chain molecules with $CH_2 - CH$ in the chain length and the benzene ring at right angles to the length of chain. In the past literature it has been established that there are characteristic high absorptions for infrared beam for some of the vibrating groups. Thus, for example, C - H aromatic has been studied and it always seemed to have a high absorption peak due to stretching at 3.3 microns, which is called an "infrared active" vibration resulting in a change of dipole moment.

Fig. 17 shows a representative portion of a C R - 39 molecule. It consists of a benzene ring with symmetrically placed parallel chains of $\overset{O}{\overset{\|}{C}} - O - CH_2 - \overset{H}{\overset{|}{C}} = CH_2$. Its chemical name is dialyll pthallate, and is a thermosetting resin. Resin is the name given to a polymer either thermoplastic or thermoset. A thermoplastic melts on heating but a thermoset starts melting first but on continued heating it sets itself and becomes rigid with an additional characteristic of forming innumerable numer of cross-links. There are some common groups, however, between polystyrene and CR - 39, namely, C - H aromatic, C - H aliphatic, C - H wagging, and C - H in the benzene ring. The additional vibrating groups in C R - 39 are C = O, C - O, C = C, C - C. The tabular statements given on pages 58 and

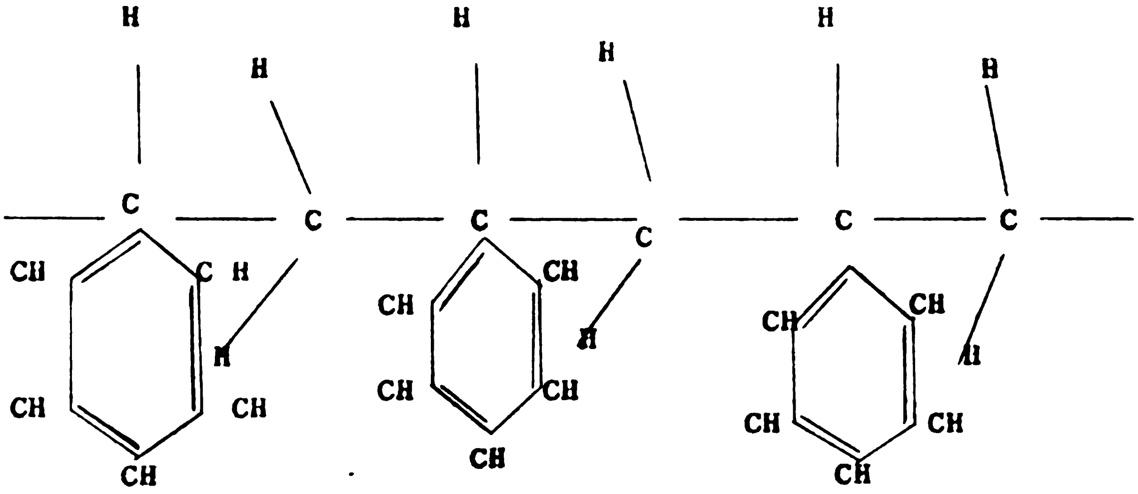


Fig. 16. Representative portion of polystyrene chain.

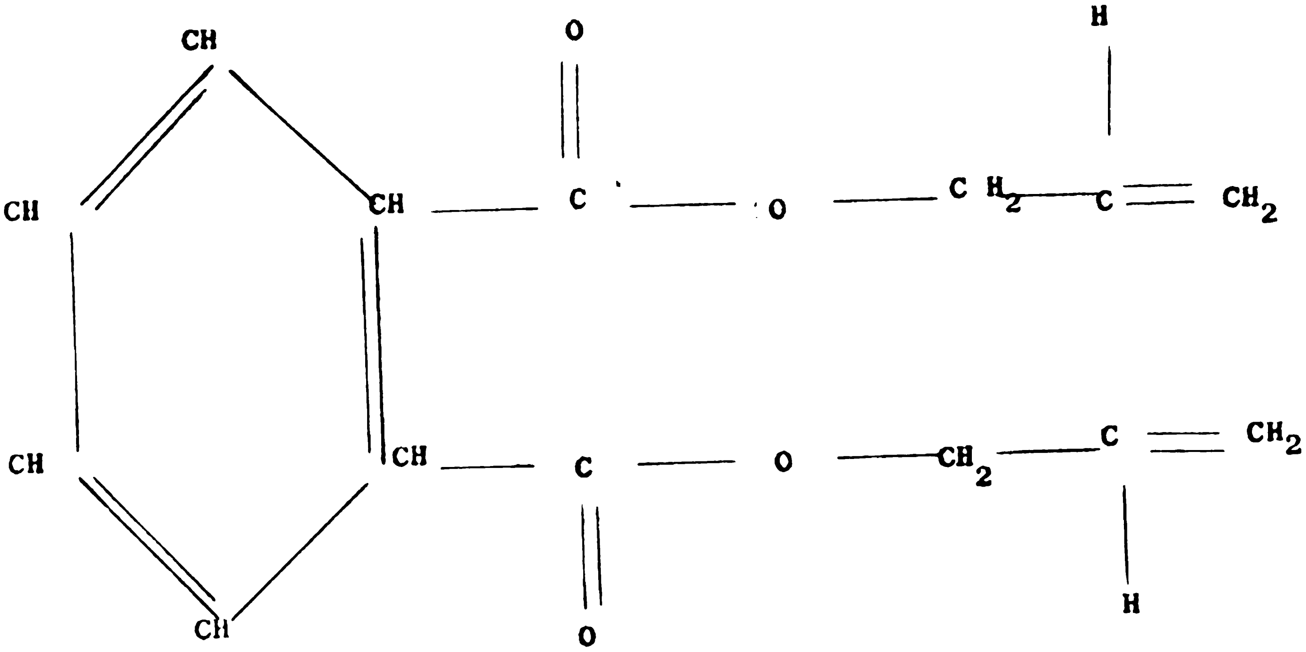


Fig. 17. Molecular structure of C R - 39.

(Dialyll Phthallate)

59 show numerically the differences in percentage absorptions of the infrared beam. C - H aromatic in polystyrene contributes an amount of 0.5 per cent towards the change in absorption at 333 psi. and 0.9 percent towards the change in absorption at 666 psi. On the other hand C - H aromatic in C R - #9 contributes an amount of 1.1 per cent towards the change in absorption at 380 psi and also at 760 psi. Considering next C - H aliphatic vibrating group it contributes 1.6 per cent to the change in absorption in polystyrene and a maximum change of 0.18 per cent at 760 psi in C R - 39. This might mean that the vibrating group C - H aliphatic undergoes greater change in dipole moment in polystyrene with consequent increase in the absorption of incident beam. However, the changes in C - H aromatic 0.9 and 1.1 in polystyrene and C R - 39, respectively, do not differ much thus leading to surmise that they do not undergo appreciable variation with stress. In other words the change in the intra-molecular activity with stress in polystyrene and C R - 39 due to the C - H aromatic group is negligible; also the change in the intra-molecular activity due to C - H aliphatic in polystyrene which is 1.6 per cent in terms of absorption might mean that any phenomenon associated with stress in polystyrene could be more due to the presence of a C - H aliphatic group.

Turning now to the C - H wagging in polystyrene we notice that there is a change in absorption of only 0.8 per cent at both 333psi and 666 psi in polystyrene, whereas there is a change in absorption of 9 to 36 per cent in the case of C R - 39. This change obviously is quite a bit and it seems that there is huge intra-molecular activity due to C - H wagging in Columbia Resin resulting in a large absorption of the incident infrared beam with increase in stress. Lastly we have the out of plane deformations of the benzene ring at about 13.5 microns. The change in percentage absorption in the case of polystyrene is zero at 333 psi and 0.8 at 666 psi. The changes in C R - 39 are 1.8 at 380 psi and 1.4 at 760 psi. Actually there is a greater absorption of the incident beam in the case of C R - 39 than in the case of polystyrene.

Besides there are other groups like C = 0, C - 0, C = C, C - C in C R - 39. The tabular statement on page 59 shows that the changes in the intensities of the incident infrared beam are not much in comparison with those of C - H wagging in C R - 39. Actually there is a decrease in absorption of 0.9 at both 380 psi and 760 psi for C = 0 and an increase in absorption of 3.6 at 380 psi and 2.7 at 760 psi for the vibrating group C - 0. The groups C = C and C - C practically contribute the same change in absorption with lead, i.e. about 2.3 per cent increase in absorption 760 psi.

Conclusion

From the previous discussion we conclude that the C - H aromatic does not contribute appreciably towards the change in absorption in polystyrene and CR - 39; and there is also a fairly greater absorption in polystyrene due to C - H aliphatic group than in CR - 39 thus leading to a surmise that stress birefringence in polystyrene might be due to the presence of a vibrating group like C - H aliphatic. However, the change in the percent absorption due to C - H wagging in the case of CR - 39 is remarkably high compared with that due to the same group in polystyrene. Taking now a look at Fig. 16 showing the structure of polystyrene and also Fig. 17 showing that of CR - 39 it seems probable that the CH aliphatic group influences the behavior of polystyrene under stress; and also the fact that the absorption of the CH aliphatic is very little (1.6 per cent) could be due to the presence of a heavy benzene ring. Presumably, if the C - H bond is stretched and released, the carbon and hydrogen atoms vibrate rapidly with a characteristic frequency and the amplitude is influenced by the presence of a heavy benzene ring close to it. But on account of the lack of such a heavy ring near the CH group in CR - 39 a greater amplitude of vibration could be possible which is revealed in the C - H wagging resulting in a greater dipole moment change and thus giving rise to relatively large absorptions of incident infrared beam for CH wagging.

Also the presence of the additional groups like C - O, C - C contribute slightly towards the absorptions with stress in CR - 39. This could be possibly due to the fact that these groups are relatively smaller compared with the benzene ring and hence could follow the vibration much better.

The discussion given in the previous pages with the concluding remarks above based on the marked difference in the infrared spectrum of CR - 39 for different loads from the spectrum of polystyrene leads one to the surmise that the high photoelastic behavior of CR - 39 compared with polystyrene could be due to 1) lack of the presence of heavy groups like benzene rather too close to other relatively small groups like CH, and 2) the presence of additional groups like C = O, C = C, C - O, C - C.

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