EFFECT OF VARIOUS SOLVENTS ON THE STRESS INDUCED BIREFRINGENCE OF PMMA.

BY

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B.ED. (SCIENCE)

A thesis submitted in partial fulfilment
for the award of the Degree of Master
of Science in Physics in the
University of Nairobi.

PHYSICS DEPARTMENT.

1987.

This thesis is my original work and has not been presented for a degree in any other University.

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This thesis has been submitted for examination with our approval as University Supervisors.

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ACKNOWLEDGEMENTS

I am greatly indebted to my major supervisor Dr. S.K. Katia who not only introduced me to Polymer Physics but also devoted a lot of time to offer constant guidance and encouragement throughout this project.

I owe a lot of gratitude to my associate supervisor, Dr. E. Maina-Ayiera for his continous guidance and suggestions in the preparation of this thesis.

I wish to extend my appreciation to Dr. Sarhene for his constructive suggestions and advice. A lot was gained from his knowledge and experience in the field of Polymer Science.

Acknowledgements are also due to the following: Mr. Muithe and staff of SEPU for the technical assistance in the preparation of my samples; Mr. Rading of Kenya Bureau of Standards for assisting in the hardness tests; Mr. Nyamai of the Department of Mines and Geology in the Ministry of Natural resources, for help with the X-ray measurements; the Mechanical engineering Department of the University of Nairobi for allowing and helping me to use their Photoelasticity laboratory and equipment and the Geology Department technical staff for their cooperation when I needed their assistance in measuring birefringence sign etc.

I am extremely grateful to the Government of Kenya for giving me the scholarship for my M.Sc. study.

Special thanks must go to Mrs. Francisca K. Osiemo who patiently typed this thesis.

Last but not least, I thank all those who directly or indirectly made this work possible more especially my parents, relatives and friends for their patience, encouragement and moral support.

THE EFFECT OF VARIOUS SOLVENTS ON THE STRESS-INDUCED BIREFRINGENCE OF POLY(METHYL METHACRYLATE)

Abstract:

The orientation and structural changes, resulting from the application of known compressive stresses in Poly(methyl methacrylate) samples conditioned in acetonitrile, n-butanol, methanol, ethylene glycol and ethanol at room temperature, have been investigated by measuring the optical double refraction or birefringence induced by the stresses. The birefringence values were obtained from the analysis of photoelastic interference fringes using a polariscope.

For samples conditioned in acetonitrile, methanol and ethanol, the stress-optical coefficient increased with duration of conditioning, although ethanol conditioning had a much smaller influence over the same period of time. The stress optical coefficient decreased with duration of conditioning in n-butanol and ethylene glycol.

These results have been explained on the basis of creation of free volume and increased chain flexibility which allow the polymer chains to assume preferred chain conformations in response to applied stress in the case of acetonitrile, methanol and ethanol conditioning. Increased rigidity as a result of desorption of residual moisture and possibly monomer units and hence increased interaction of polymer chains have been used to explain the reduction of the stress-optical sensitivity for poly(methyl methacrylate) conditioned in n-butanol and ethylene glycol.

The results also show that the refractive index and the density of the polymer decreased with duration of conditioning in all the solvents used. The molecular polarizability anisotropies calculated from the stress-optical coefficient values, show an increase with duration, for samples conditioned in acetonitrile, methanol and ethanol, while they decrease with duration of conditioning in n-butanol and ethylene glycol.

Acetonitrile which has a cohesive energy density close to that of poly(methyl methacrylate) and which is weakly hydrogen bonded showed the greatest effect.

CONTENTS

PAGE

CHAPTER 1 INTRODUCTION

CHAPTER 2 LITERATURE REVIEW

CHAPTER 3 THEORY OF BIREFRINGENCE IN POLYMERS

CHAPTER 6. ANALYSIS AND DISCUSSION OF RESULTS

APPENDICES

List of Tables

LIST OF FIGURES

LIST OF SYMBOLS

a	amplitude of light emerging from polarizer
A	amplitude of light emerging from analyzer
A	Surface area
b	constant
c	velocity of light in air or vacuum
C	stress optical coefficient
d	density
D	diameter of a circular disk
f_σ	material stress-fringe value
F	force, applied load
k	Boltzman's constant
k_2	constant
m	molecular weight
n	index of refraction
n_o	index of refraction in an unstressed medium
n_1, n_2, n_3,	index of refraction along the principal directions
$\bar{n}$	average index of refraction $\frac{1}{3}(n_3 + 2n_1)$
N	fringe order

N_A	Avogadro's number
r_o	unperturbed chain end to end distance
r	actual chain end to end distance
R	radius of a circular disk
s	degreee of swelling
t	thickness
T	absolute temperature
T_g	glass transition temperature
v	velocity of light in a medium
v_i	molar volume
w	equilibrium weight after drying samples
w_s	swollen weight
α	expansion coefficient
$\bar{\alpha}_e$	electronic polarizability
$\alpha, \beta, \theta, \rho, \phi$	angles
β	Polarizability per unit volume
$\beta_1, \beta_2, \beta_3$	Principal polarizabilities
δ	relative retardation

δ	solubility parameter
δ_1	solvent solubility parameter
δ_2	polymer solubility parameter
Δ	birefringence
$\lvert\Delta\rvert$	absolute birefringence
ΔE^V_i	solvent molar energy of vaporization
E	deformation
ε_{jk}	componets of deformation
ε_{11}	Polymer chemical potential
ε_{22}	solvent chemical potential
ε_{12}	polymer-solvent chemical potential
λ	wavelength
σ	Stress
σ_{jk}	cartesian components of stress
$\sigma_1, \sigma_2, \sigma_3$	principal normal stresses

σ_x , σ_y, σ_2	normal stress components in cartesian coordinates
τ_{12} , τ_{xy}	shear stress

CHAPTER 1

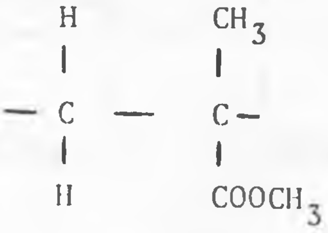
INTRODUCTION

Polymer solids are of immense technological importance and wide scientific interest because of their numerous applications in industry and their variety of forms ranging from amorphous to crystalline. They also exhibit fine textures consisting of complex combinations of crystalline and amorphous forms giving rise to multi-phase systems. These fine textures and the complicated architecture of the atomic arrangements play a dominant part in controlling the physical and chemical properties of these solids.

Crystalline polymers have high densities and refractive indices. They are generally transluscent although their clarity can be improved by quenching or by random copolymerization. Amorphous polymers do not have enough chemical regularity and so do not crystallize appreciably when cooled from the molten state. Polymers that are amorphous at room temperature and contain no discrete particles of any form are highly transparent to visible light. These form polymeric glasses. Examples of these materials are poly(methyl methacrylate), polycarbonate, atactic polystyrene and cellulose acetate butyrate. These polymeric glassy materials are widely used because of their good optical transparency, and this study seeks to investigate the stress-optical behaviour of PMMA after conditioning it in various solvents.

1.1.0 Poly(methyl methacrylate)

Poly(methyl methacrylate) is an amorphous linear polymer which relies on its high transparency and favourable mechanical properties for its utility. Unlike the fragile, easily broken inorganic glasses, poly(methyl methacrylate) has a good degree of toughness. Some of the numerous important applications of PMMA are in outdoor advertising, display demonstration models, edge lighted signs and air-craft windows The polymer is fundamentally composed of the monomer units.

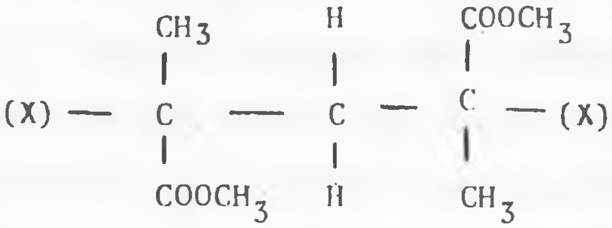


$$-\underset{\displaystyle \mathrm{H}}{\overset{\displaystyle \mathrm{H}}{\underset{|}{\overset{|}{\mathrm{C}}}}}-\underset{\displaystyle \mathrm{COOCH_3}}{\overset{\displaystyle \mathrm{CH_3}}{\underset{|}{\overset{|}{\mathrm{C}}}}}-$$

Fig. 1.

Because of the $COOCH_3$ group, the polymer is polar. Pure form of PMMA transmits extensively in the ultraviolet range. Commercial grades are usually supplied with an added ultra-violet radiation absorber {1}. The polymer has a solubility parameter of 18.6-19.4 $(J/cm^3)^{\frac{1}{2}}$ {2}. Being polar PMMA is likely to be affected in its physical properties by some polar solvents.

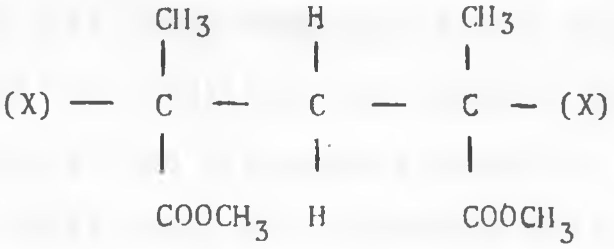
Apart from the amorphous form of poly(methyl methacrylate), stereoregular forms exist. These are the isotactic and the syndiotactic PMMA. The syndiotactic PMMA has the following configuration



$$\begin{array}{ccccccccc} & & CH_3 & & H & & COOCH_3 & & \\ & & | & & | & & | & & \\ (X) & — & C & — & C & — & C & — & (X) \\ & & | & & | & & | & & \\ & & COOCH_3 & & H & & CH_3 & & \end{array}$$

Fig. 2

and the isotactic PMMA has the form



$$\begin{array}{ccccccccc} & & CH_3 & & H & & CH_3 & & \\ & & | & & | & & | & & \\ (X) & — & C & — & C & — & C & — & (X) \\ & & | & & | & & | & & \\ & & COOCH_3 & & H & & COOCH_3 & & \end{array}$$

Fig. 3.

These stereoregular forms of PMMA which can be prepared using stereospecific catalysts {3} are able to crystallize.

Crystalline PMMA is harder than the amorphous one. It has high density, low solubility and high refractive index {4}. Stereoregular poly(methyl methacrylate) such as the isotactic one has a melting point of 160°C, while the syndiotactic type has a melting point greater than 200°C {5}. In this study non-crystalline transparent PMMA was used because of its impact strength and excellent glassy properties.

1.2.0 Present work.

Most transparent non-crystalline materials become doubly refracting (birefringent) when stressed with the line of stress corresponding to the optical axis of a natural doubly refracting crystal. This stress normally persists while the loads are maintained but vanishes when they are removed, either instantaneously or after some interval of time depending on the material and the conditions of loading. In particular, non-crystalline transparent materials such as rubbers and glasses which are ordinarily optically isotropic show birefringence when stressed, which is an indicator of the structural dissymmetry induced by the stress.

Birefringence studies of polymers have been extensively persued because of reasons ranging from getting information about the shapes of molecules to the determination of the structural behaviour when the polymer is subjected to physical factors like temperature.

Polymeric solids depend on their rigidity for utility in varying environments. Knowledge on the changes of their physical properties in the utility environment is very necessary for design purposes. Although the influence of water on methacrylate polymer properties has been widely investigated {6, 7, 8} little work has been done on the influence of other solvents on the stress-optical properties of poly(methyl methacrylate). The commercial use of poly(methyl methacrylate) as an acrylic thermoplastic glassy polymer used mainly for outdoor activities makes the polymer come in contact with many more physical and environmental factors such as temperature, humidity, atmospheric contaminants and industrial chemicals which may have adverse effects on the polymer.

In this study an attempt is made to investigate the effect of solvents on the stress induced birefringence of PMMA. The work will involve the measurement of stress birefringence in solvent conditioned samples of PMMA. The study is expected to provide information on the deformational process of the polymer as a function of external mechanical stresses and how this is influenced by solvents; hence leading to a better understanding of the molecular process which controls the response of the polymer to mechanical and environmental stresses. The study will also focus on the influence of various solvents conditioning on the manner and degree of orientation of the PMMA used in this study in response to stress, and how the solvents influence the correlation between mechanical and optical properties in terms of the stress-optical law. (see section 3.3.0).

This study also attempts to investigate the effect of the solvents on the density and refractive index of PMMA. The refractive index, being a fundamental property of transparent materials, is a very important property to a design engineer involved in designing lenses, cameras, microscopes and other optical equipment. It would therefore be important in this study to determine how the solvents influence this property.

In Chapter 2, a review of previous work related to this study will be given. A theory of birefringence in polymers is presented in chapter 3, while Chapter 4 deals with the experimental procedures and techniques used in the study. The mechanical and structural properties of the PMMA used, obtained from characterization tests, experimental results obtained from photoelastic measurements and refractive index measurements for different solvent conditioned PMMA samples, are presented in chapter 5. Chapter 6 deals with the analysis of data and discussion of the results.

CHAPTER 2

LITERATURE REVIEW

2.1.0 Introduction

Birefringence has many uses in the study of polymers. Streaming birefringence gives information about the shape of molecules in solution while the disappearance of birefringence in crystalline polymers marks the crystalline melting point. Birefringence also reflects the extent of molecular orientation in polymers and in amorphous polymers it indicates the presence of stresses.

Molecular orientation is known to have an important effect on the mechanical properties of polymeric materials {9}. It has been the desire of researchers to determine molecular orientation in filaments and fibres. Since molecular orientation produces optical anisotropy, birefringence measurement have been used as reported by Andrews {10} to measure the extent of orientation in polystyrene monofilaments. Many birefringence studies have concentrated on property behaviour of polymers as a function of temperature and plasticizers {11}. Andrews and Kazama {12} studied the birefringence effects of PVC as a function of stress, temperature and plasticizer content; using dioctyl phthalate, dioctyl adipate and tricresyl phosphate as plasticizers. They noted that the stress optical coefficient increased with plasticizer content and the orientation birefringence increased with temperature.

2.1.1 Previous work on Poly(methyl methacrylate).

Several studies on the influence of various physical factors on the Photoelastic and mechanical properties of poly(methyl methacrylate) and related thermoplastic polymers have been reported in several references. Kolsky and shearman {13} studied the orientation and structural effects of poly(methyl methacrylate) by applying known stresses and also studied the effect of temperature on the birefringence of poly(methyl methacrylate) under a constant load. They showed that the stress optical coefficient of PMMA at room temperature was negative and its birefringence under constant load increased with temperature. These effects observed on PMMA were attributed to the behaviour of the strongly polar carbo-methoxy groups on heating and stretching the sample. Robbinson,Rugy and Slantz {14} in 1944 showed that the stress optical coefficient for PMMA varied markedly with temperature showing a maximum of -45 Brewsters at 93^{o}C as compared to -3.8 Brewsters at

27^{o}C. A study by Tsvetkov and Petrova {15} on poly(methyl methacrylate) using acetone, ethylacetate, chloroform, dichloroethane, benzene, chlorobenzene and bromoform as solvents showed that the sign of streaming birefringence of PMMA in solution in these solvents was positive and that the streaming birefringence is a parabolic function of the refractive index of the solvent and has a minimum value when the solvent has the same refractive index as the polymer. The effect of plasticisers on the photoelastic properties of PMMA in the glassy state, reported by Lamble and Dahmouch {16 } showed that, the stress-optical coefficient for PMMA changed from -4.55 Brewsters for unplasticised polymer to +4.4 Brewsters for polymer plasticised with 20% dibutyl phthalate. Another plasticiser, polyethylene glycol when used in the same proportion by weight as for dibutyl phthalate had a much smaller influence on the stress optical coefficient. Jenkel and Hesch {17 } have reported on the effects of solvents and plasticisers on the glass transition in polystyrene and PMMA, determined by measuring the change of refractive index. The results for PMMA showed a lower value of T_g 84.5^{o}C as compared to the normal value of 105^{o}C. The PMMA used was also an industrial sample as the one used in this study. The effect of water concentration on the mechanical and rheo-optical properties of PMMA reported by Moore and Flick {18} showed from birefringence measurements, a strong enhancement of orientation at short times when the response was in terms of reduced variables for PMMA samples with higher water content (2.2%).

In the present study, poly(methyl methacrylate) was especially chosen because of its widespread utility as a thermoplastic glass, used both for its excellent optical and mechanical properties. The lack of information concerning the effect of various solvents on the stress-optical properties of the polymer also motivated the choice.

CHAPTER 3

THEORY OF BIREFRINGENCE IN POLYMERS

3.1.0 Introduction

In Chapter 1, it was noted that polymers could be crystalline, semi-crystalline or amorphous. The exhibition of birefringence by amorphous polymers when stressed was introduced in section 1.2.0. Since birefringence is very useful in the study of structural changes in polymers, several theories have been developed. The theory of birefringence of amorphous polymers was first worked out by Kuhn and Grun {19} and later set out in detail for rubbers by Treloar {20}. Gurnee {21} gave a theoretical discussion of birefringence of linear amorphous polymers with emphasis on polystyrene. Stein {22} and other workers have put forward models for birefringence of semi-crystalline polymers. In this chapter the theory of birefringence of amorphous polymers will be outlined. Photoelasticity as a way of measuring birefringence is discussed with a detailed account of the use of circular geometries to determine photoelastic parameters.

3.2.0 Birefringence of Amorphous Polymers

The optical properties of any material can be described if the three refractive indices n_1, n_2, n_3

measured along three mutually perpendicular axes in the medium are known. When the three indices of refraction are equal, the medium is optically isotropic. For an optically anisotropic medium, the refractive indices n_1, n_2, n_3 are such that either $n_1 \neq n_2 \neq n_3$ or there is at least one pair of these indices which is not equal.

Birefringence Δ for an optically anisotropic medium is defined as the difference between any two refractive indices {23} (see Fig. 4). Optical anisotropy in small molecules and in repeating units of higher polymers is caused by the electric field associated with the light striking the medium. The electric field distorts the electron clouds and induces a dipole moment. The moment of the induced dipole is proportional to the electric field and the ratio of the induced dipole moment to the field strength is a measure of the molecular polarizability of the medium.

In an optically anisotropic medium, the optical properties are respresented by the refractive index ellipsoid {24}; the principal axes of which represent the three principal refractive indices

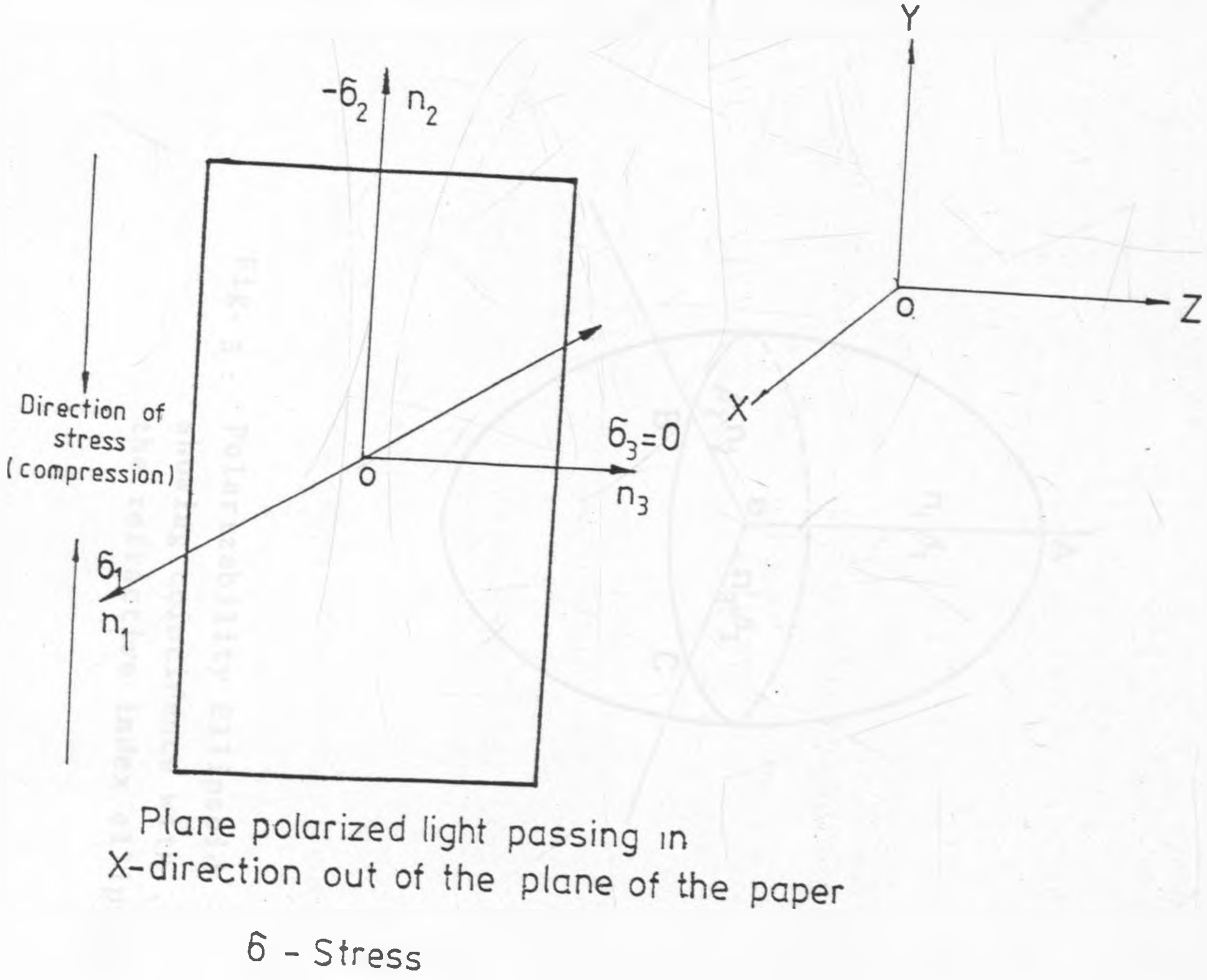


Fig. 4. Diagram illustrating the defination of birefringence in compression, $\Delta = n_2 - n_1 = C(-\sigma_2 - \sigma_1)$.

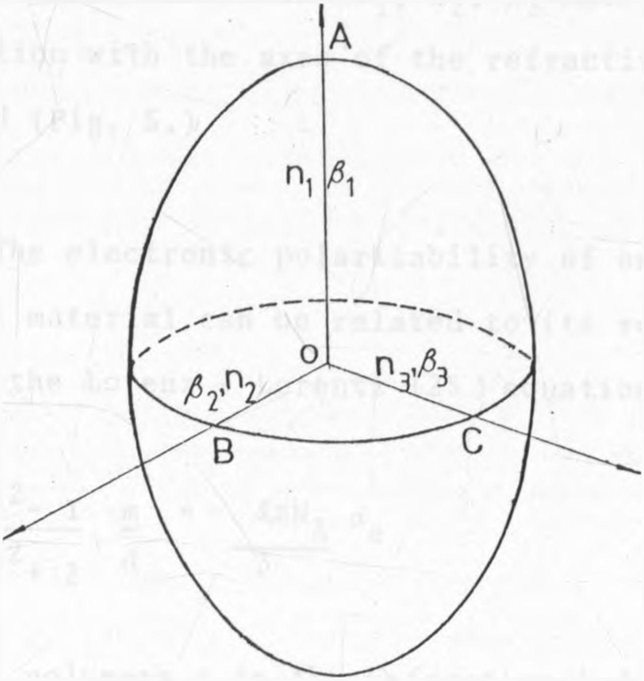


Fig. 5 . Polarizability Fllipsoid showing coincidence with the refractive index ellipsoid.

n_1, n_2, and n_3 in mutually perpendicular directions. This in turn is related to the polarizability ellipsoid whose axes correspond to the three principal polarizabilities β_1, β_2, β_3 and coincide in direction with the axes of the refractive index ellipsoid (Fig. 5.)

The electronic polarizability of an optically isotropic material can be related to its refractive index by the Lorenz - Lorentz {25} equation

$$\frac{n^2-1}{n^2+2}\ \frac{m}{d} = \frac{4\Pi N_A}{3}\alpha_e \qquad \ldots(1)$$

where in polymers n is the refractive index of the polymer, m is the molecular weight of a monomer unit, N_A is the Avogadro's number and d is the density of polymer. If a polymer is composed of monomer units that are optically anisotropic, for example, where the electronic polarizability of a unit monomer in the x-direction, α_1, is not identical with the electronic polarizability α_3 in the z-direction then the Lorentz-Lorenz equation (1) can be re-written as

$$\left[\frac{n_3^2 - 1}{n_3^2 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2}\right]\frac{m}{d} = \frac{4\pi N_A(\alpha_3 - \alpha_1)}{3} \qquad \ldots(2)$$

where n_3 and n_1 are the refractive indices in the z and x - directions respectively. Similarly an equation of type (2) would be obtained if α_2 in the y- direction was considered. For small values of birefringence we make use of the approximation

$$\frac{n_3^2 - 1}{n_3^2 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2} \approx \frac{6\bar{n}(n_3 - n_1)}{(\bar{n}^2 + 2)^2} \qquad \ldots(3)$$

where $\bar{n}$ is the arithmetic average of n_3 and n_1 given by

$$\bar{n} = \frac{1}{3}(n_3 + 2n_1) \qquad \ldots(4)$$

By combining equations (2) and (3) we obtain the relationship between birefringence and polarization anisotropy as

$$\Delta = n_3 - n_1 = \frac{2\pi}{9}\,\frac{N_A d}{m}\,\frac{(\bar{n}^2 + 2)^2}{\bar{n}}\,(\alpha_3 - \alpha_1) \qquad \ldots(5)$$

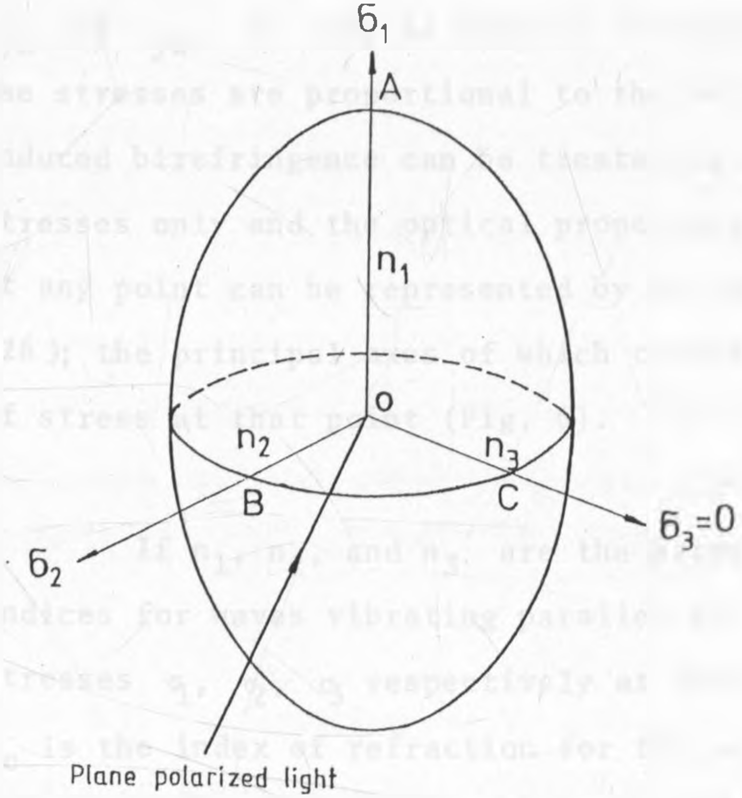


Fig. 6. Index ellipsoid for a point in a biaxial stress field.

3.3.0 Stress Optic Law

In a birefringent crystal the orientation of the principal axes and the respective refractivities change under stress. The stresses σ and deformations ε change the refractivity; the changes being linear functions of σ_{jk} and ε_{jk}. As long as Hooke's law applies, i.e. where the stresses are proportional to the deformations, the induced birefringence can be treated as a function of the stresses only and the optical properties of the material at any point can be represented by an index ellipsoid {26}; the principal axes of which coincide with the axes of stress at that point (Fig. 6).

If n_1, n_2, and n_3 are the principal refractive indices for waves vibrating parallel to the principal stresses σ_1, σ_2, σ_3 respectively at any point and if n_o is the index of refraction for the unstressed material, then according to Maxwell {27} the principal refractive indices are related to the principal stresses as

$$(n_1 - n_o) = a\sigma_1 + b(\sigma_2 + \sigma_3) \quad \ldots(a)$$

$$(n_2 - n_o) = a\sigma_2 + b(\sigma_3 + \sigma_1) \quad \ldots(b) \quad (6)$$

$$(n_3 - n_o) = a\sigma_3 + b(\sigma_1 + \sigma_2) \quad \ldots(c)$$

in which a and b are constants depending on the material. The stress birefringence is given by

$$n_1 - n_2 = a(\sigma_1 - \sigma_2) - b(\sigma_1 - \sigma_2)$$

$$\text{or } n_1 - n_2 = (a-b)(\sigma_1 - \sigma_2)$$

$$\text{or } n_1 - n_2 = C(\sigma_1 - \sigma_2) \qquad \ldots(a)$$

where $C=a-b$.

similarly

$$n_1 - n_3 = C(\sigma_1 - \sigma_3) \qquad \ldots(b) \quad (7)$$

$$\text{and } n_2 - n_3 = C(\sigma_2 - \sigma_3) \qquad \ldots(c)$$

In general, the sample investigated is a thin sheet with $\sigma_3 = 0$ so that the stress induced birefringence becomes

$$\Delta = C(\sigma_1 - \sigma_2) \qquad \ldots (8)$$

where C is the relative stress optical coefficient. C, which is a strain-independent parameter is given by

$$C = \frac{2\pi}{45kT} \frac{(\bar{n}^2 + 2)^2}{\bar{n}} (\alpha_1 - \alpha_2) \qquad \ldots (9)$$

where k is the Boltzman's constant, T is the absolute temperature, $\bar{n}$ is the average refractive index given by equation (4) and α_1 and α_2 are electronic polarizabilities in x and y directions.

3.4.0 Methods of measuring stress birefringence

The photoelastic effect of a material provides a useful method of measuring the birefringence of transparent materials such as PMMA {28} . This is the property where some transparent solids become doubly refracting (birefringent) when subjected to stress. The induced birefringence can be measured using a photoelastic polariscope. The polarising microscope used with compensators such as the Berek type provides an alternative method for determining quantitatively any induced birefringence or orientation in transparent polymers. A hot stage polarising microscope {29} combined with a compensator may be used to measure any changes of birefringence in semi-crystalline polymers.

In this study the photoelastic method using a 'Sharples' diffuse polariscope was used to determine the stress induced birefringence of PMMA conditioned in different solvents.

3.4.1 Photoelasticity

Fig. 7 shows a light source emitting random trains of waves containing vibrations in all possible planes. On introducing a polarizing filter P only one

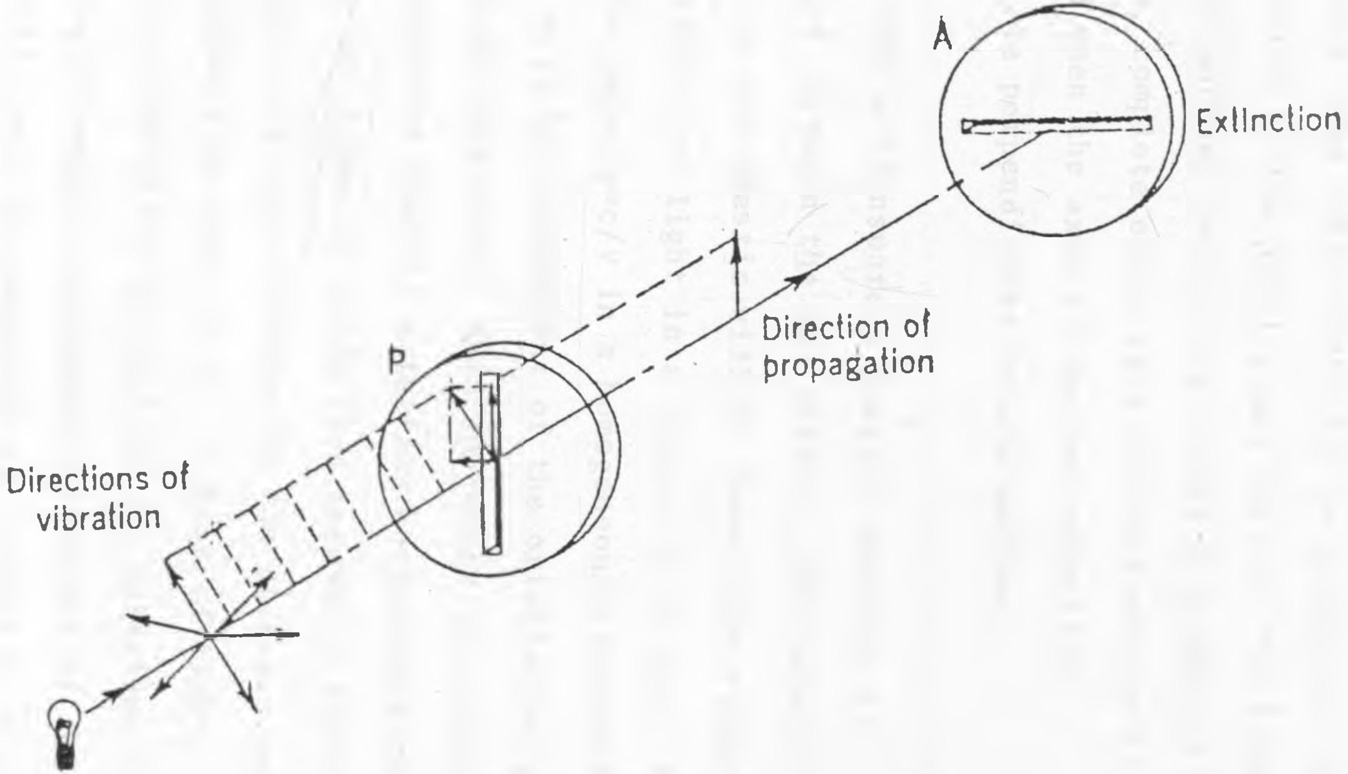


Fig. 7: Action of crossed polarizers on unpolarized light.

component of the vibrations will be permitted (the one parallel to the priviledged axis of the filter [30]. If another polarizing filter A is placed in the beam, complete extinction of the beam can be obtained when the axes of the two polarizing filters are perpendicular to one another.

When a transparent plastic material is introduced between the two filters, the velocity v of light in the plastic will be lower than either the velocity c of light in a vacuum or in air. The refractive index n=c/v in a homogeneous isotropic material will be independent of the orientation of the plane of vibration. When subjected to stress most transparent plastic materials become heterogeneous, hence the index of refraction becomes a function of the magnitude and direction of the stresses applied (see equation 8 in chap. 3.3). A beam of light polarized in the plane defined by the polarizer P and propagating through a transparent material of thickness t, will cross the material at a point O (Fig. 8) where the principal stresses σ_1, σ_2 and σ_3 are oriented along x, y, and z directions respectively. This light will split into two independent components vibrating in the directions of the principal stresses x and y and travelling through the material with different velocities v_1 and v_2. Emerging from the plastic material, one of the two waves will be retarded with respect to the other one. The extent of the relative retardation depends on the degree of birefringence at the point O; which in turn depends upon the magnitude of the two principal stresses at the point. The relative retardation δ is given by

$$\delta = t(n_1 - n_2) \qquad \ldots(10)$$

where t is the thickness, n_1 and n_2 are the principal refractive indices in x and y directions respectively.

If n_o represents the index of refraction of the unstressed material, the photoelastic effect can be expressed as function of stresses σ_1, σ_2 and σ_3 as shown in equation 6(a-c).

3.4.2 Principle of the Polariscope

The Polariscope is an instrument used to measure the relative retardations or phase differences when polarized light passes through a stressed transparent material.

3.4.2.1 Plane Polariscope

The plane polariscope used to determine stress directions consists of a light source and two

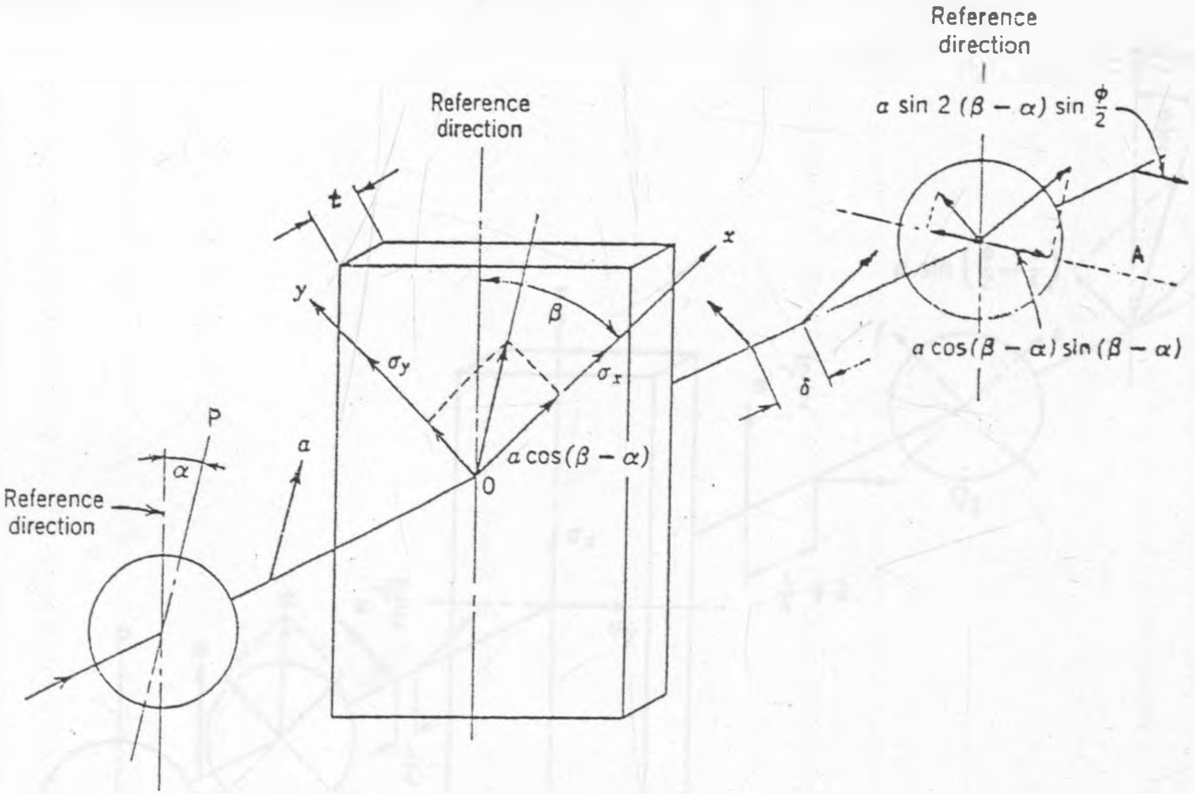


Fig. 8. Principle of a plane polariscope: P, plane of axis of polarizer; α, angle between polarizer and reference direction; a, amplitude of light polarized in plane P; t, thickness of sample containing stresses σ_x and σ_y in the x and y directions; β, angle between principal direction x and reference direction; δ, relative retardation of Y with respect to X wave; A, plane of axis of analyzer.

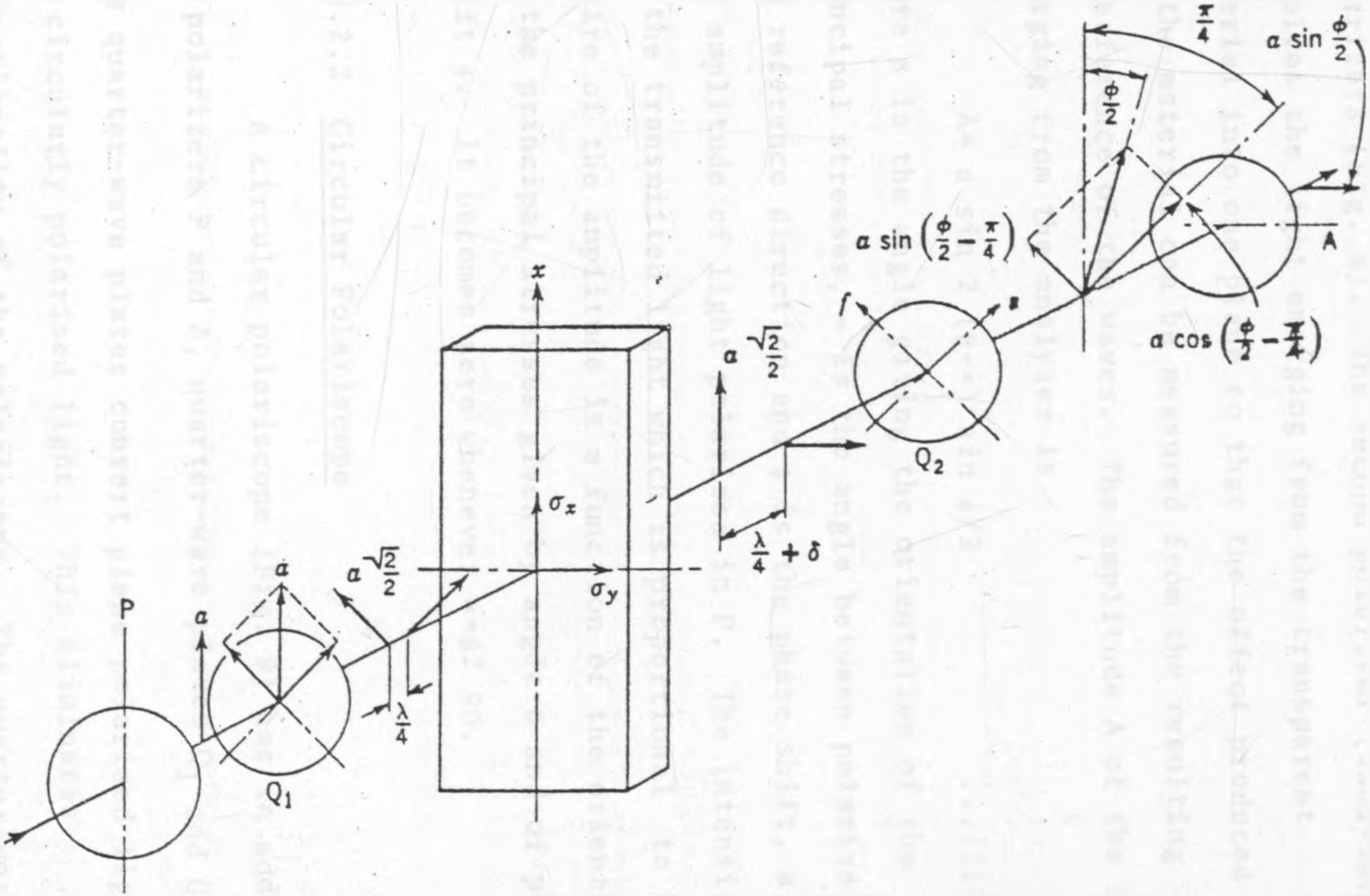


Fig. 9. Principle of a circular polariscope. Q_1 and Q_2 are quarter-wave plates; λ is wavelength; f and s are axes of quarter-wave plate Q. Other symbols are as in Figure 5.

polarizers (Fig. 8). The second polarizer (analyser) resolves the light emerging from the transparent material into one plane so that the effect produced by the material can be measured from the resulting interference of the waves. The amplitude A of the light emerging from the analyser is

$$A = a \sin 2(\beta - \alpha) \sin \phi/2 \qquad \ldots(11)$$

where β is the angle giving the orientation of the principal stresses, α is the angle between polarizer and reference direction and ϕ is the phase shift, a is the amplitude of light polarized in P. The intensity of the transmitted light which is proportional to the square of the amplitude is a function of the orientation of the principal stresses given by angle β and of phase shift ϕ. It becomes zero whenever $\alpha = \beta \pm 90$.

3.4.2.2 Circular Polariscope

A circular polariscope (Fig. 9) has in addition to polarizers P and A, quarter-wave plates Q_1 and Q_2. The quarter-wave plates convert plane polarised light to circularly polarised light. This eliminates directionality of the polariscope. The quarter-wave plates are thin retardation plates of uniform thickness which are stressed uniformly such that they exhibit a constant retardation

$$\delta = \lambda/4 \qquad \ldots(12)$$

where λ is the wavelength of incident light. As a result of stresses in the plastic material, the plane of polarization of light passing through the polariscope is rotated by an angle $\delta = \phi/2$, regardless of the direction of the principal stresses. If the analyzer remains perpendicular to the polarizer in a crossed arrangement, the amplitude of the light emerging from the analyzer is given by

$$A = a \sin \phi/2 \qquad \ldots(13)$$

where a is the amplitude of light polarized in the plane of the polarizer. The intensity will be proportional to the square of the amplitude A. When the analyzer is rotated in its own plane, the amplitude A is given by

$$A = a \sin (\phi_{/2} - \rho) \qquad \ldots(14)$$

where ρ represents the angular rotation of the analyzer; ϕ is phase shift and a is the amplitude of light polarised in P.

3.4.2.3 Material Fringe Value f_σ (fringe-stress coefficient).

In the circular polariscope, the amplitude A of the light emerging from the analyzer is described by equation (13), for the case of the analyzer perpendicular to the polarizer and by equation (14) for the case of analyzer rotated through angle ρ. The light intensity is independent of angle β. In the crossed arrangement, the light intensity becomes zero when $\phi/2 = N\Pi$, $N = 0, 1, 2,$ or when

$$\delta = \frac{\phi\lambda}{2\Pi} = N\lambda \qquad \ldots(15)$$

where N is a whole number, and λ is the wavelength of incident light. When the analyzer is rotated from its crossed position, the intensity is zero

when $\delta = (N + \rho/\Pi)\lambda \qquad \ldots(16)$

where ρ/Π is a fraction of an order.

If monochromatic light is used in a crossed polariscope, fringes of constant orders $N = 0, 1, 2, \ldots$ are observed When the analyzer is rotated through 90°, the isochromatic fringes are shifted to new positions where the relative retardation δ is given by

$$\delta = (N + \tfrac{1}{2})\,\lambda \qquad \ldots(17)$$

These are the half-order fringes. The relationship between the retardation and stress gives

$$\sigma_1 - \sigma_2 = \frac{\delta}{tC} = \frac{N\lambda}{tC} = \frac{Nf_\sigma}{t} \qquad \ldots(18)$$

where t is the thickness of the material, C is the stress optical coefficient and $f_\sigma = \lambda/C$ called the material fringe value is a property for the material for a given wavelength of light which represents the principal stress difference necessary to produce unit change in the fringe order in a material of unit thickness.

3.4.3 The circular disk

The circular disk subjected to stress is one of the geometrical forms which can be used to measure induced birefringence and other photoelastic parameters like the stress optical coefficient.

3.4.3.1. Stresses in a circular disk

The state of stress in a circular disk subjected to concentrated diametrical loads {31} F (Fig. 10) is given by

$$\sigma_x = \sigma_1 = \frac{-2F}{\pi t}\left[\frac{(R-y)x^2}{r_1^4} + \frac{(R+y)x^2}{r_2^4} - \frac{1}{D}\right] \quad \ldots(a)$$

$$\sigma_y = \sigma_2 = \frac{-2F}{\pi t}\left[\frac{(R-y)^3}{r_1^4} + \frac{(R+y)^3}{r_2^4} - \frac{1}{D}\right] \quad \ldots(b) \quad 19$$

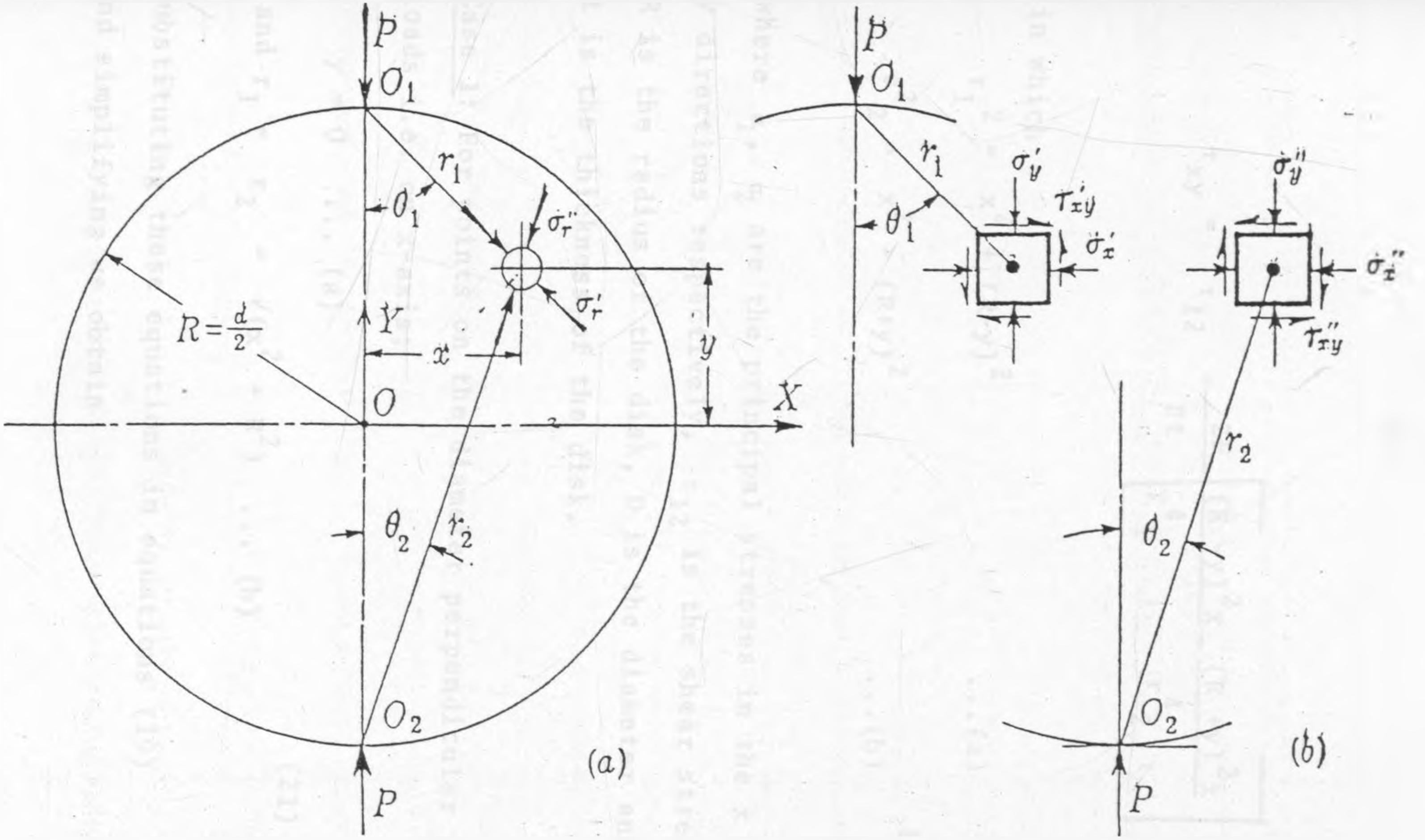


Fig. 10. Sketches showing notation for rectangular stress components in a disk under the action of two diametrically opposite concentrated loads.

$$\tau_{xy} = \tau_{12} = \frac{2F}{\pi t}\left[\frac{(R-y)^2 x}{r_1^4} - \frac{(R+y)^2 x}{r_2^4}\right] \quad \ldots(c)$$

in which

$$r_1^2 = x^2 + (R-y)^2 \quad \ldots(a)$$

$$(20)$$

$$r_2^2 = x^2 + (R+y)^2 \quad \ldots(b)$$

where σ_1, σ_2 are the principal stresses in the x and y directions respectively, τ_{12} is the shear stress, R is the radius of the disk, D is the diameter and t is the thickness of the disk.

Case 1: For points on the diameter perpendicular to the loads i.e. on x-axis;

$$y = 0 \quad \ldots(a)$$

$$(21)$$

$$\text{and } r_1 = r_2 = \sqrt{(x^2 + R^2)} \quad \ldots(b)$$

substituting these equations in equations (19) and simplifying we obtain

$$\sigma_x = \sigma_1 = \frac{-2F}{\pi tD}\left[\frac{16D^2x^2}{(D^2+4x^2)^2} - 1\right]$$

$$= \frac{2F}{\pi tD}\left[\frac{D^2-4x^2}{D^2+4x^2}\right]^2 \qquad \ldots (a)$$

$$\sigma_y = \sigma_2 = \frac{-2F}{\pi tD}\left[\frac{4D^4}{(D^2+4x^2)^2} - 1\right] \ldots (b) \qquad (22)$$

$$\tau_{xy} = \tau_{12} = 0 \qquad \ldots (c)$$

where all parameters are defined as in (19)

Case 2: For points on the Y-axis (Fig. 10)

where $x = 0$ ... (a)

$r_1 = R-y$ ... (b) (23)

and $r_2 = R + y$, ... (c)

We have

$$\sigma_x = \sigma_1 = \frac{2F}{\pi tD} \qquad \ldots (a)$$

(24)

$$\sigma_y = \sigma_2 = \frac{-2F}{\pi t}\left[\frac{2}{D-2y} + \frac{2}{D+2y} - \frac{1}{D}\right] \ldots (b)$$

$$\tau_{xy} = \tau_{12} = 0 \qquad \ldots(c)$$

The negative sign on the principal stress σ_2 shows that σ_2 is compressive while the principal stress in the x - direction is tensile.

The material fringe value f_σ defined in section 3.4.2.3 is given by

$$f_\sigma = \lambda / C \qquad \ldots(25)$$

where λ is the wavelength of incident light and C is the stress optical coefficient. The difference in the principal stresses σ_2, σ_1 is

$$\sigma_2 - \sigma_1 = \sigma_y - \sigma_x = \frac{Nf_\sigma}{t} \qquad \ldots(26)$$

where N is the fringe order number and t is the material thickness.

For points on the y- axis

$$\sigma_2 - \sigma_1 = \frac{-4F}{\pi t}\left[\frac{1}{D-2y} + \frac{1}{D+2y}\right] \qquad \ldots(a)$$

Hence the load is

$$F = \pi f_\sigma N \Big/ 4\left[\frac{1}{D-2y} + \frac{1}{D+2y}\right] \qquad \ldots(b) \qquad (27)$$

For points along the x -axis, the load F is given by

$$F = \frac{\Pi f_\sigma (D^2 + 4x^2)^2 N}{8D(D^2 - 4x^2)} \qquad \ldots(28)$$

and for any general point (x, y), the load F is given by

$$F = \frac{\Pi f_\sigma t \left[(x^2 + R^2 + y^2)^2 - 4r^2y^2\right] N}{2R(R^2 - x^2 - y^2)} \qquad \ldots(29)$$

The material fringe value f_σ is obtained from a plot of load (F) against fringe order number (N). From equation 27-b, the material fringe value f_σ is evaluated using

$$f_\sigma = \frac{-4F}{\Pi N}\left[\frac{1}{D - 2y} + \frac{1}{D + 2y}\right] \qquad \ldots(30)$$

where F/N is obtained from the slopes of the load fringe order plots.

In this study, the diffused - light {32} Polariscope (see chap. 3.4.2.) was used to determine relative retardations δ in stressed PMMA circular samples. This was achieved by measuring the fringe order number at a reference point for every applied load. The method used to measure fringe orders will be discussed in detail in chapter 4.

CHAPTER 4

EXPERIMENTAL TECHNIQUES

4.1.0 Introduction

The PMMA used in this study was a commercial grade. No information concerning the preparation of the material was available and so it was necessary to carry out some analysis to characterise it. Chemical analysis was carried out to give structural information. Physical properties of the material were obtained using physical measurements. The study centred on the measurement of stress induced birefringence in samples conditioned in various solvents. The birefringence results would provide information on the deformational and orientation characteristics of the PMMA and how these characteristics are affected by the solvents. In this chapter the various experimental techniques used are given.

4.2.0 Materials

The PMMA used was a Thailand made sheet of thickness 0.5 ± 0.02 cm provided by Habattullah glass merchants in Nairobi. The solvents used in this study were mainly poor and medium solvents to PMMA. These were acetonitrile, n-butanol, methanol, ethylene glycol and ethanol. Some properties and the

TABLE 1

SOLUBILITY PARAMETERS AND HYDROGEN BONDING TENDENCY FOR SOLVENT USED

SOLVENT	*SOLUBILITY PARAMETER, $\delta(J/cm^3)^{\frac{1}{2}}$	HYDROGEN BONDING TENDENCY	MOLECULAR FORMULA
Acetonitrile	24.3	low	CH_3CN
n-Butanol	23.3	strong	$CH_3CH_2CH_2CH_2OH$
Methanol	29.6	strong	CH_3OH
Ethylene Glycol	29.0	strong	CH_2OHCH_2OH
Ethanol	26.0	strong	CH_3CH_2OH

* The square of the solubility parameter represents the cohesive energy density of a substance and for small molecules is approximately its energy of vaporization per unit volume.

respective molecular formulae of these solvents are summarised in table 1.

4.3.0 Sample preparation for characterization

4.3.1 X-Ray and Infra-red spectra samples

10.0 ± 1 gm of PMMA was dissolved in 20ml of ethyl acetate at room temperature. The solution was poured and allowed to spread on a flat glass surface. The solvent was allowed to evaporate and thin films of thickness 0.5 ± 0.02 mm were cast on the glass substrate. The films were dried in air for three weeks to ensure complete solvent evaporation. Samples for X-ray and infra-red spectra analysis were cut from these films.

4.3.2. Samples for tensile and compressive strength tests

Rectangular strips of width 1.30 ± 0.01 cm, thickness 0.5 ± 0.02 cm and gauge length 6.0 ± 0.1 cm were cut for tensile strength testing. Cylindrical pieces of PMMA of diameter 0.8 ± 0.05 cm were prepared using a lathe machine. These were used for compressive strength testing.

4.3.3. Density and Hardness Test samples

Rectangular PMMA pieces were cut out for density measurements. A circular flat piece of diameter 10.0 ± 0.05 cm was used for hardness test.

4.3.4. Refractive index measurement samples

Rectangular PMMA samples of dimensions 2.0 cm x 1 cm x 0.5 cm suitable for refractive index measurements on the Abbe' refractometer were cut out from the flat sheet.

4.3.5. Samples for Photoelastic measurements

Circular PMMA discs of diameter 4.0 ± 0.02 cm for diametrical loading were cut out from the flat sheet using a lathe machine. The cutting error was ± 0.01 cm.

4.4.0 Experimental Procedures

4.4.1. Tensile and compressive strengths

The tensile and compressive mechanical properties of the unconditioned PMMA were measured using a table Hounsfield Tensometer-model W3344.

The machine has a capacity of 20 KN. (the results are shown in tables 2 and 3).

4.4.2 X-Ray analysis

An X-ray spectrum to determine whether the PMMA used was crystalline or amorphous was run using films prepared as in section 4.3.1. The spectrum was obtained using an X-ray diffractometer Philips model operating with a current of 20mA and a voltage of 40KV(see Fig. 18)

4.4.3 I.R. analysis

An infra-red spectrum was obtained for structural analysis of the PMMA used in this study. To obtain the spectrum a thin film of PMMA was placed at the window of an Elmer-Perkin I.R. machine and a spectrum was obtained. The spectrum together with reported spectra for the polymer are given in Figs. 19 and 20 and discussed in chapter 5.

4.4.4. NMR analysis

40± 0.5 g of PMMA was dissolved in 1cm^3 of deuterated chloroform. The solution was put into an NMR tube and an NMR spectrum was run in a 60 MHZ NMR machine. The spectrum in Fig. 21 was obtained.

4.4.5 Density

The density of unconditioned PMMA was measured by measuring the volume and mass of cut samples. The measurement was done at room temperature and for several samples then an average density was obtained. The density was found to be 1.183 ± 0.0009 g/cm^3.

4.4.6 Hardness

The hardness of the unconditioned PMMA was tested using a hardness tester for plastics HT2004 at the Kenya Bureau of Standards. The Standard used was DIN 53456. The identation ball of the tester was pressed into the sample of PMMA, prepared as per section 4.3.3., by a small contact load to fix the ball. The ball was then pressed by a large test load F= 358N. The identation depth produced by the additional test load F was measured. From the depth, the identation surface area A was computed. The hardness was calculated using

$$\text{hardness} = \frac{\text{test load } F}{\text{surface } A} \qquad \ldots(31)$$

The measurements were repeated for different parts of the sample and the average result obtained is given in section 5.1.3.

4.4.7 Refractive index measurement.

There are a number of methods for measuring refractive index of polymers. The basic ones commonly used are the microscopical and the refractometric methods. The latter method was used in this study.

The refractometric method requires the use of a refractometer. The Abbe' refractometer type IT, 4T shown schematically on Fig. 11 was used. The measurement in this refractometer is carried out by placing a specimen in contact with the main prism using a drop of contacting liquid. The refractive index is determined by moving the index arm of the refractometer so that the field seen through the eyepiece is half dark. A compensator is adjusted to remove all colour from the field. The index arm is then adjusted using a vernier to coincide the dark and light portion of the field at the intersection of cross hairs. The value of the refractive index is read from sodium D lines.

In this study, the PMMA samples were placed in contact with the main prism using monobromonaphthalene of refractive index $nD^{20} = 1.64$ as

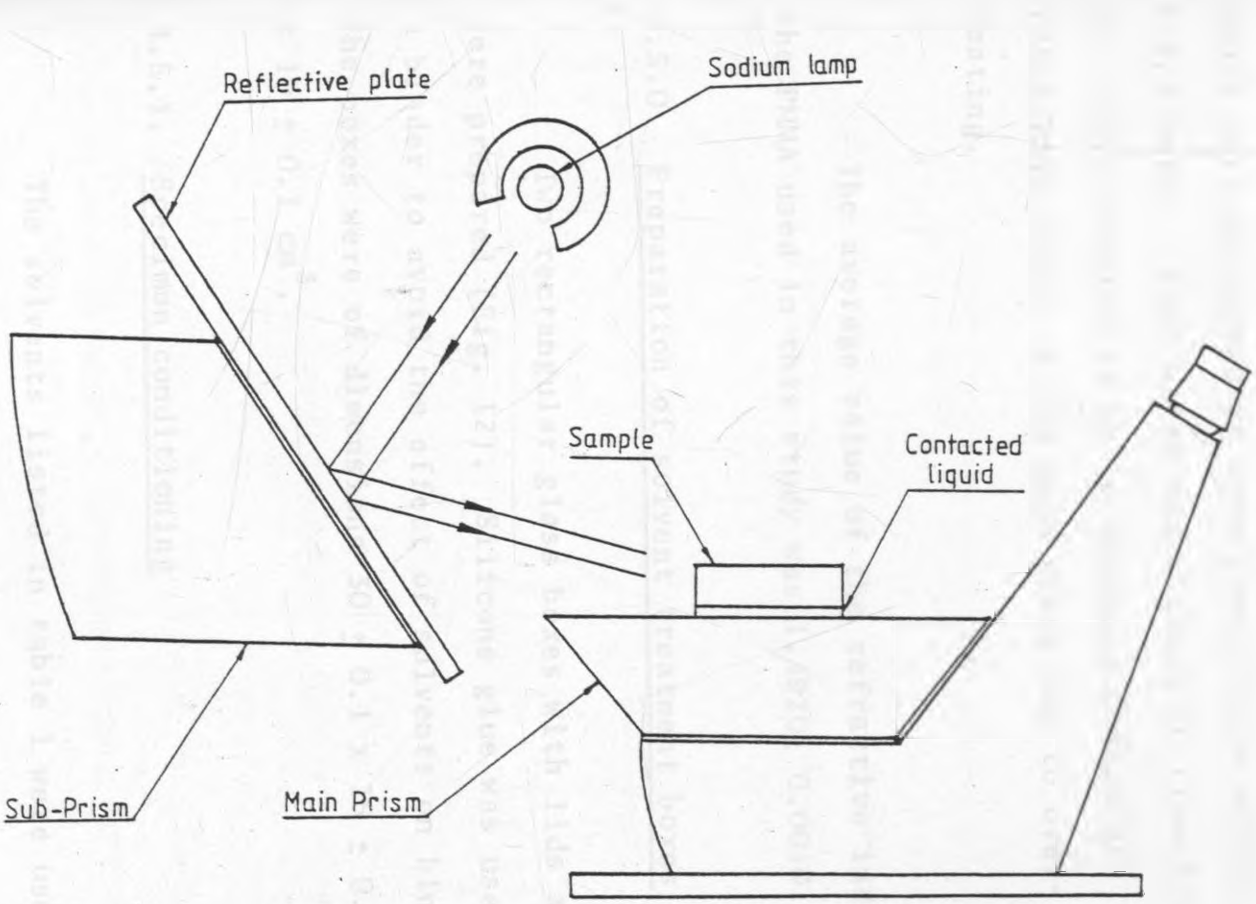


Fig. 11. The Abbe' Refractometer.

a contacting liquid. All refractive index measurements were performed at room temperature and in triplicate. Cold water was allowed to flow into the refractometer so as to minimize change of refractive index of the main prism due to overheating.

The average value of the refractive index for the PMMA used in this study was 1.4920 ± 0.0010.

4.5.0 Preparation of solvent treatment boxes

Two rectangular glass boxes with lids as covers were prepared (Fig. 12). Silicone glue was used as a binder to avoid the effect of solvents on binder. The boxes were of dimensions 30 ± 0.1 x 15 ± 0.1 x 10 ± 0.1 cm^3.

4.5.1. Specimen conditioning

The solvents listed in table 1 were used to provide the environments for conditioning the PMMA samples before birefringence measurements were performed. The samples were first weighed in air and their thickness measured using a micrometer screw gauge. Six values of the thickness were

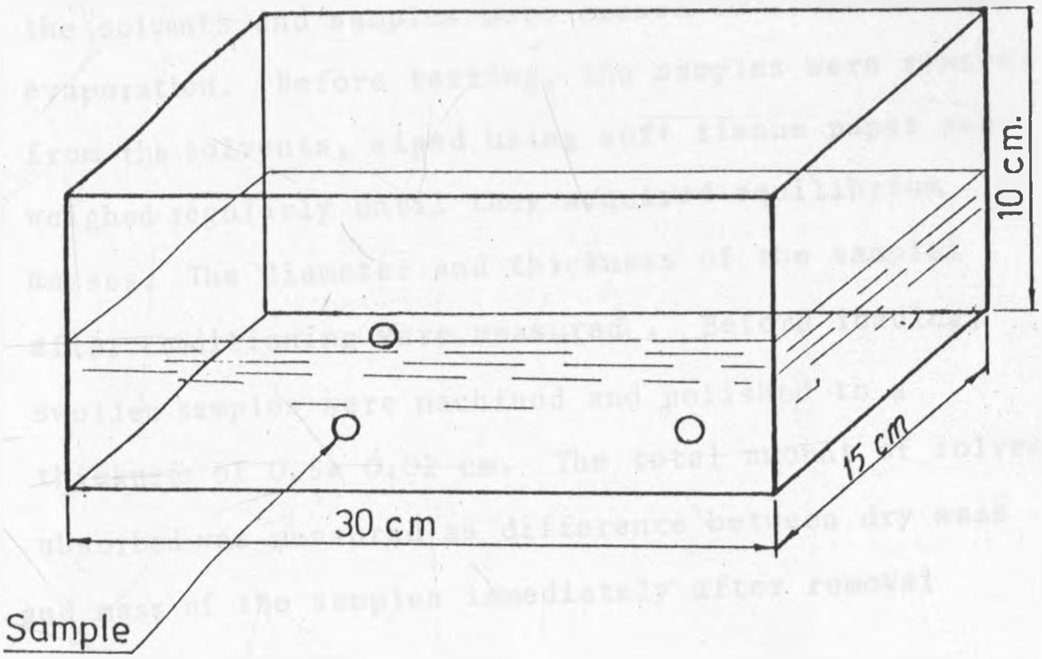


Fig. 12. * Glass solvent conditioning box.

* (Inorganic glass was used for the box).

obtained and averaged. The diameter of the samples were measured using a vernier calipers. The circular PMMA discs were immersed in the solvents for durations ranging from half an hour to 21 days. All conditioning was done at room temperature. The boxes containing the solvents and samples were closed to avoid solvent evaporation. Before testing, the samples were removed from the solvents, wiped using soft tissue paper and weighed regularly until they acquired equilibrium masses. The diameter and thickness of the samples after conditioning were measured . Before loading, swollen samples were machined and polished to a thickness of 0.5± 0.02 cm. The total amount of solvent absorbed was measured as difference between dry mass and mass of the samples immediately after removal from the solvents.

4.6.0 Measurement of birefringence

It was noted in section 3.4.0 that the photoelastic effect could be used to measure stress induced birefringence in polymers. In this study, analysis of photoelastic interference patterns from which birefringence values were obtained was carried out using a photoelastic polariscope and the Tardy compensation method.

Fig. 13. The Sharpless Polariscope.

A. Loading beam

B: Sample position

C: Sodium light

D: Weights.

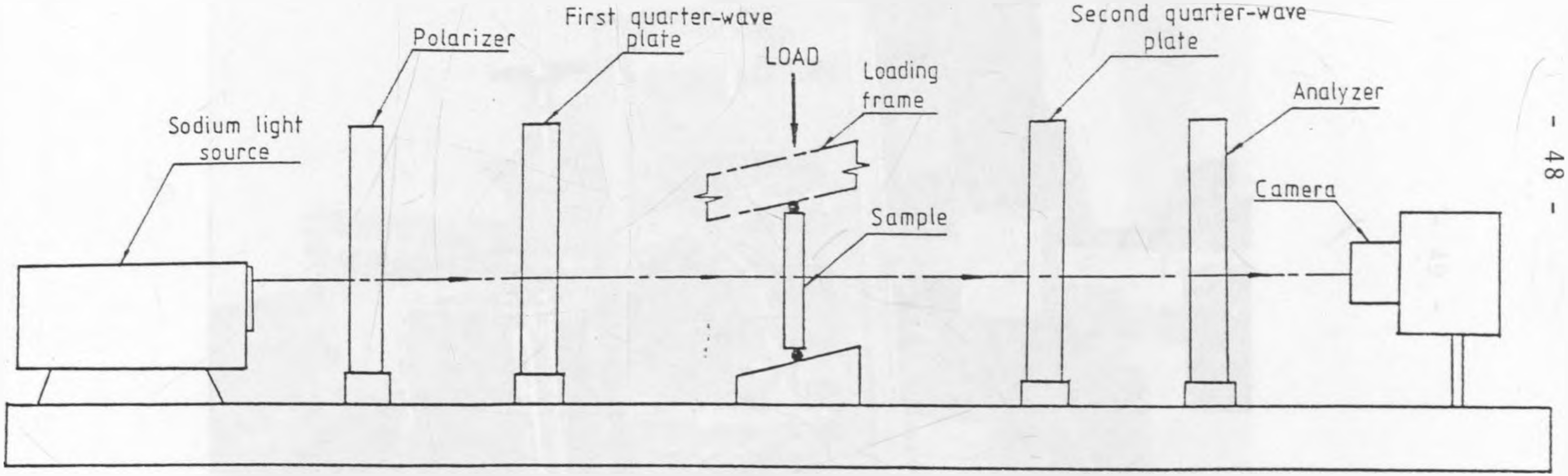


Fig. 14. Schematic diagram of the birefringence apparatus.

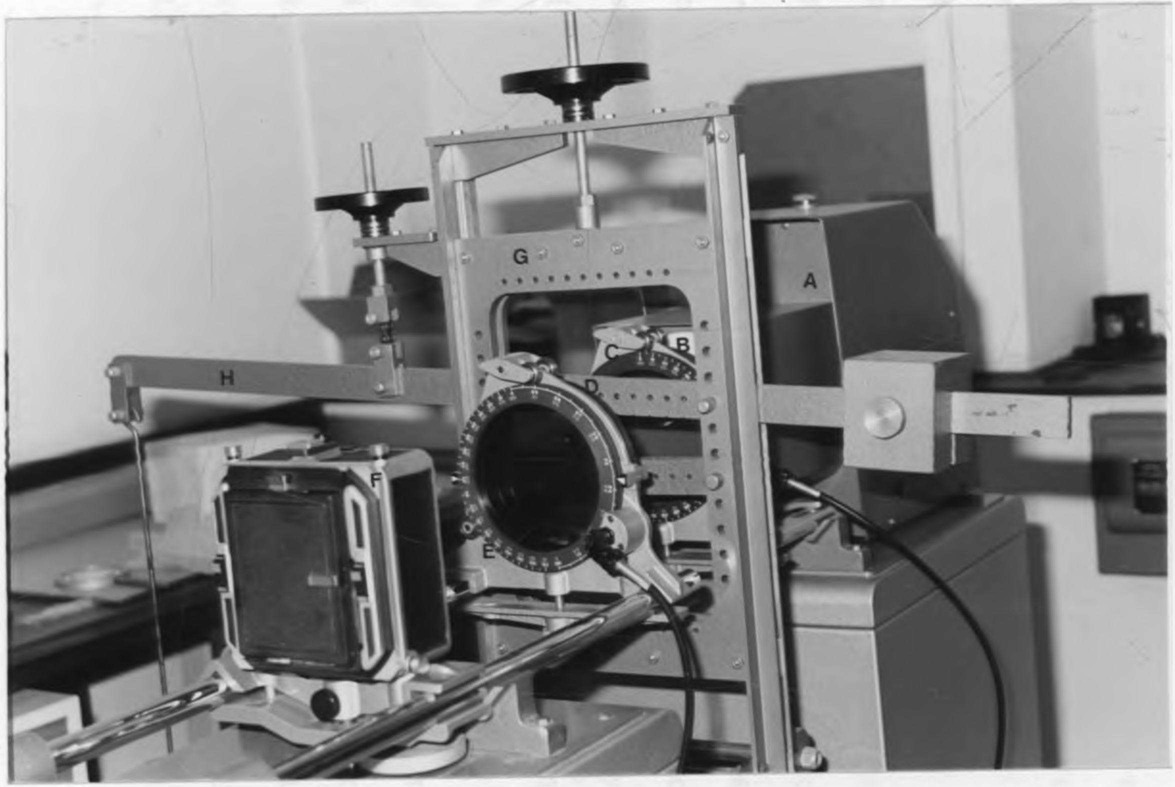


Fig. 15. Optical components of the polariscope.

A:	Sodium light source	E:	Analyser
B:	Polarizer	F:	Camera
C:	First Quarter-wave plate	G:	Loader
D:	Second Quarter-wave plate	H:	Loading beam.

4.6.1 Apparatus

The apparatus used for birefringence measurements was a 'Sharples' diffused-light polariscope arrangement with polarizing filters of 14 cm diameter (Fig. 13 and Fig.15). The source of light was a sodium lamp. The diffused light polariscope as opposed to the lens polariscope, requires only one lens. The field of this polariscope can be made very large since its diameter depends on the size of the linear polarizers and quarter-wave plates only. It consists of (1) a light house,..(11) monochromatic light source, (111) 300W tungsten-filament as white-light source ; (1V) diffusing plates which are made of flashed opal glass, (V) polarizer, (V1) first quarter wave plate, (V11) Loading frame, (V111) second quarter-wave plate, (1X) analyzer and (X) camera. The lens polariscope {33} employs a lens system to expand the field of view.

4.6.2 Experimental Procedure

To measure stress birefringence, a line was drawn as the diameter on each of the solvent conditioned PMMA samples. Points S and R were marked on the line, 0.4 cm from the rim (Fig. 16). The samples were diametrically loaded under compression

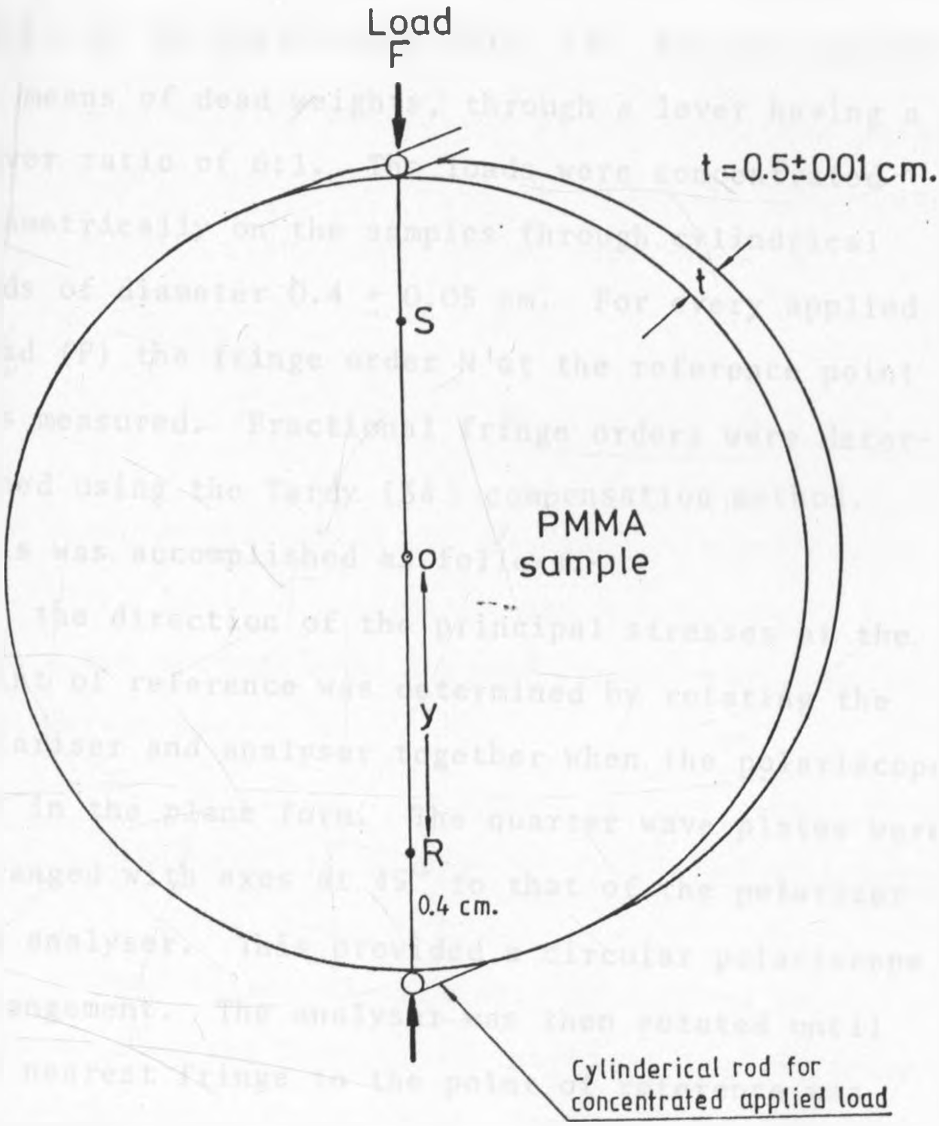


Fig. 16. Illustrating the loading of a circular PMMA sample in compression.

(Fig. 16). The loading was facilitated in the loading frame of the polariscope (Fig. 13); and was applied by means of dead weights, through a lever having a lever ratio of 6:1. The loads were concentrated diametrically on the samples through cylindrical rods of diameter 0.4 ± 0.05 cm. For every applied load (F) the fringe order N at the reference point was measured. Fractional fringe orders were determined using the Tardy {34} compensation method. This was accomplished as follows:-

the direction of the principal stresses at the point of reference was determined by rotating the polariser and analyser together when the polariscope was in the plane form. The quarter wave plates were arranged with axes at 45^o to that of the polarizer and analyser. This provided a circular polariscope arrangement. The analyser was then rotated until the nearest fringe to the point of reference was displaced to intersect with that point. The angle θ through which the analyser had been rotated was noted. If the rotation of the analyser moved the N^{th} order fringe in the direction of increasing fringe order to give extinction at the reference point, then the fringe order there would be

$$(N + \frac{\theta}{180})$$

If the rotation had been in the opposite direction the next higher fringe order would have been moved to give extinction at the reference point and the angle of rotation of the analyzer would have been (180-θ). The fringe order would then be

$$N - \frac{(180 - \theta)}{180}$$

From these measurements the material fringe value, the stress optical coeffienct and birefringence values for various PMMA solvent conditioned samples were determined.

4.6.3 Determination of sign of residual birefringence

Thin slices of thickness 1± 0.01 mm were prepared from the plastically strained loading points on the samples. These slices were used to determine the sign of the residual birefringence. The sign was obtained from interference figures using a polarising microscope and a 1st order red compensator. All tests were done in triplicate for every solvent conditioned PMMA.

4.7.0 Measurement of density and refractive index

The densities and refractive indices for the samples conditioned in the various solvents were measured as described in 4.4.5 and 4.4.7.

4.8.0 Concluding Remarks

The use of the experimental techniques described in this chapter depended upon their availability, cheap design requirements and relevancy to the study. The use of the photoelastic polariscope for birefringence measurements has been reported by many workers {35} . Measurement of the relative retardations using the Se'rnarmont compensator has also been reported {36}. In this study, the Tardy compensation method was used because of its simplicity and accuracy. It also has the advantage of not requiring any extra accessories other than the quarter-wave plates and the polarizers of the polariscope. The results obtained from the measurements are presented and discussed in chapter 5 and 6.

CHAPTER 5

RESULTS

5.0.0 Introduction

The tensile and compressive strengths of the PMMA used in this work were measured to provide information on the mechanical behaviour of the material in both tension and compression. The hardness of the PMMA was measured in order to get an idea on the resistance of the material to indentation. X-ray, Infra-red and NMR spectra for the material were obtained for structural and compositional analysis. From the X-ray spectrum information about the crystallinity or amorphousness of the material would be deduced. By comparing the obtained Infra-red spectrum with reported spectra for PMMA, information on its chemical structure would be obtained. The NMR spectrum would provide information on compositional functional groups and the stereo-chemical configuration of the polymer.

This study centred mainly on the stress induced birefringence in PMMA and how it is influenced by solvents. Solvent effect on the refractive index and the density of PMMA was also investigated. The results of these tests and investigations are presented and discussed in the following sections under the sub-headings

(a) "Mechanical and structural properties of PMMA", which characterize the material, and

(b) 'Photoelasticity results' from which birefringence values for solvent conditioned PMMA samples are obtained.

5.1.0 Mechanical and structural properties of PMMA

5.1.1.0 Mechanical properties

5.1.1.1 Tensile strength

Figure 17 gives a typical stress-strain curve obtained by stretching unconditioned PMMA in a tensometer. The curve shows that the PMMA is brittle in tension. This is depicted by the instantaneous fracture of the PMMA upon subjecting it to 6.62 KN/cm^2 load. Summary of the results for PMMA stretching is given in table 2.

5.1.1.2 Compressive strength

The stress-strain relation for compressed samples of solvent unconditioned PMMA is given in Fig. 17. The curve shows a yield maximum which is

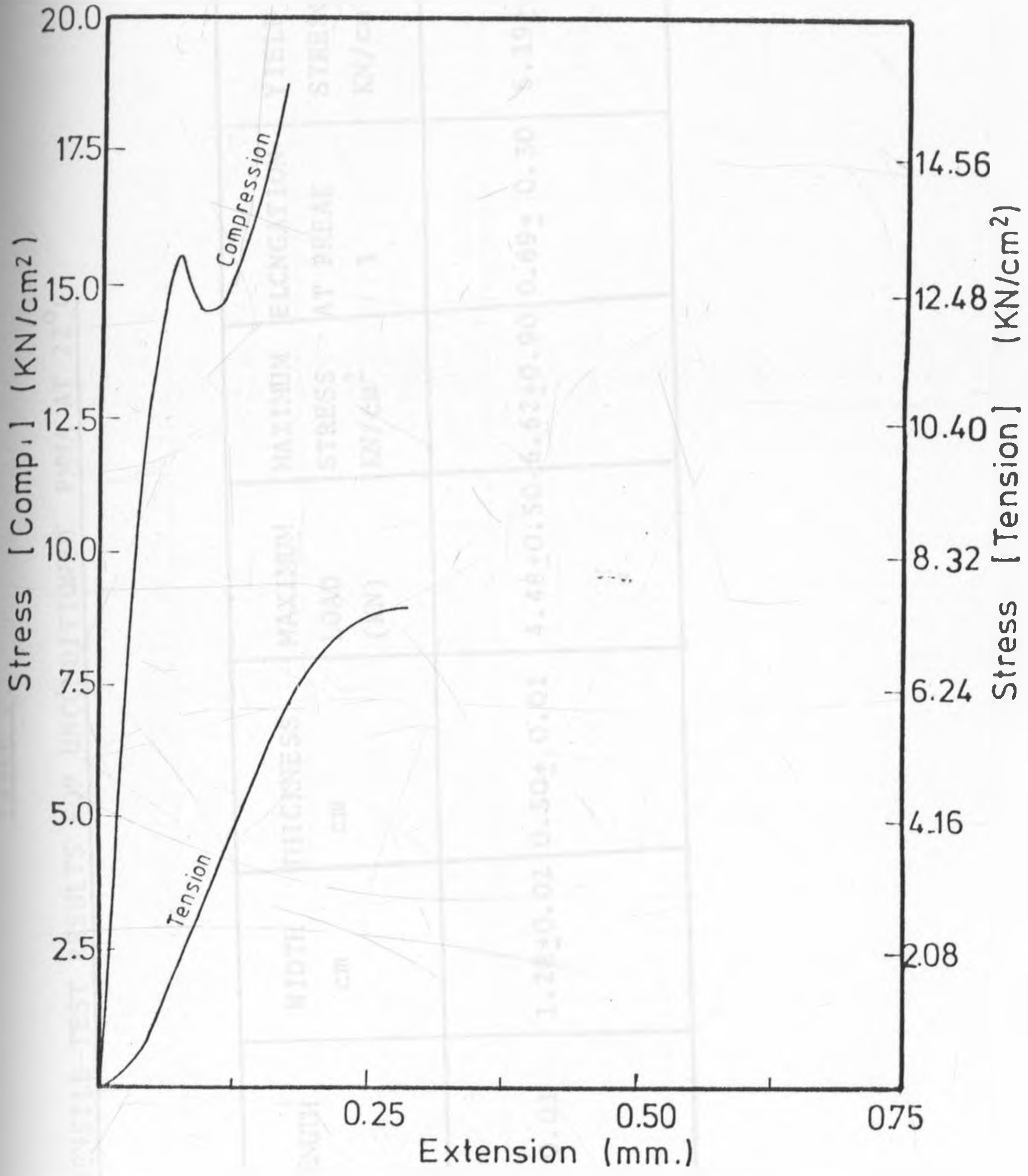


Fig. 17. Stress-Extension behaviour of unconditioned PMMA in compressive and in Tensile Loading.

TABLE 2.

TENSILE TEST RESULTS FOR UNCONDITIONED PMMA AT 22°C

GAUGE- LENGTH cm	WIDTH cm	THICKNESS cm	MAXIMUM LOAD (KN)	MAXIMUM STRESS KN/cm^2	ELONGATION AT BREAK %	YIELD STRESS KN/cm^2	TENSILE MODULUS x10^5 N/cm^2
6.0 ± 0.01	1.28±0.02	0.50± 0.01	4.48±0.50	6.62±0.90	0.69± 0.30	6.19±0.07	3.81± 0.05

is associated with some uncoiling and straightening of polymer chains. The compression modulus is $(4.10 \pm 0.30) \times 10^5$ N/cm^2. The results are given in Table 3. It is noted that the compressive yield strength of the PMMA is higher than its tensile strength. (see tables 2 and 3).

5.1.1.3 Hardness

The hardness number of the PMMA used in this study was measured against Din 53456 standard of the Kenya Bureau of Standards. The value obtained for the PMMA is 162.0 ± 3.0 N/mm^2.

5.1.2.0 Structural Properties

5.1.2.1 X-ray spectrum

Figure 18 shows the x-ray spectrum for the PMMA used. From this spectrum it is observed that the PMMA was highly amorphous. There were no distinct peaks characteristic of crystalline materials.

5.1.2.2 Infra-red spectrum

The infra-red spectrum (Fig. 19) shows high characteristics of syndiotactic PMMA. However

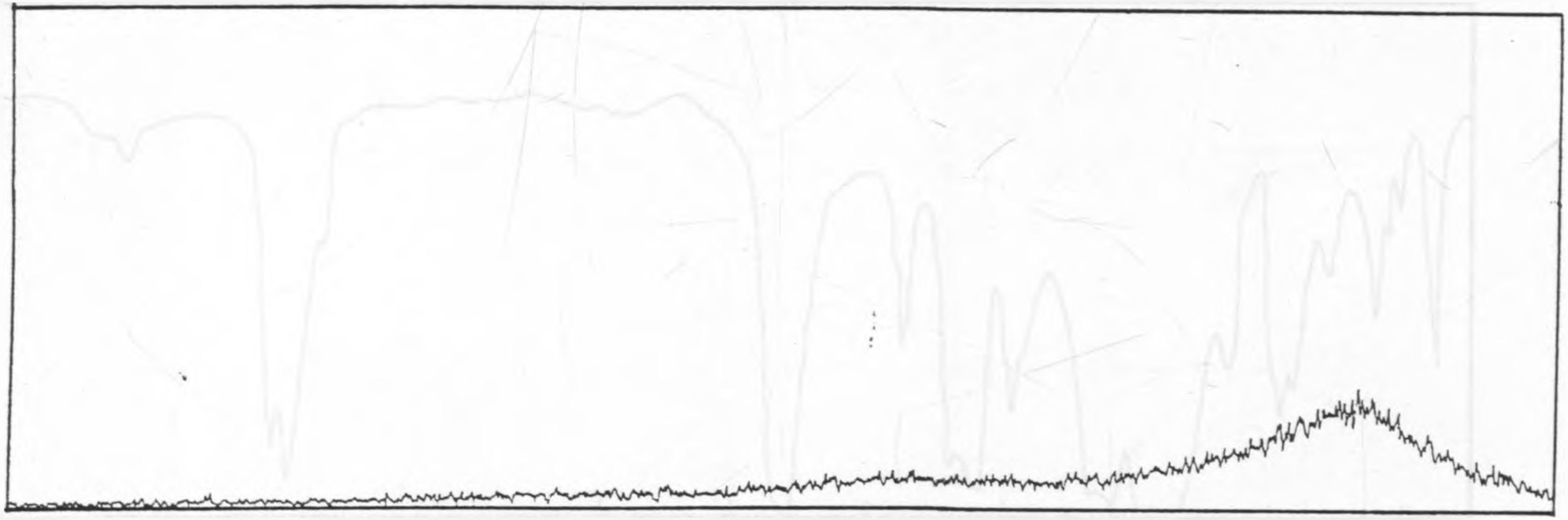


Fig. 18: X-ray spectrum for the unconditioned PMMA.

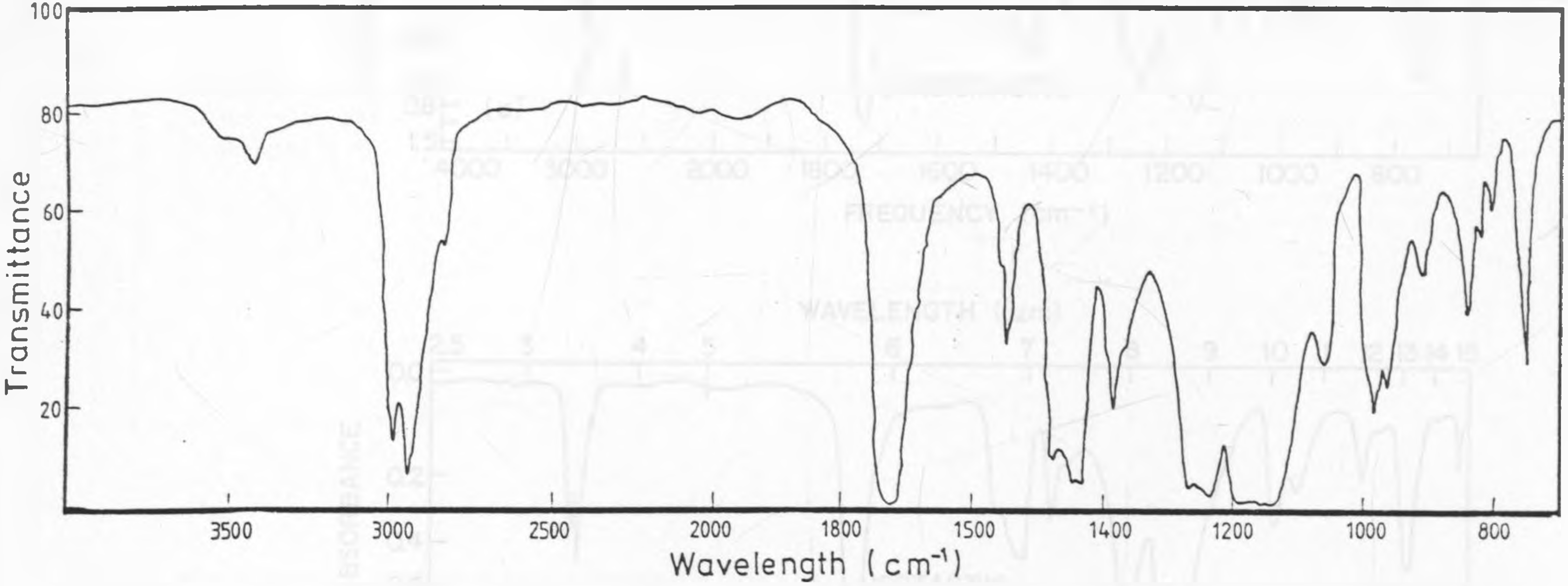


Fig. 19. Infra-red spectrum for the PMMA used in the study, (film from Ethyl acetate solution).

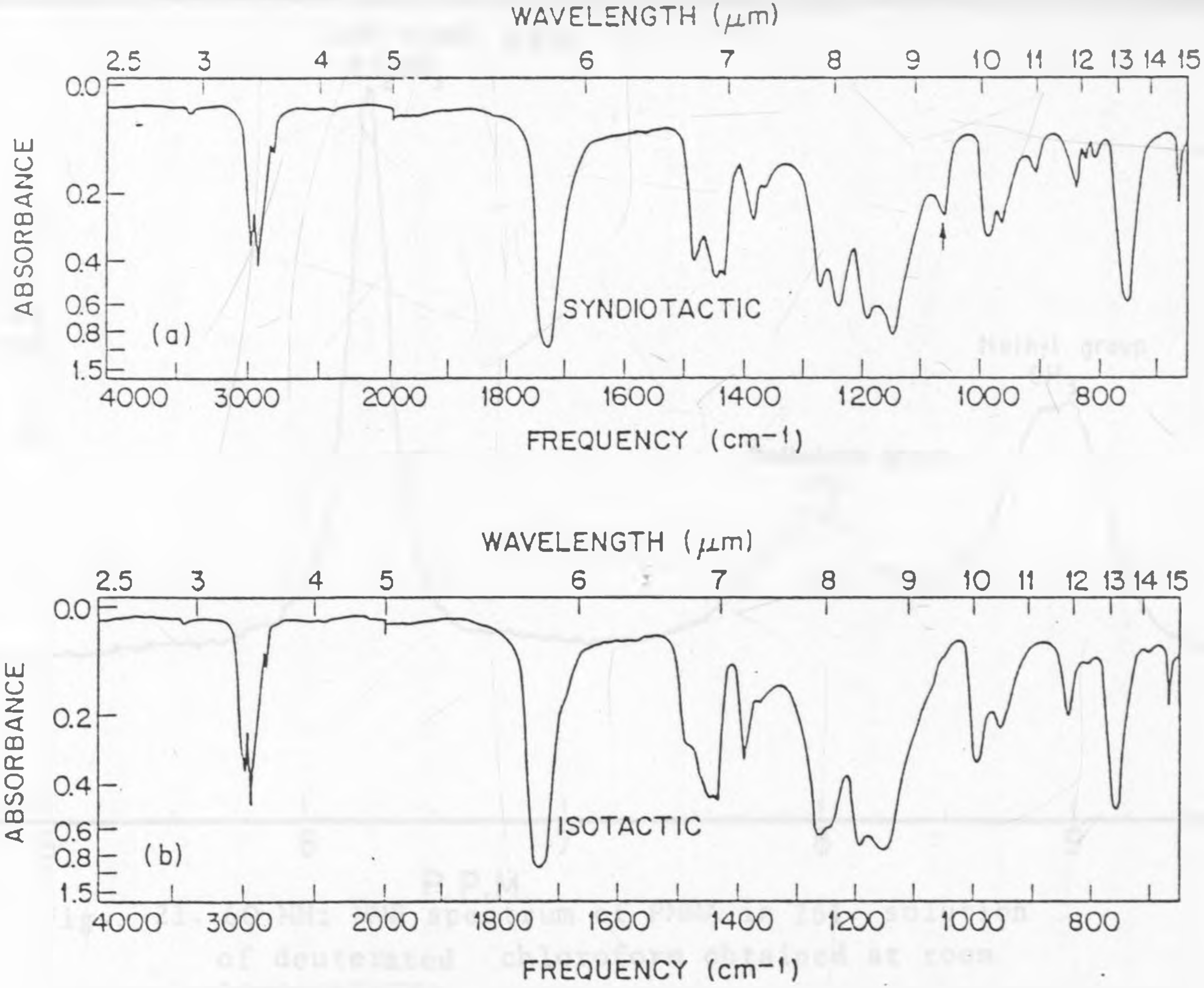


Fig. 20. Infrared spectra of predominantly (a) syndiotactic and (b) isotactic films of polymethyl methacrylate.

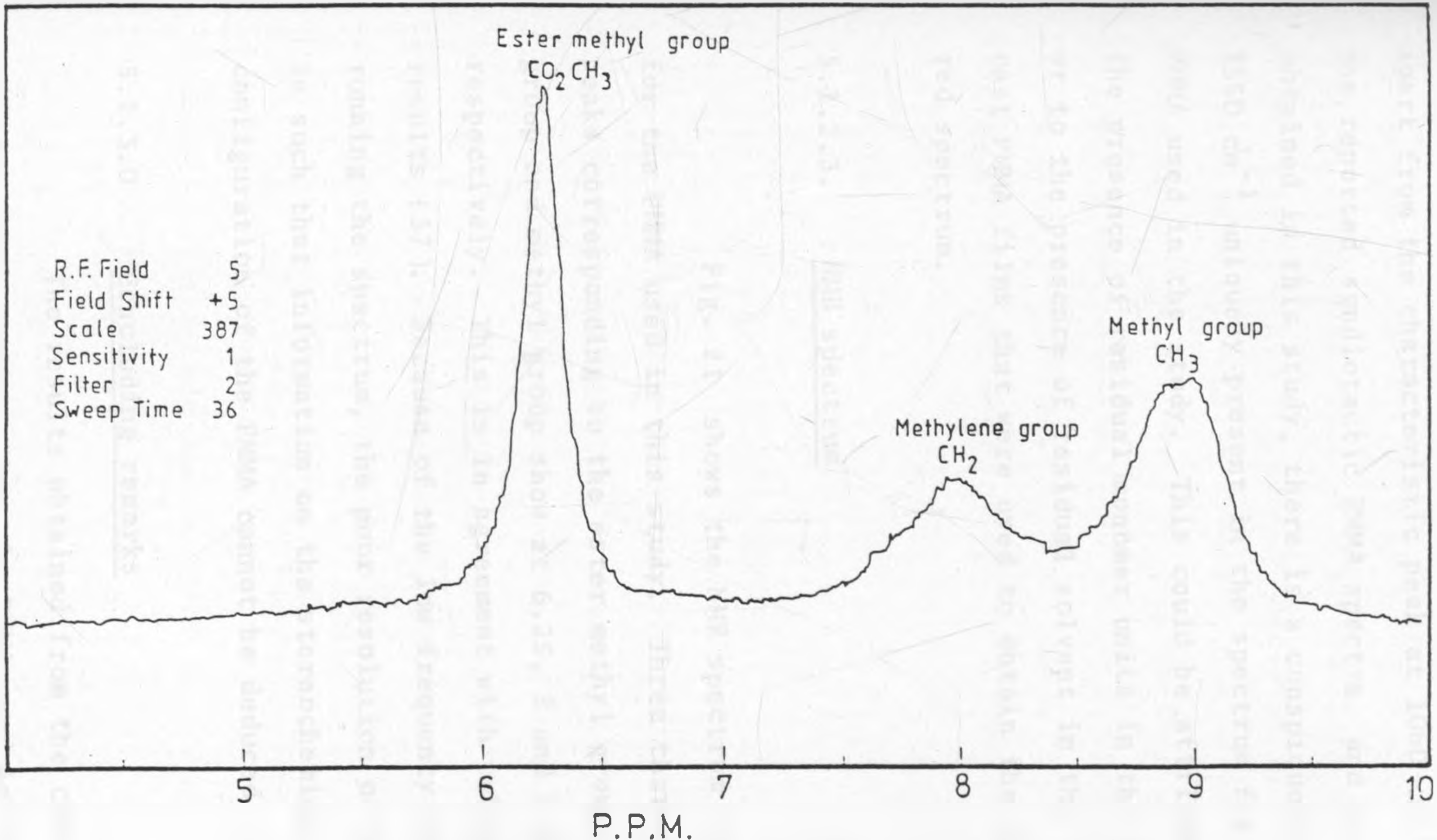


Fig. 21. 60 MHz NMR spectrum of PMMA in 26% solution of deuterated chloroform obtained at room temperature.

comparison with spectra for either predominantly syndiotactic or isotactic PMMA (see Fig. 20) shows that apart from the characteristic peak at 1060 cm^{-1} in both the reported syndiotactic PMMA spectra and the spectra obtained in this study, there is a conspicuous band at 1550 cm^{-1} uniquely present in the spectrum for the PMMA used in the study. This could be attributed to the presence of residual monomer units in the polymer or to the presence of residual solvent in the solvent-cast PMMA films that were used to obtain the infra-red spectrum.

5.1.2.3. NMR spectrum

Fig. 21 shows the NMR spectrum obtained for the PMMA used in this study. Three characteristic peaks corresponding to the ester methyl group, methylene group and methyl group show at 6.25, 8 and 9 p.p.m. respectively. This is in agreement with published results {37}. Because of the low frequency used in running the spectrum, the poor resolution of the peaks is such that information on the stereochemical configuration of the PMMA cannot be deduced.

5.1.3.0 Concluding remarks

The results obtained from the characterization tests suggest that the PMMA used in this study was amorphous and didn't have any residual stresses.

The density of the material was 1.183± 0.0009 g/cm^3 which is within the range of reported value of [38]. Because the PMMA had a higher compressive yield strength than the tensile strength, the birefringence measurements were performed in compression. This provided a wider loading range before the material yields than if tensile loading was used. The birefringence measurements which form the main theme of the study are presented and discussed in the following section.

5.2.0 Photoelasticity Results

The photoelasticity results of PMMA conditioned in acetonitrile, n-butanol, methanol, ethylene glycol and ethanol respectively are presented. All photoelastic measurements were performed in compression. From these results, the material fringe values and stress optical coefficients for PMMA samples conditioned in the various solvents are deduced. Also presented in this section are the refractive indices and densities of the solvent conditioned PMMA samples.

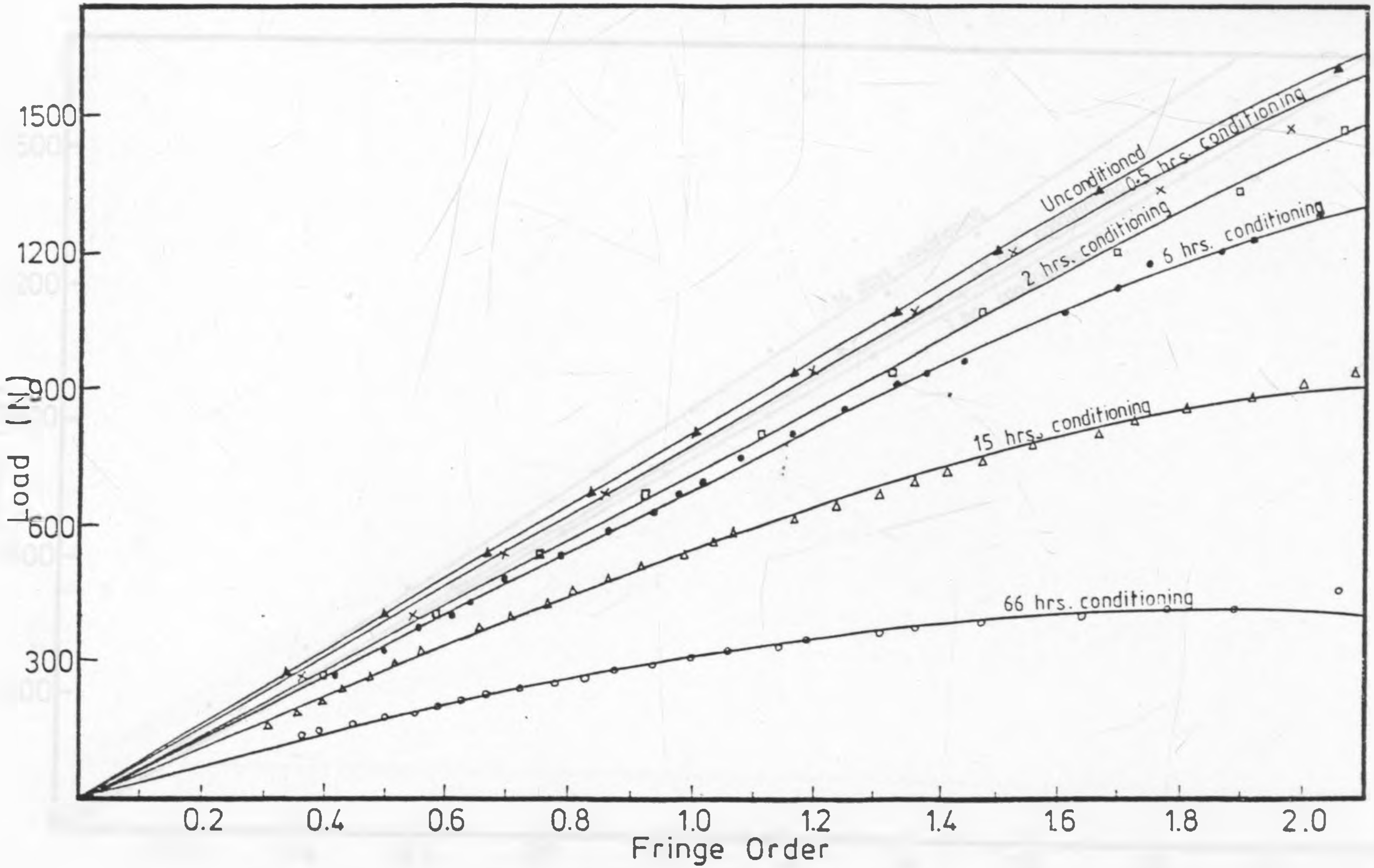


Fig. 22. Load-Fringe order relation for PMMA conditioned in acetonitrile for various durations.

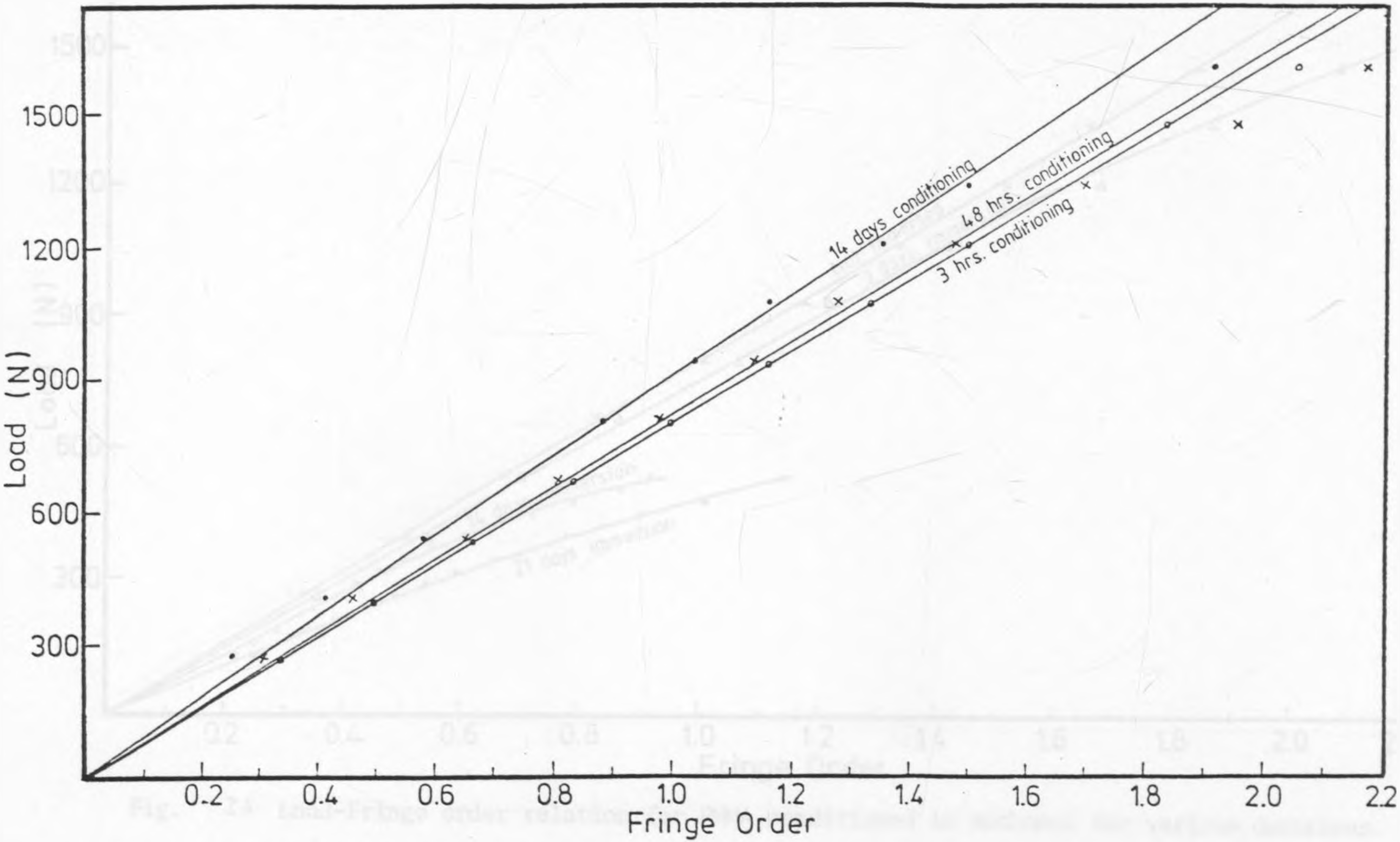


Fig. 23. Load-Fringe order relation for PMMA conditioned in n-butanol for various durations.

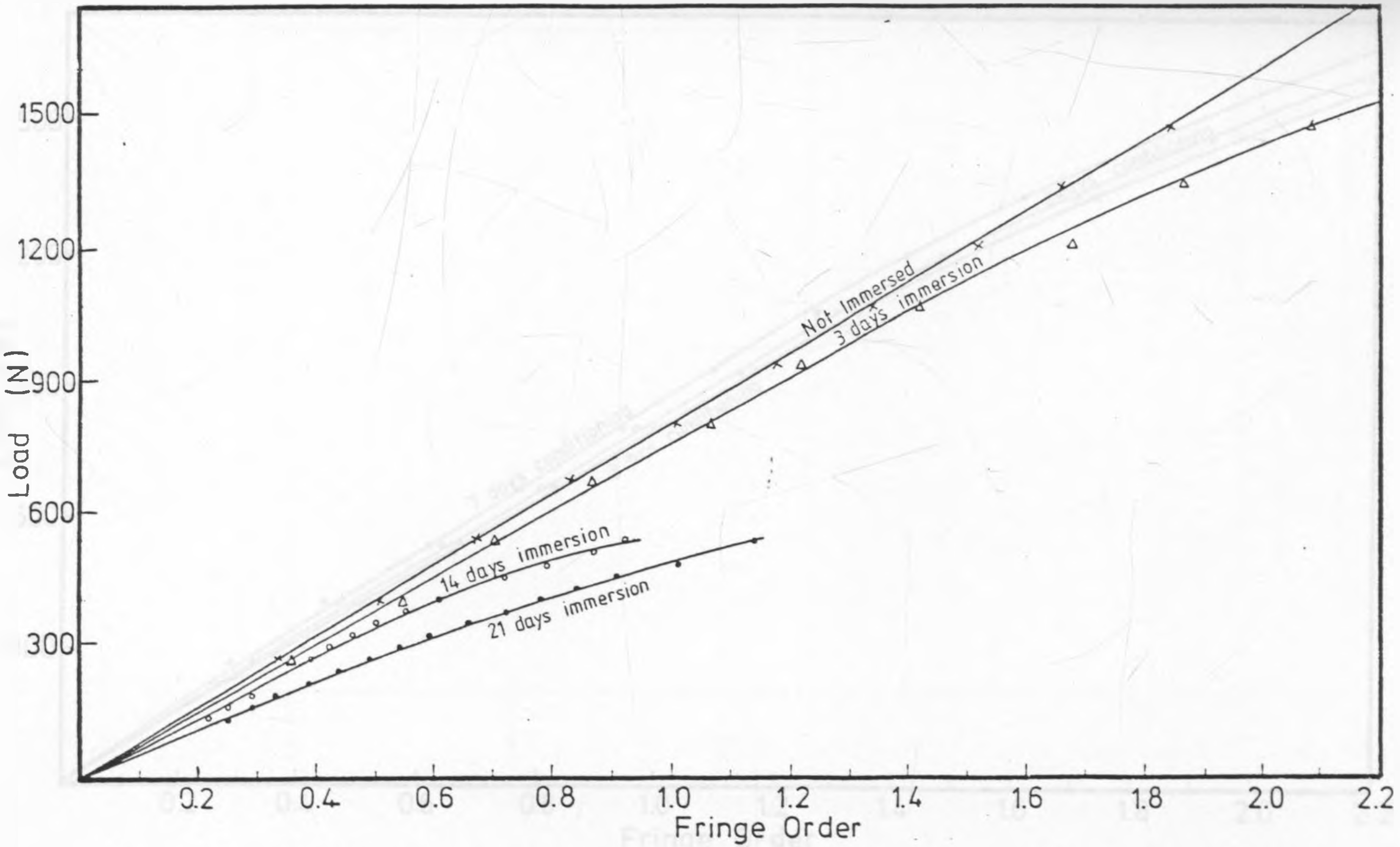


Fig. 24 Load-Fringe order relation for PMMA conditioned in methanol for various durations.

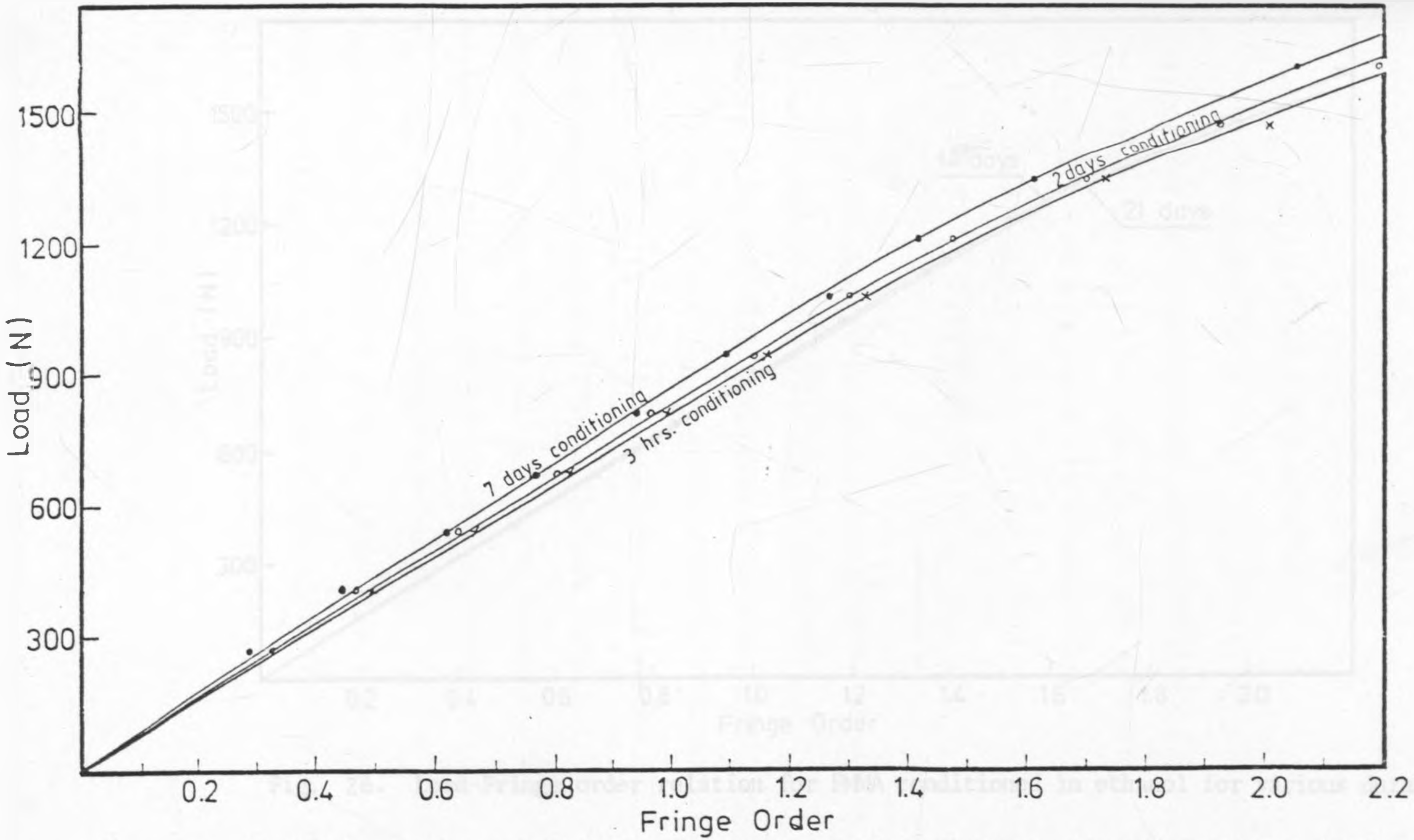


Fig. 25. Load-Fringe order relation for PMMA conditioned in ethylene glycol for various durations.

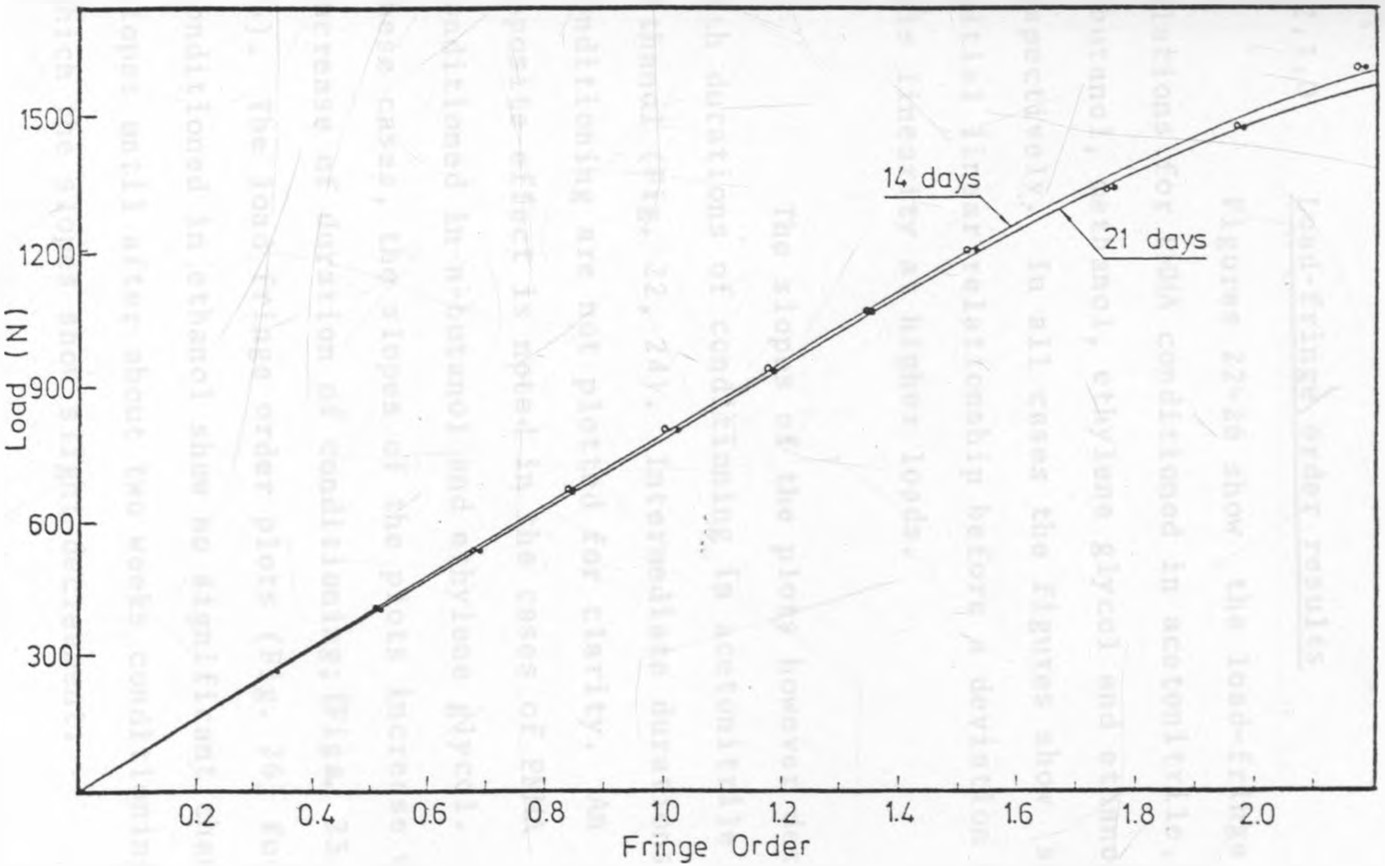


Fig. 26. Load-Fringe order relation for PMMA conditioned in ethanol for various durations.

5.2.1.0 Load-fringe order results

Figures 22-26 show the load-fringe order relations for PMMA conditioned in acetonitrile, n-butanol, methanol, ethylene glycol and ethanol respectively. In all cases the figures show some initial linear relationship before a deviation from this linearity at higher loads.

The slopes of the plots however decrease with durations of conditioning in acetonitrile and methanol (Fig. 22, 24). Intermediate durations of conditioning are not plotted for clarity. An opposite effect is noted in the cases of PMMA conditioned in n-butanol and ethylene glycol. In these cases, the slopes of the plots increase with increase of duration of conditioning; (Figs. 23, and 25). The load fringe order plots (Fig. 26) for PMMA conditioned in ethanol show no significant change in slopes until after about two weeks conditioning after which the slopes show slight decreament.

5.2.1.1. Relative retardations

The relative retardations δ at the reference point for every load were calculated using the equation $\delta = N\lambda$

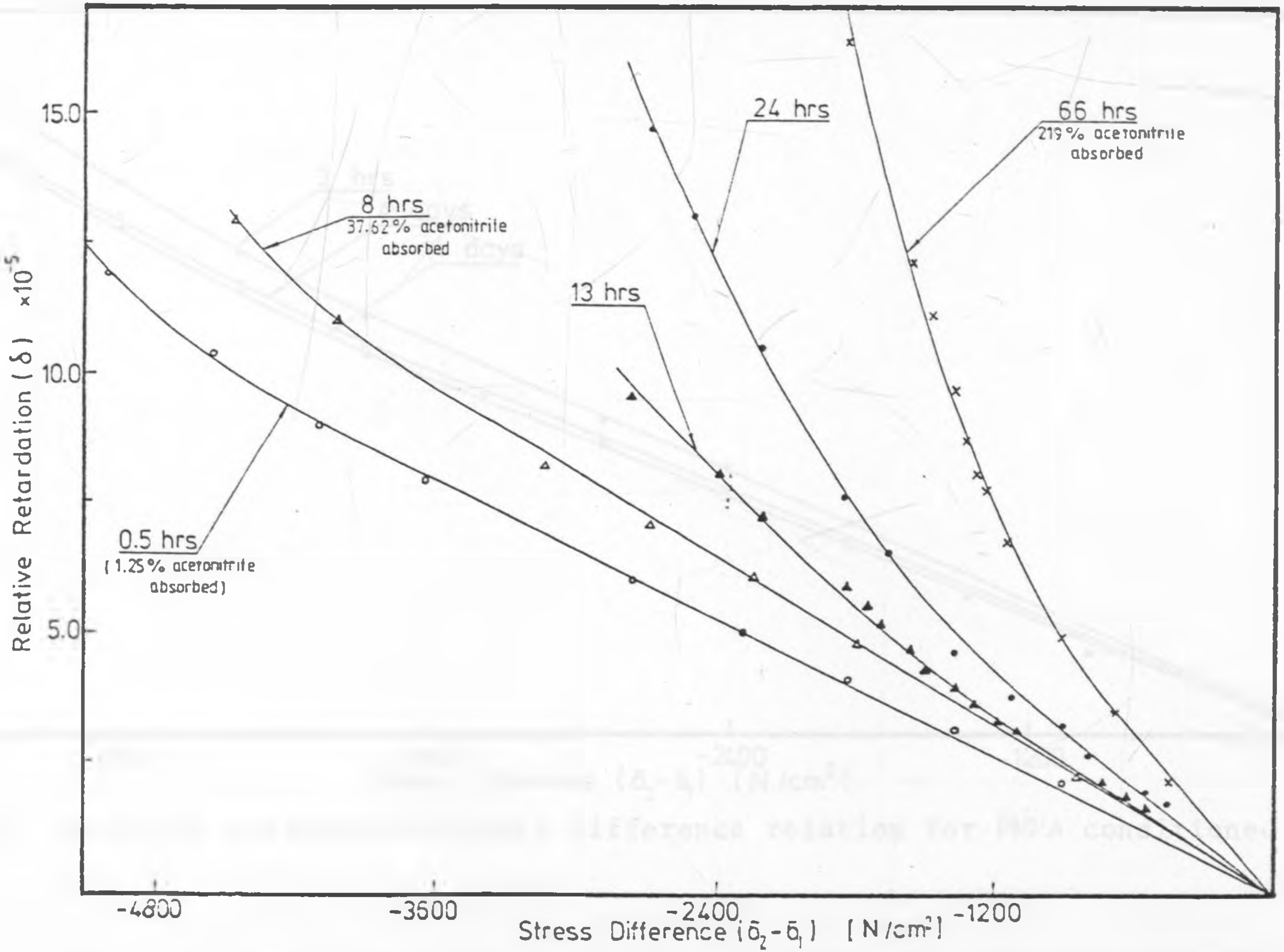


Fig. 27. Relative retardation-Stress difference relation for PMMA conditioned in acetonitrile.

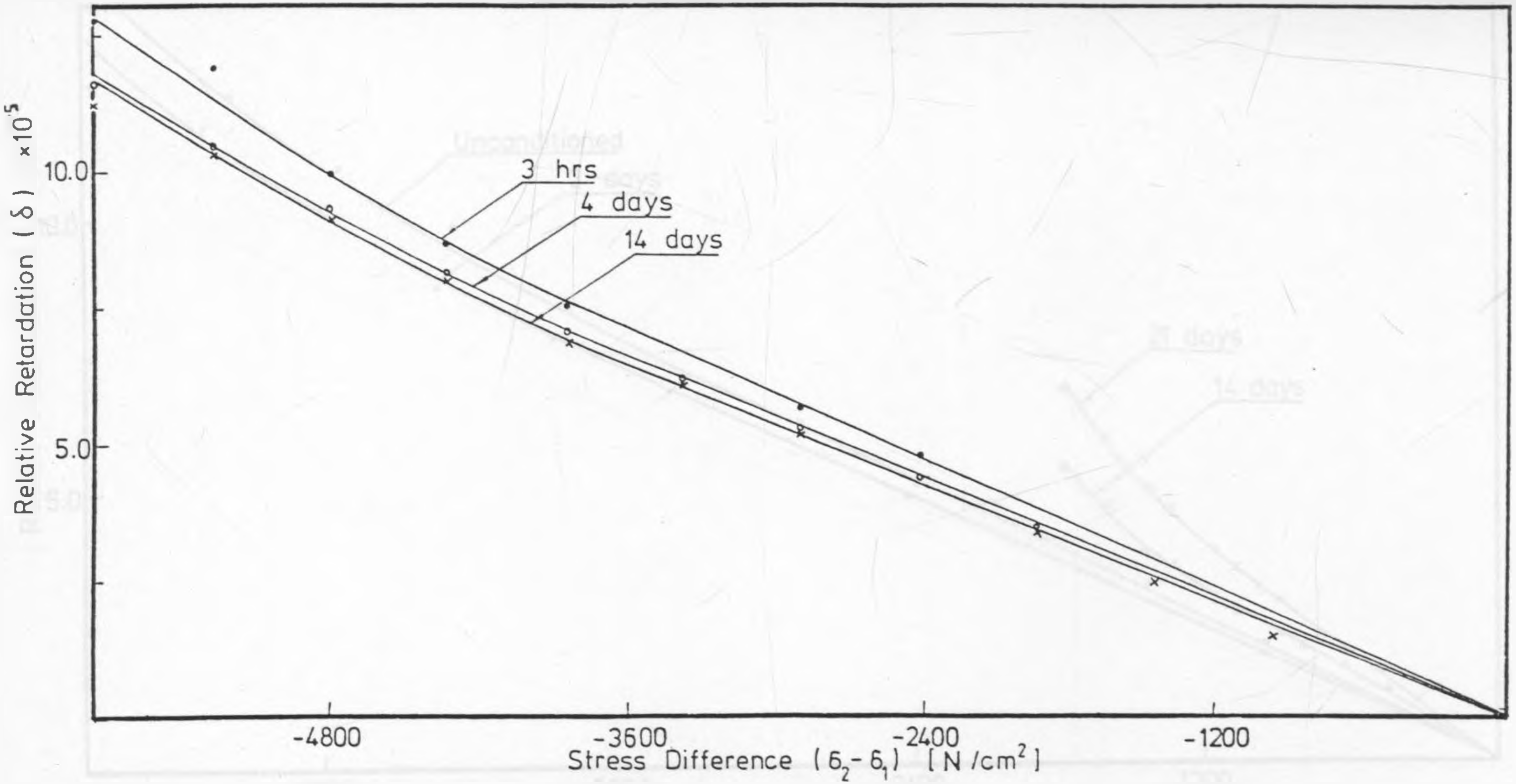


Fig. 28. Relative retardation-Stress difference relation for PMMA conditioned in n-butanol.

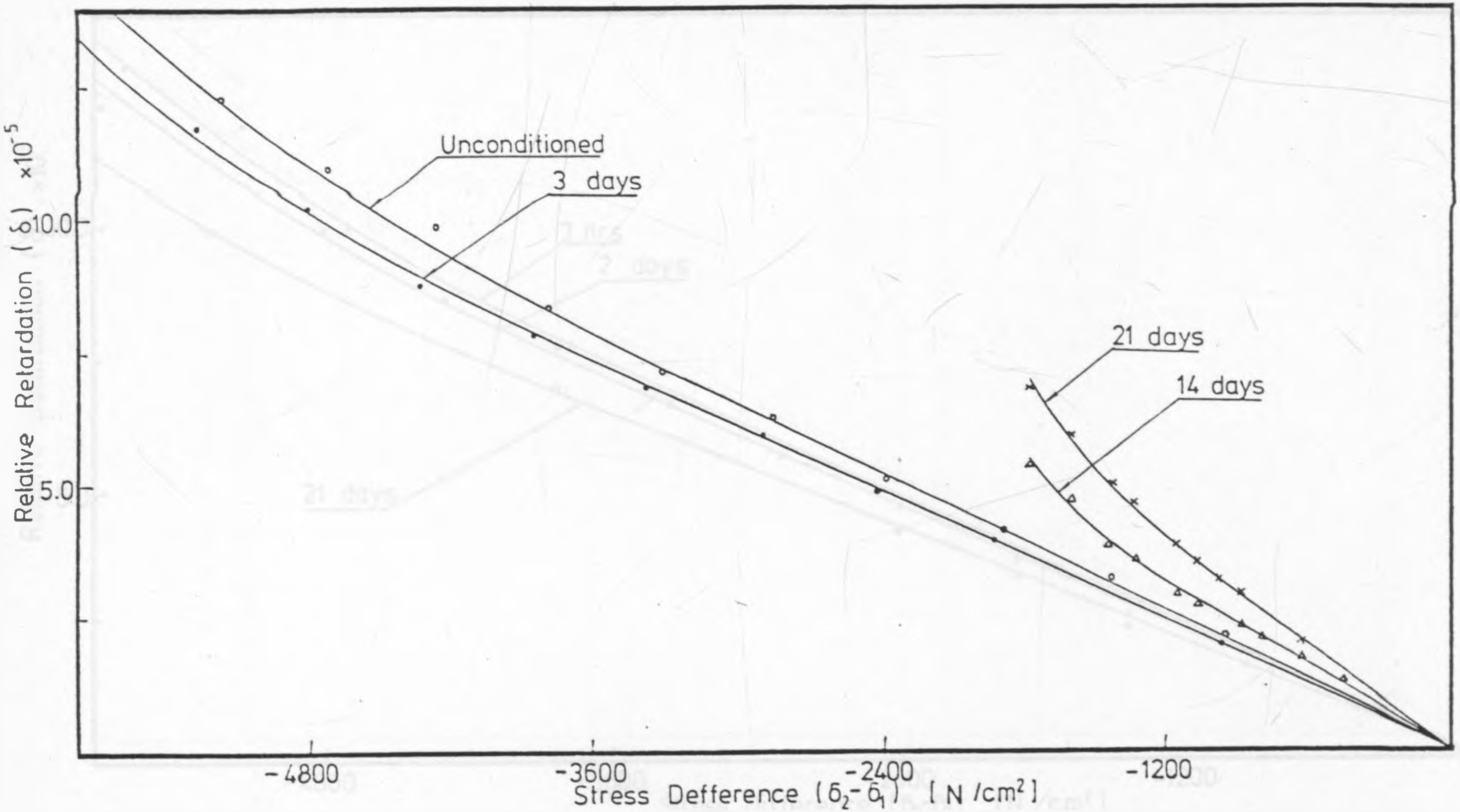


Fig. 29. Relative retardation-Stress difference relation for PMMA conditioned in methanol.

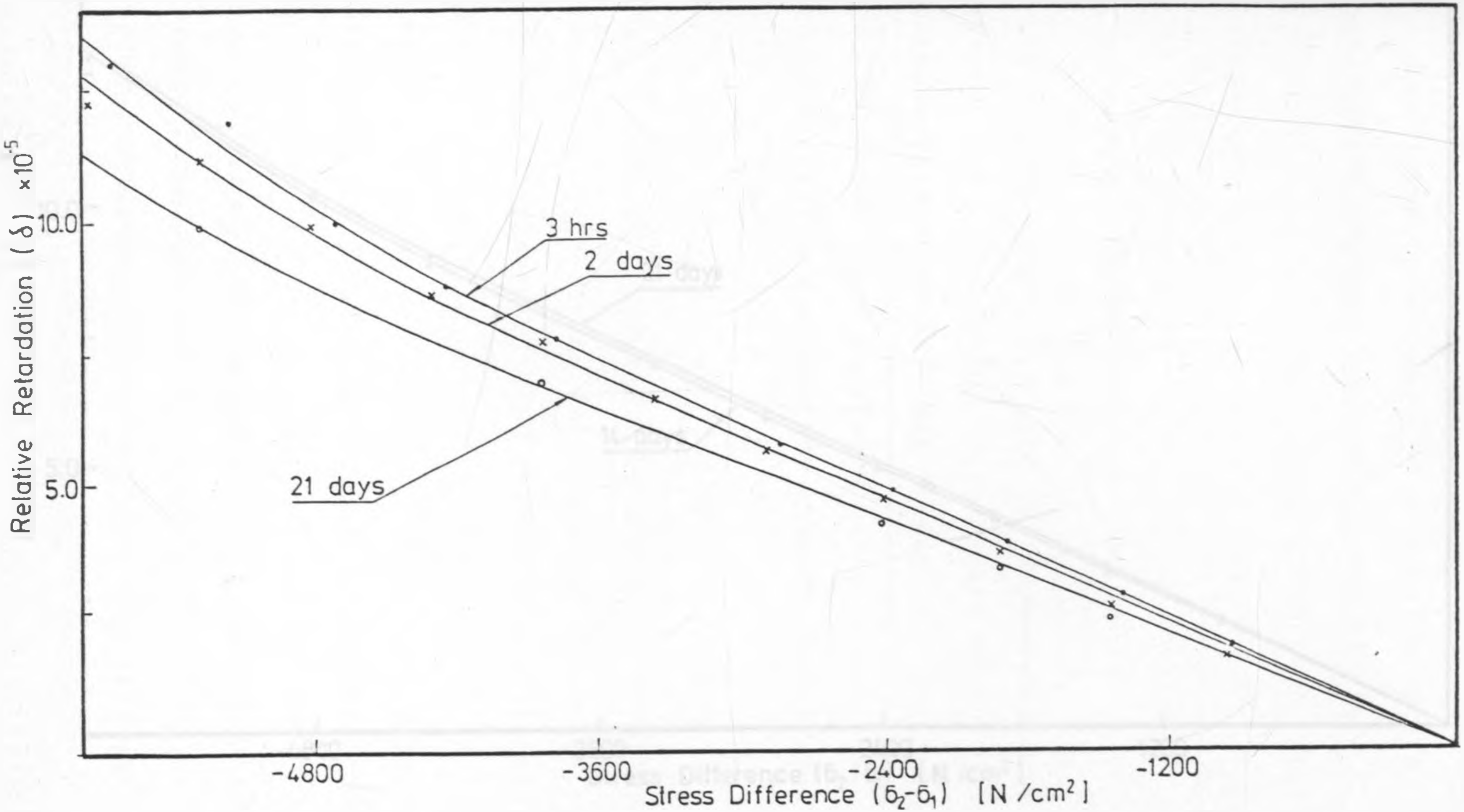


Fig. 30. Relative retardation-Stress difference relation for PMMA conditioned in ethylene glycol.

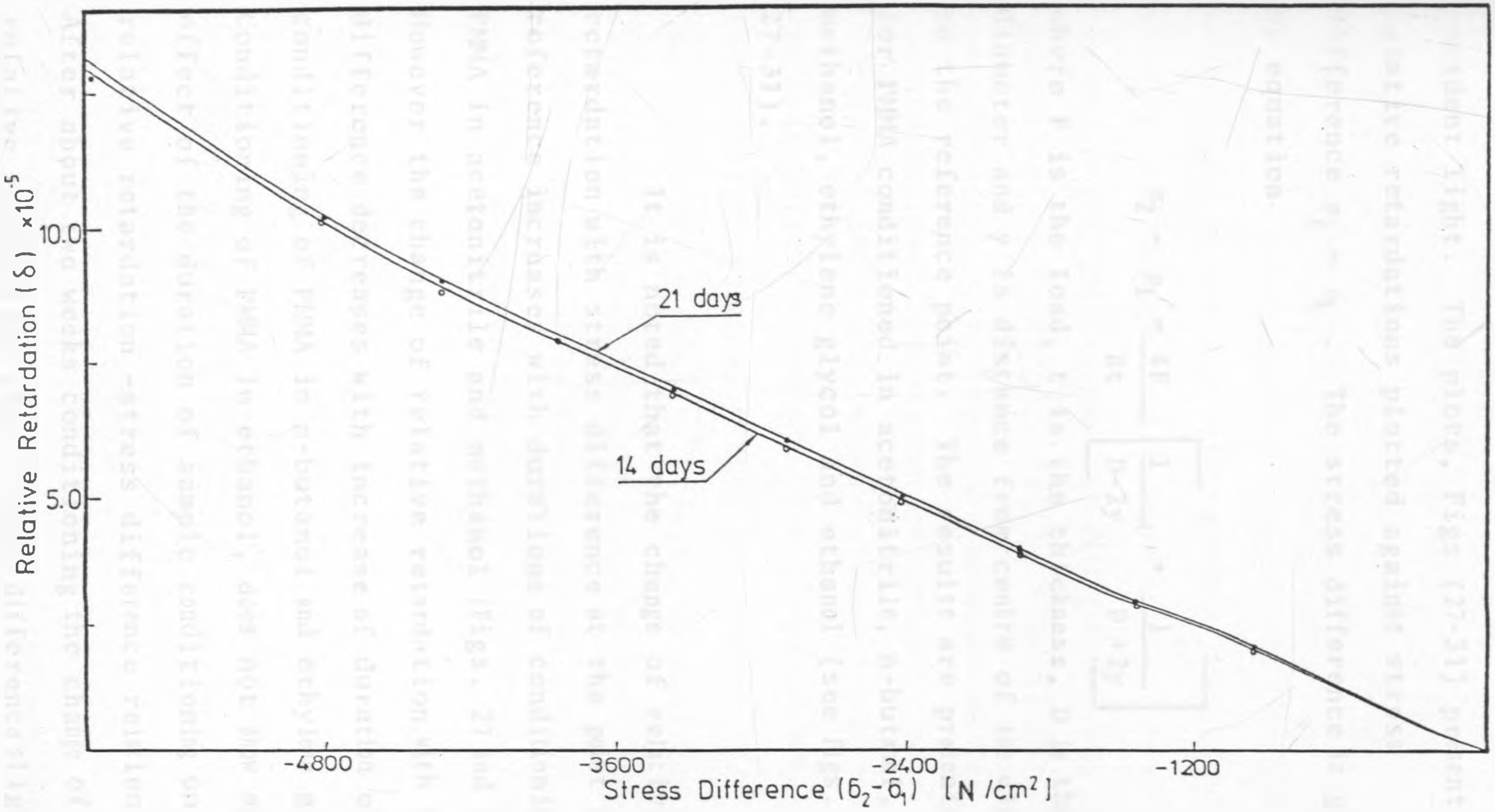


Fig. 31. Relative retardation-Stress difference relation for PMMA conditioned in ethanol.

where N is the fringe order and λ is the wavelength of incident light. The plots, Figs (27-31) present the relative retardations plotted against stress difference $\sigma_2 - \sigma_1$. The stress difference is given by equation

$$\sigma_2 - \sigma_1 = \frac{4F}{\Pi t}\left[\frac{1}{D-2y} + \frac{1}{D+2y}\right]$$

where F is the load, t is the thickness, D is the diameter and y is distance from centre of the disk to the reference point. The results are presented for PMMA conditioned in acetonitrile, n-butanol, methanol, ethylene glycol and ethanol (see Figs. 27-31).

It is noted that the change of relative retardation with stress difference at the point of reference increases with durations of conditioning of PMMA in acetonitrile and methanol (Figs. 27 and 29). However the change of relative retardation with stress difference decreases with increase of duration of conditioning of PMMA in n-butanol and ethylene glycol. Conditioning of PMMA in ethanol, does not show any effect of the duration of sample conditioning on the relative retardation -stress difference relation. After about two weeks conditioning the change of relative retardation with stress-difference slightly increases. This shows in the increase of the slope of retardation-stress difference plots.

5.3.0 Percentage change in mass

The percentage changes of mass for PMMA conditioned in acetonitrile, methanol, n-butanol, ethanol and ethylene glycol were obtained by finding the percentage difference between the dry mass of the samples and the mass immediately after removal from the solvents. It was observed as shown in Figs. 32 and 34 that the percentage change of mass increased with the durations of conditioning in acetonitrile and methanol. The masses of samples of PMMA conditioned in n-butanol and ethylene glycol decreased with increasing duration of conditioning (Fig. 33 and 35). The percentage change of mass was negative. Samples conditioned in ethanol show slight increase in percentage change in mass after about one week (Fig. 36).

5.4.0. Density values

The densities of samples of PMMA conditioned in the various solvents were measured as described in chapter 4. The densities were measured when the samples had acquired equilibrium mass. A pronounced effect on the density for samples conditioned in methanol and acetonitrile environments was observed.

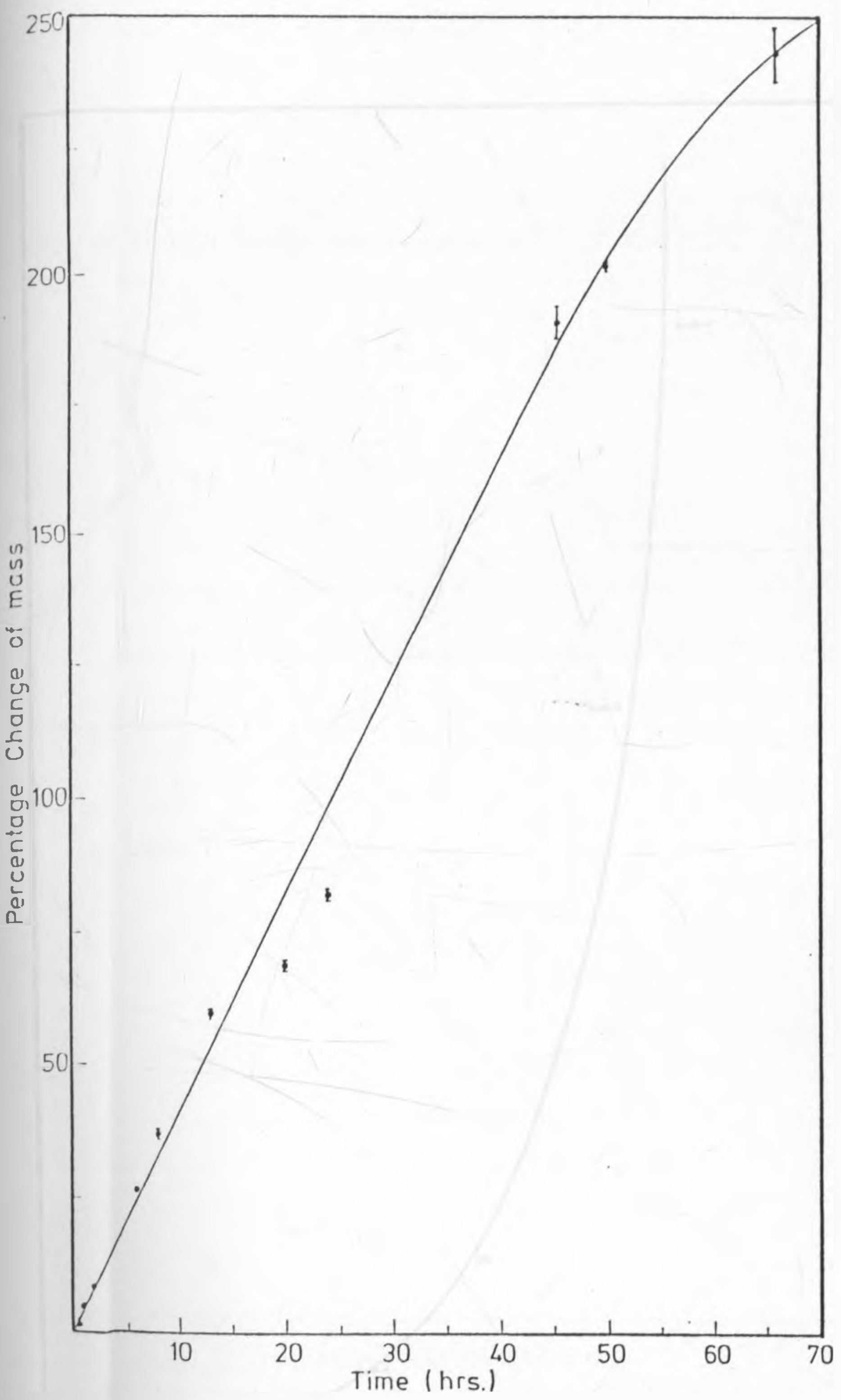


Fig. 32. Percentage change in mass with duration of conditioning of PMMA in acetonitrile.

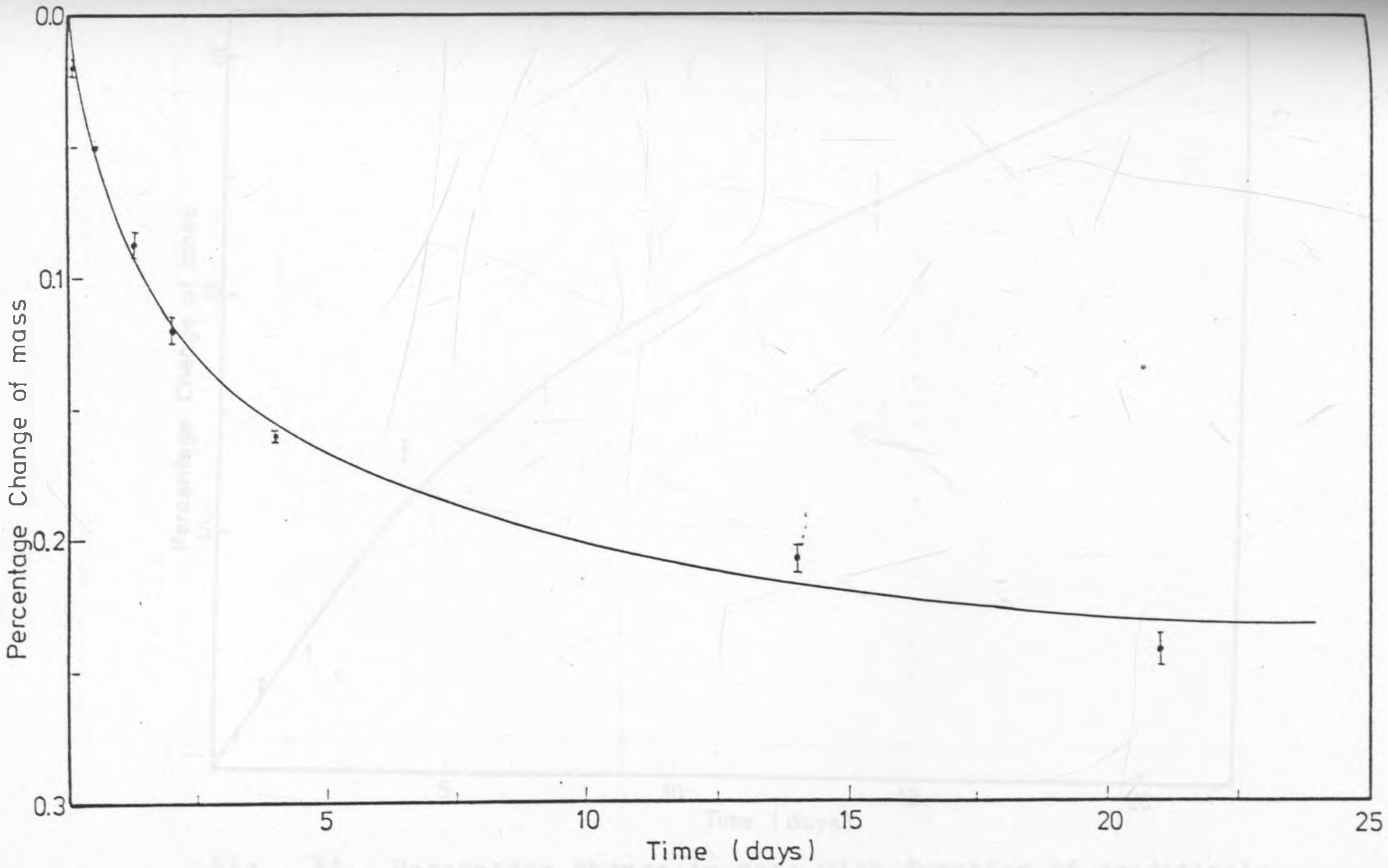


Fig. 33. Percentage change in mass with duration of conditioning of PMMA in n-butanol.

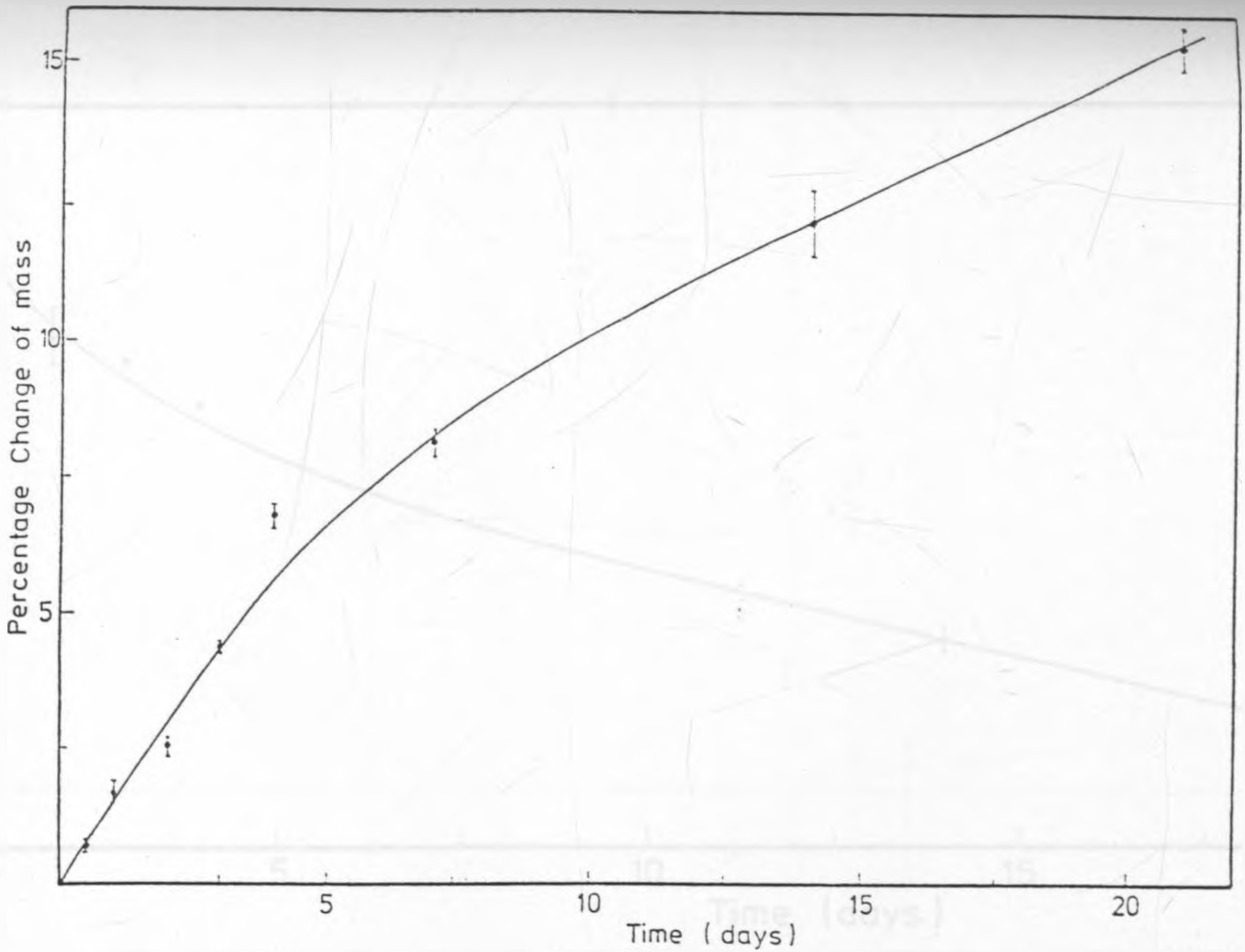


Fig. 34. Percentage change in mass with duration of conditioning of PMMA in methanol.

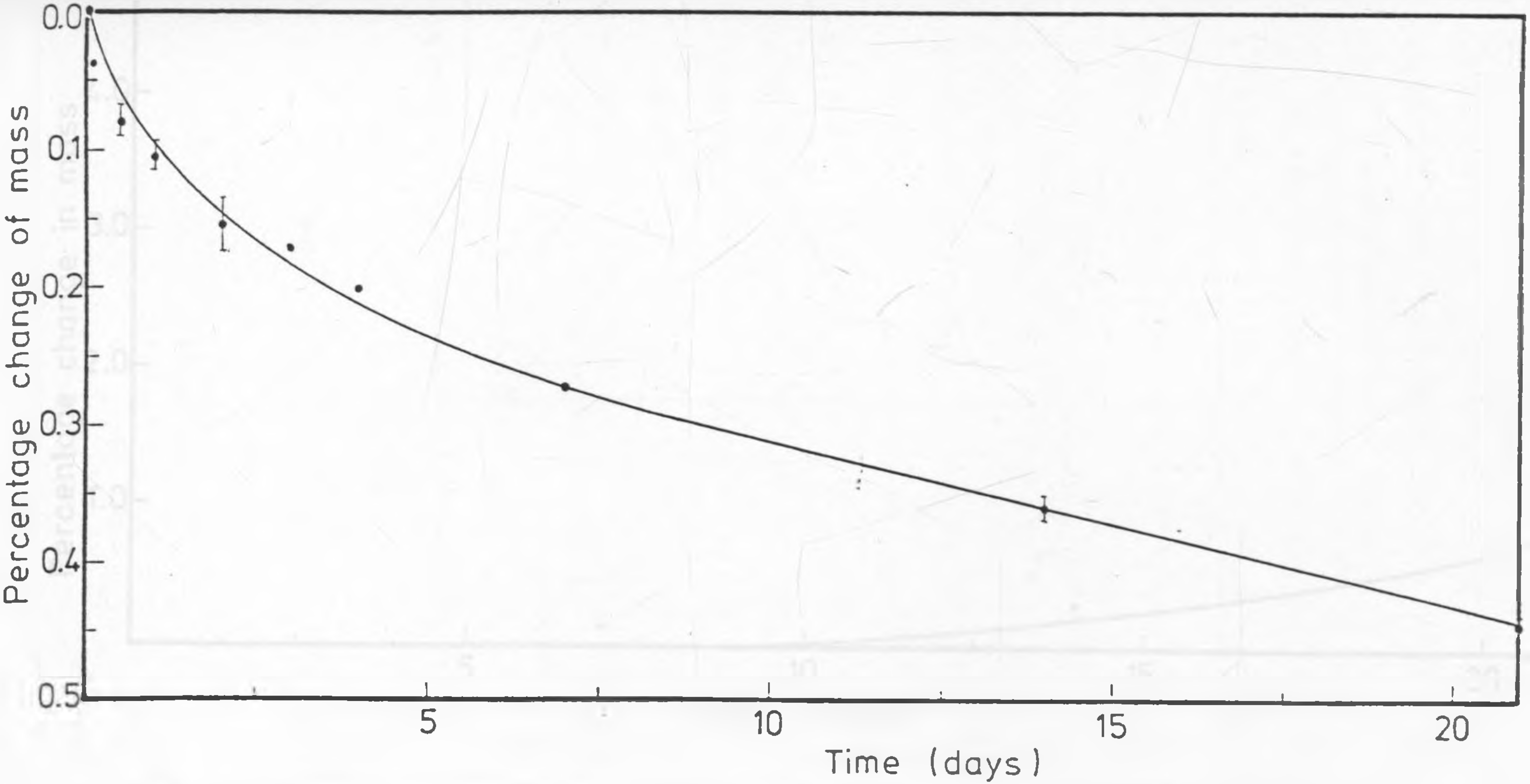


Fig. 35. Percentage change in mass with duration of conditioning of PMMA in ethylene glycol.

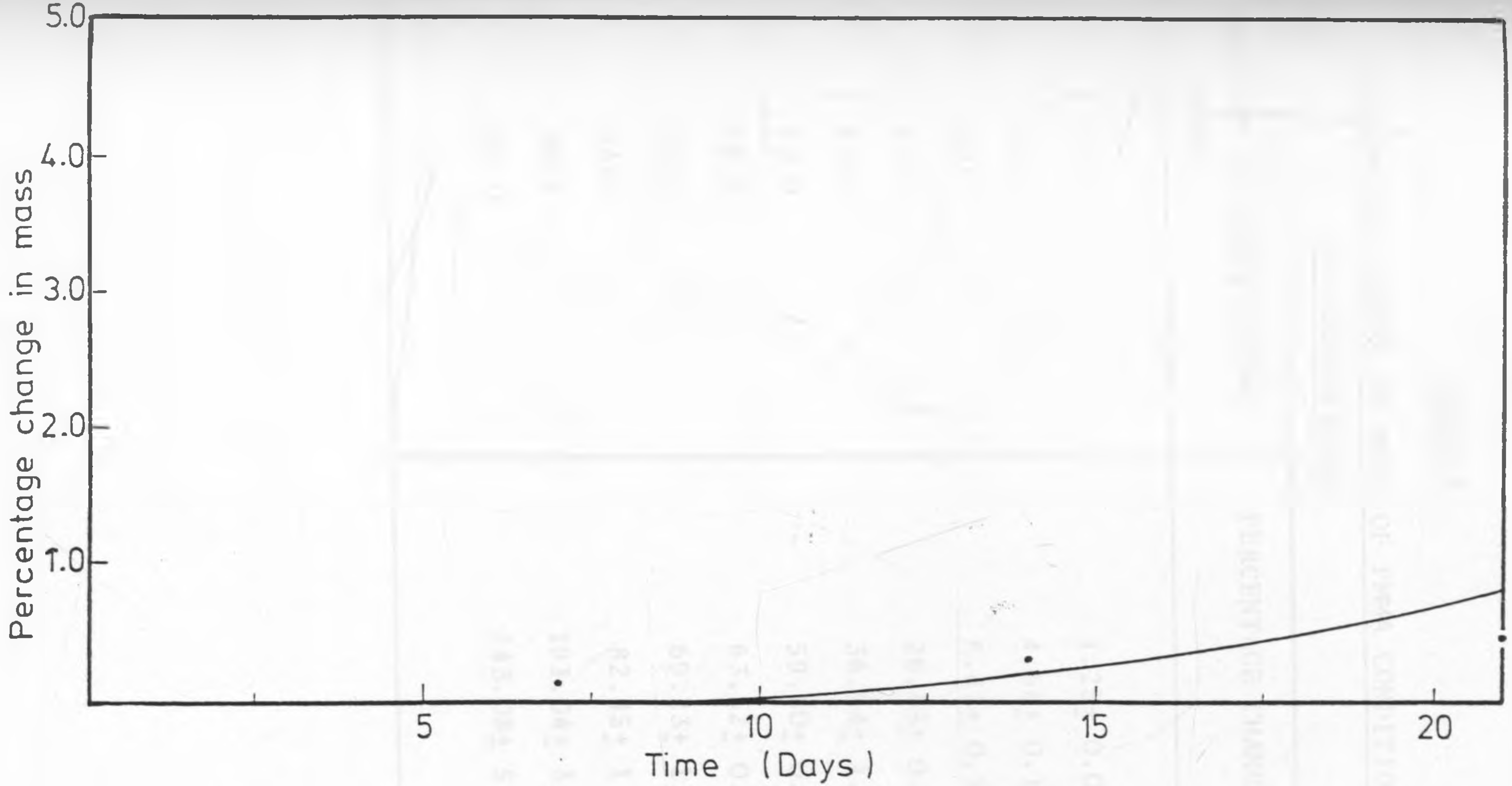


Fig. 36. Percentage change in mass with duration of conditioning of PMMA in ethanol.

TABLE 4

PERCENTAGE CHANGE OF MASS OF PMMA CONDITIONED IN ACETONITRILE

DURATION OF CONDITIONING (HRS)	PERCENTAGE CHANGE IN MASS
0.5	1.25 ± 0.06
1.0	4.68 ± 0.13
2.0	8.43 ± 0.50
6.0	26.83 ± 0.06
8.0	36.94 ± 1.3
13.0	59.80 ± 0.60
15.0	63.52 ± 0.60
20.0	69.23 ± 1.0
24.0	82.45 ± 1.0
45.5	191.04 ± 3.0
66.0	243.08 ± 5.0

TABLE 5

PERCENTAGE CHANGE OF MASS OF PMMA IN n-BUTANOL

DURATION OF CONDITIONING 'HRS'	PERCENTAGE DECREASE IN MASS
3	0.020 ± 0.005
6	0.030± 0.003
12	0.051± 0.002
24	0.086± 0.003
30	0.090± 0.004
48	0.133± 0.005
72	0.151± 0.002
96	0.161± 0.001
168	0.183± 0.002
336	0.204± 0.002
504	0.221± 0.003

TABLE 6

PERCENTAGE CHANGE OF MASS OF PMMA CONDITIONED IN METHANOL

DURATION OF CONDITIONING HRS	PERCENTAGE CHANGE IN MASS
3	0.10± 0.01
6	0.30± 0.01
12	0.72 ±0.10
24	1.90± 0.10
48	3.60± 0.10
96	7.00 ± 0.20
168	8.15± 0.25
336	12.21± 0.60
504	15.36± 0.41

TABLE 7

PERCENTAGE CHANGE OF MASS OF PMMA CONDITIONED IN ETHYLENE GLYCOL

DURATION OF IMMERSION (HRS)	PERCENTAGE CHANGE IN MASS (DECREASE)
3 hrs	0.038 ± 0.004
6 hrs	0.046 ± 0.002
12 hrs	0.088 ± 0.010
24 hrs	0.105 ± 0.010
48 hrs	0.156 ± 0.021
72 hrs	0.266 ± 0.020
96 hrs	0.200 ± 0.008
168 hrs	0.271 ± 0.004
336 hrs	0.361 ± 0.010
504 hrs	0.445 ± 0.010

TABLE 8.

PERCENTAGE CHANGE OF MASS OF PMMA AFTER CONDITIONING IN ETHANOL

DURATION OF CONDITIONING (DAYS)	PERCENTAGE CHANGE OF MASS
7	0.142 ± 0.020
14	0.326 ± 0.0005
21	0.459 ± 0.010

TABLE 9

DENSITY OF PMMA AFTER CONDITIONING IN ACETONITRILE

DURATION OF CONDITIONING (IN HRS)	DENSITY* g/cm^3
0.5	1.1832±0.0009
1.0	1.1795±0.0009
2.0	1.1748±0.0009
6.0	1.1720±0.0020
8.0	1.1604±0.0005
13.0	1.1347± 0.001
15.0	1.1236± 0.001
20.0	1.1134± 0.002
24.0	1.1079± 0.002
45.5	1.0912± 0.001
66	1.0439± 0.009

* Densities were measured for the PMMA samples that had acquired equilibrium mass.

TABLE 10

DENSITY OF PMMA AFTER CONDITIONING IN METHANOL

DURATION OF CONDITIONING (HRS)	DENSITY g/cm^3
3	1.1807 ± 0.001
6	1.1792 ± 0.001
12	1.1778 ± 0.003
24	1.1787 ± 0.0003
48	1.1763 ± 0.0008
96	1.1602 ± 0.001
168	1.1528 ± 0.0009
336	1.1384 ± 0.0009
504	1.1265 ± 0.002

TABLE 11

DENSITY OF PMMA AFTER CONDITIONING IN ETHYLENE GLYCOL

DURATION OF CONDITIONING (DAYS)	DENSITY g/cm^3
7	1.1822 ± 0.002
14	1.1812 ± 0.0004
21	1.1780 ± 0.0003

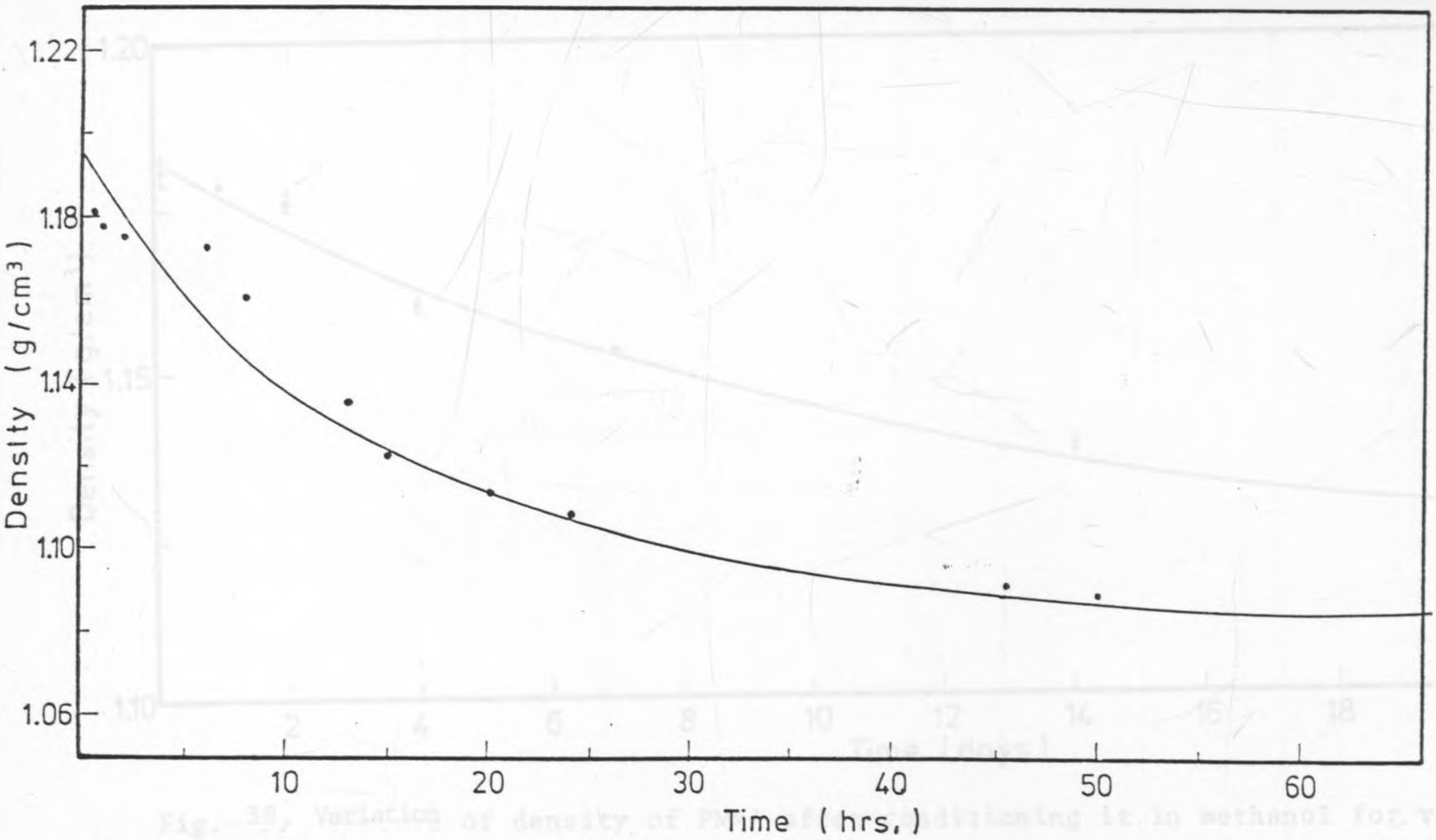


Fig. 37. Variation of density of PMMA after conditioning it in acetonitrile for various durations.

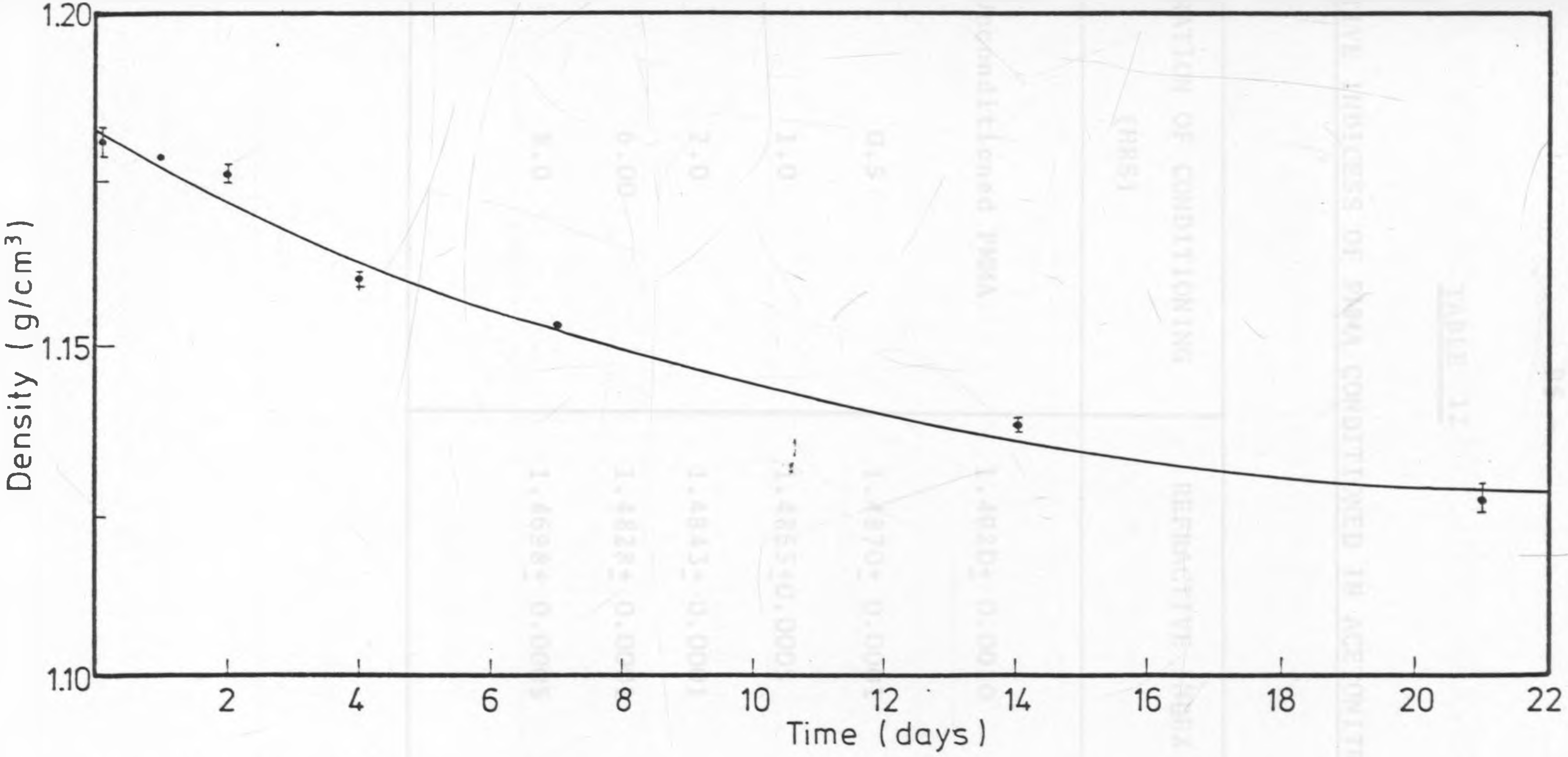


Fig. 38. Variation of density of PMMA after conditioning it in methanol for various durations.

TABLE 12

REFRACTIVE INDICESS OF PMMA CONDITIONED IN ACETONITRILE

DURATION OF CONDITIONING (HRS)	REFRACTIVE INDEX
Unconditioned PMMA	1.4920± 0.0010
0.5	1.4870± 0.0001
1.0	1.4855±0.0005
2.0	1.4843± 0.0001
6.00	1.4828± 0.0001
8.0	1.4698± 0.0005

TABLE 13

REFRACTIVE INDICES OF PMMA AFTER CONDITIONING IN n-BUTANOL

DURATION OF CONDITIONING (HRS)	REFRACTIVE INDEX
3	1.4919 ± 0.0001
6	1.4914 ± 0.0020
12	1.4912 ± 0.0004
30	1.4911 ± 0.0002
48	1.4909 ± 0.0009
72	1.4907 ± 0.0007
96	1.4904 ± 0.0005

TABLE 14

REFRACTIVE INDICES OF PMMA AFTER CONDITIONING IN METHANOL

DURATION OF CONDITIONING (HRS)	REFRACTIVE INDEX
3	1.4909 ± 0.0002
6	1.4882 ± 0.0001
12	1.4880 ± 0.0001
24	1.4865 ± 0.0002
48	1.4863 ± 0.0004
72	1.4860 ± 0.0001
96	1.4850 ± 0.0003

TABLE 15

REFRACTIVE INDICIES OF PMMA CONDITIONING IN ETHYLENE GLYCOL

DURATION OF CONDITIONING (HRS)	REFRACTIVE INDEX
3	1.4916 ± 0.0001
6	1.4912 ± 0.0004
12	1.4910 ± 0.0002
24	1.4902 ± 0.0001
48	1.4900 ± 0.0003
72	1.4897 ± 0.0001
96	1.4892 ± 0.0010

TABLE 16

REFRACTIVE INDICES OF UNSTRESSED PMMA AFTER CONDITIONING IN ETHANOL

DURATION OF CONDITIONING (HRS)	REFRACTIVE INDEX
3	1.4923± 0.0001
6	1.4922±0.0003
12	1.4917± 0.0003
24	1.4918± 0.0004
48	1.4916± 0.0004
72	1.4913± 0.0001
96	1.4910± 0.0001

The variation of density with duration of conditioning is illustrated in Figs. 37 and 38. The variation of density for PMMA conditoned in n-butanol, ethylene glycol and ethanol was comparatively less significant. The change of density for samples conditioned in n-butanol and ethylene glycol was mainly due to the decrease in mass. However in all environments, the density showed a decrease with time.

5.5.0 Refractive indices

Tables (12-16) show the refractive indices of PMMA conditioned in acetonitrile, n-butanol, methanol, ethylene glycol and ethanol as measured using the sodium D lines. It was observed that the refractive index of PMMA decreased with duration of conditioning in these solvents.

5.6.0 Concluding remarks

The results presented in this section show that the solvents used in this study had definite effects on the photoelastic properties of PMMA. The extent of the effect depended on the duration for which the PMMA was conditioned in the solvents. The refractive indices and density values showed general decrease with the duration of conditioning. A detailed analysis and discussion of these results will be given in chapter 6.

CHAPTER 6

ANALYSIS AND DISCUSSION OF RESULTS.

6.0.0. Introduction

In this chapter, the influence of the solvents used in this study on the stress-induced birefringence of PMMA is analysed and discussed. From the load-fringe order relations presented in chapter 5, the material fringe value and stress-optical coefficient for the PMMA used in this study, are deduced for various solvents conditioning. The influence of the solvents on the polarizability per unit volume (β), resulting from changes of refractive indices (see equation 1) and the influence of the solvents on molecular polarizability anisotropy ($\alpha_2 - \alpha_1$) (see equation 9), deduced from stress-optical coefficient values for solvent conditioned PMMA are presented and discussed. Finally discussions of these observations at the macromolecular level is presented and conclusions drawn.

6.1.0 The influence of solvents on stress induced birefringence

The absolute values of the stress-induced birefringence $|\Delta|$ were obtained from the measured relative retardation values presented in chapter 5, using the equation

$$|\Delta| = \delta/t \qquad \ldots(32)$$

where δ is the relative retardation and t is the thickness of the PMMA sample. For the linear part of the load-fringe order plots (Figs. 22-26), the strains are very small and therefore negligible. The thickness t is thus taken to be that of the unstressed sample.

Figs. 39-43 show the plots of the absolute birefringence values versus stress difference (σ_2 - σ_1), under compression for poly(methyl methacrylate) conditioned in acetonitrile, n-butanol, methanol, ethylene glycol and ethanol respectively, for various durations. The plots for PMMA conditioned in acetonitrile and methanol (see Figs 39 and 41) respectively, show that the absolute stress-induced birefringence increases with increase in stress difference. The effect of long durations of conditioning the PMMA in these solvents is to increase the change of birefringence per stress difference. This is shown by the increase of slopes of the initial linear parts of these curves. Tables 17 and 19 give the values of these slopes as a function of the duration of conditioning of the PMMA in both acetonitrile and methanol.

The initial linear variation of the stress-induced birefringence with stress-difference, at low levels of the stress-difference, is in agreement with

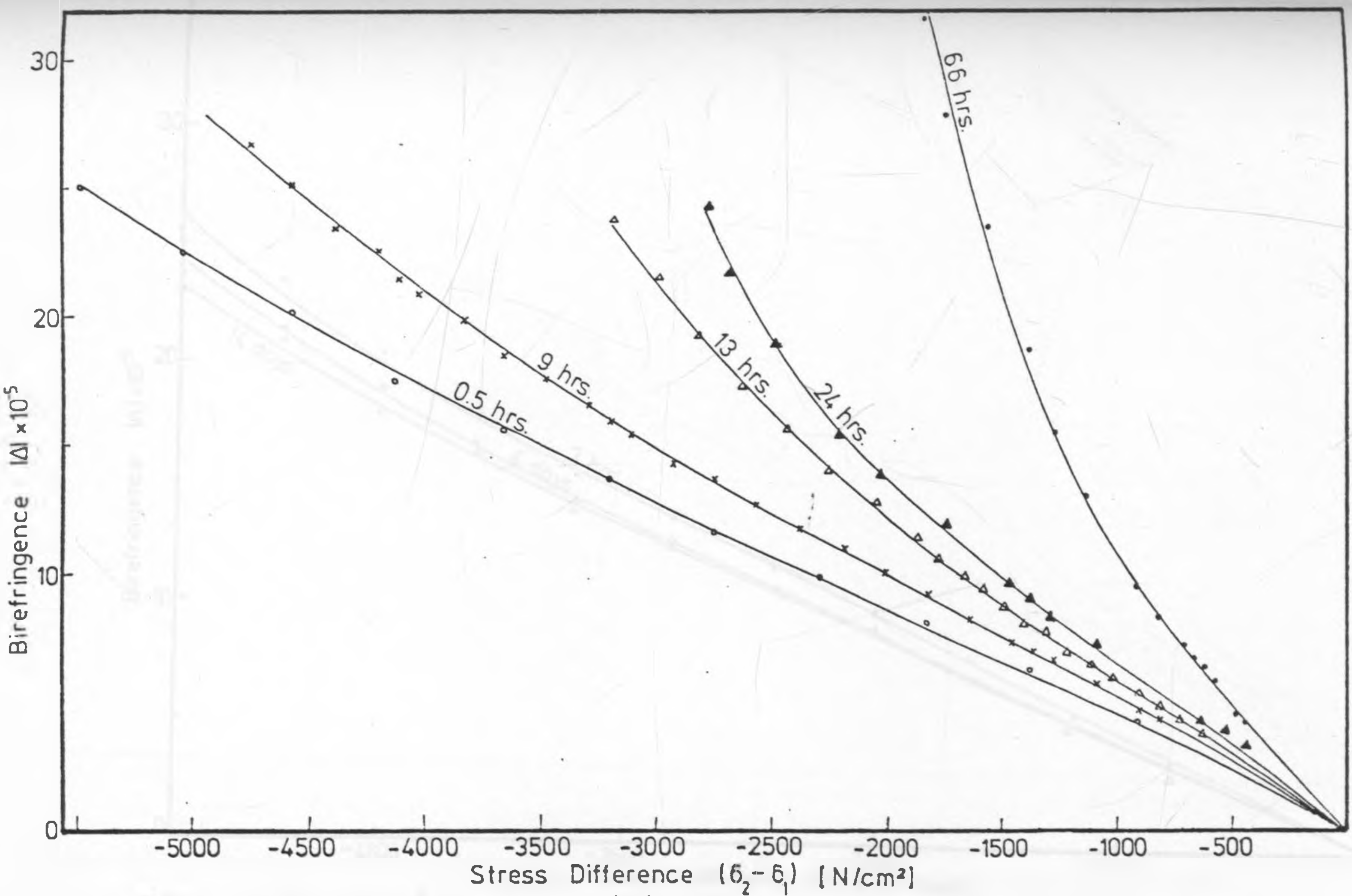


Fig. 39. Absolute Birefringence |Δ|- Stress difference relation for PMMA conditioned in acetonitrile for various durations.

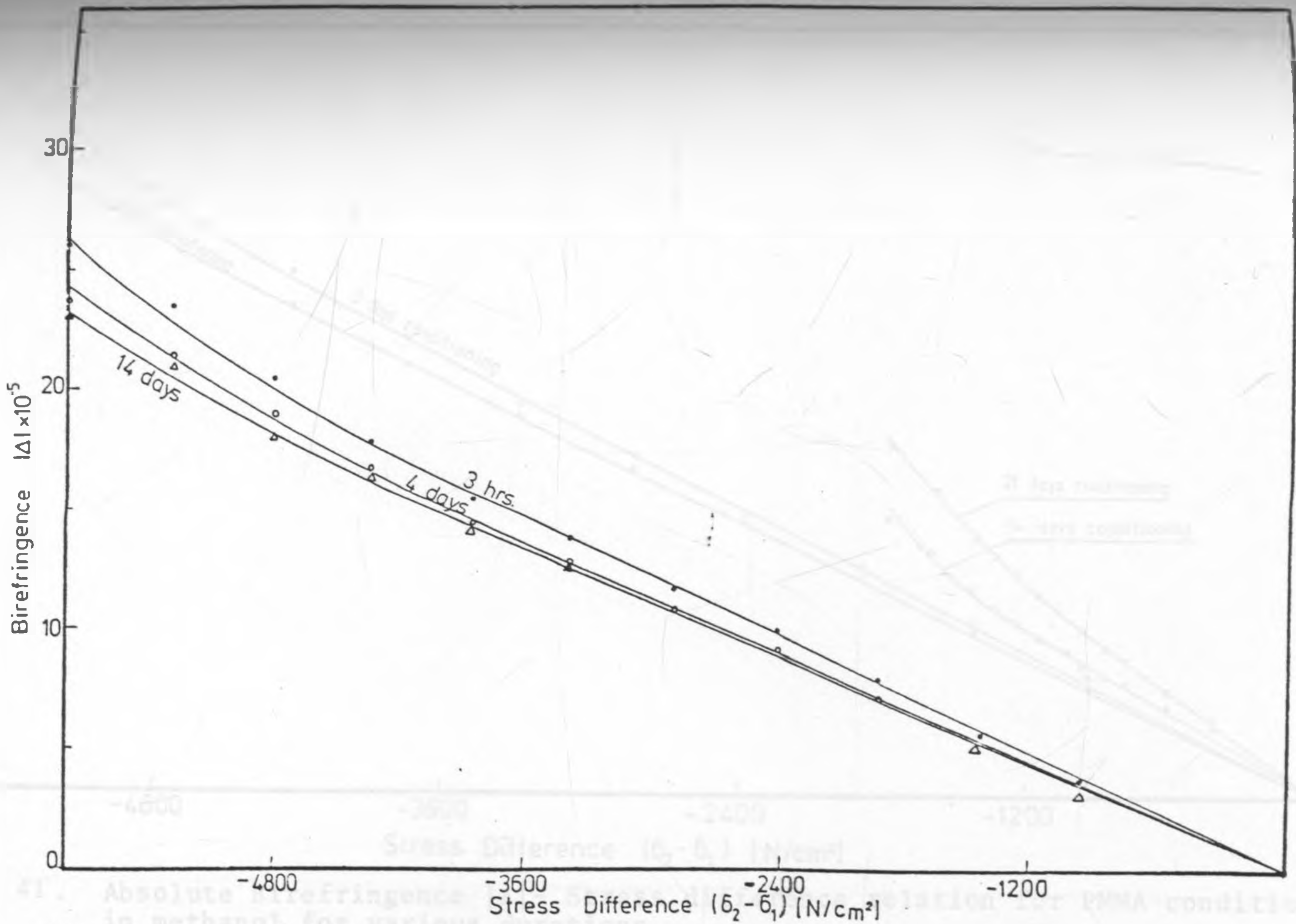


Fig. 40. Absolute Birefringence $|\Delta|$- Stress difference relation for PMMA conditioned in n-butanol for various durations.

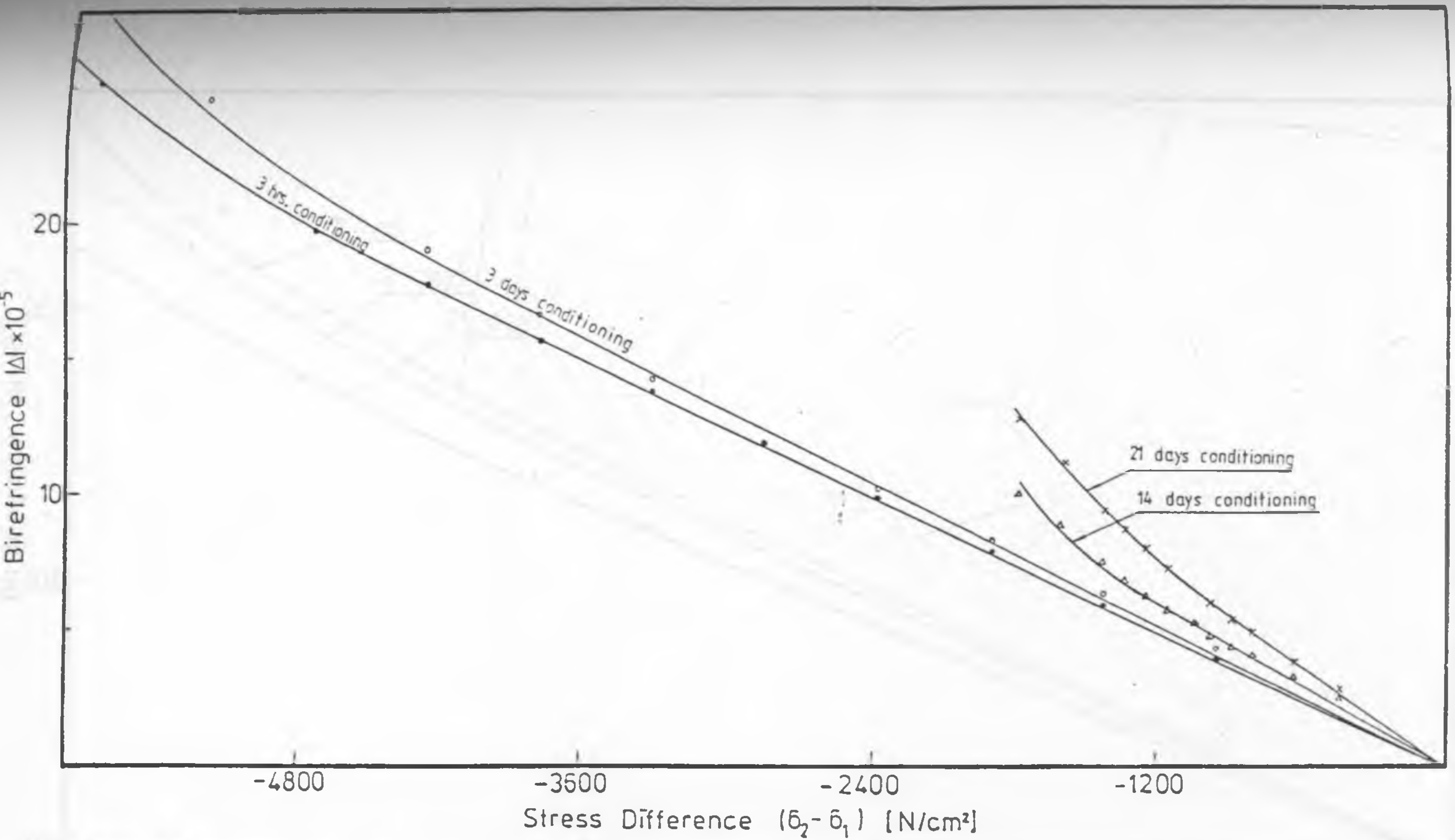


Fig. 41. Absolute Birefringence $|\Delta|$ - Stress difference relation for PMMA conditioned in methanol for various durations.

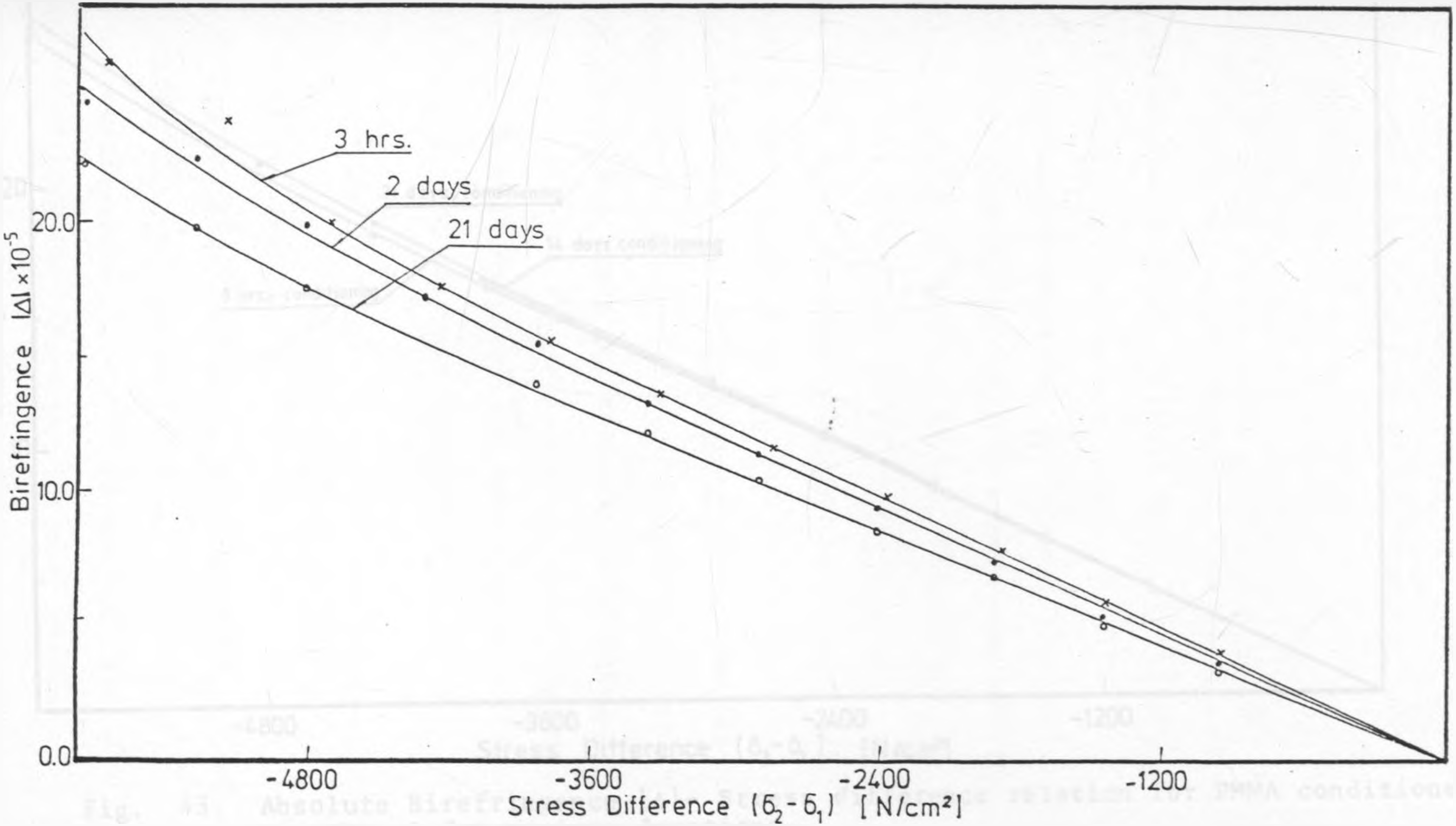


Fig. 42. Absolute Birefringence |Δ| - Stress difference relation for PMMA conditioned in. ethylene glycol for various durations.

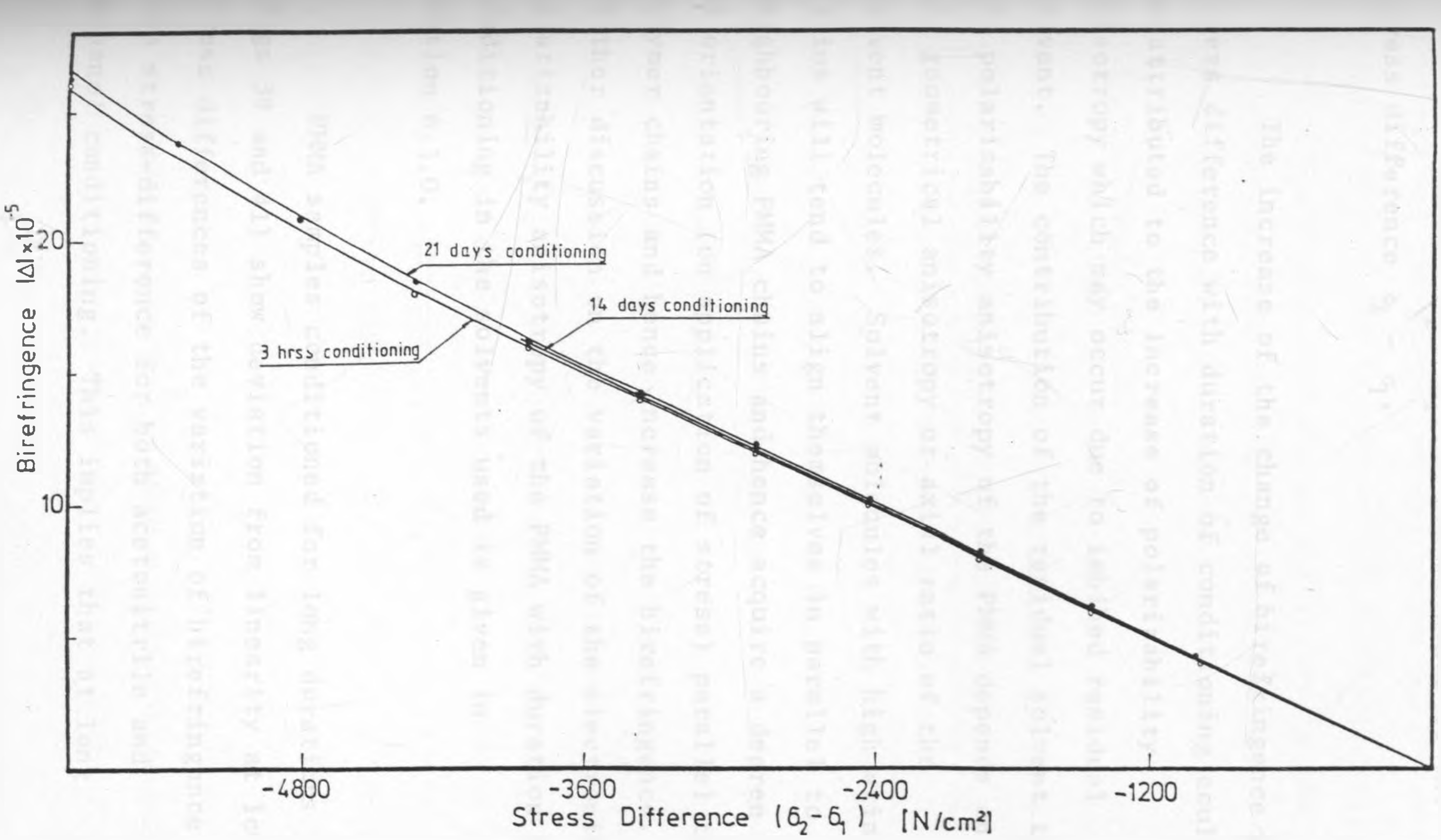


Fig. 43. Absolute Birefringence |Δ|- Stress difference relation for PMMA conditioned in ethanol for various durations.

Brewster's law which generally postulates that the birefringence $|n_2 - n_1|$ is proportional to the stress difference $\sigma_2 - \sigma_1$.

The increase of the change of birefringence per stress difference with duration of conditioning could be attributed to the increase of polarizability anisotropy which may occur due to imbibed residual solvent. The contribution of the residual solvent to the polarizability anisotropy of the PMMA depends on the geometrical anisotropy or axial ratio of the solvent molecules. Solvent molecules with high axial ratios will tend to align themselves in parallel to neighbouring PMMA chains and hence acquire a degree of orientation (on application of stress) parallel to polymer chains and hence increase the birefringence. Further discussion on the variation of the electronic polarizability anisotropy of the PMMA with duration of conditioning in the solvents used is given in section 6.3.0.

PMMA samples conditioned for long durations (Figs 39 and 41) show deviation from linearity at low stress differences of the variation of birefringence with stress-difference for both acetonitrile and methanol conditioning. This implies that at long durations of conditioning, more intermolecular bonds are broken and the polymer chains become more flexible. On application of stress, the chains deform elastically at very low stresses. At higher stress levels the chains undergo plastic deformation which may be accompanied by flow due to enhanced chain mobility.

Figs. 40 and 42 show the plots of birefringence versus stress difference for PMMA conditioned in n-butanol and ethylene glycol, respectively. It is also clear that the birefringence increases with increase in stress difference. The variation of the stress-induced birefringence with stress difference is linear to fairly high stress levels for both short and long duration conditioned samples in both solvents. Contrary to what was observed for both acetonitrile and methanol conditioning, the change of the stress-induced birefringence per stress difference, $|\Delta|/(\sigma_2 - \sigma_1)$ decreases with duration of conditioning of PMMA in n-butanol and ethylene glycol respectively. Tables 18 and 20 give the values of $|\Delta|/(\sigma_2 - \sigma_1)$ as a function of duration of conditioning in n-butanol and ethylene glycol.

The decrease in the change of birefringence with stress difference means that the ease with which

TABLE 17.

THE CHANGE OF BIREFRINGENCE PER STRESS DIFFERENCE FOR PMMA CONDITIONED IN ACETONITRILE.

DURATION OF CONDITIONING HRS	$\lvert\Delta\rvert / \sigma_2 - \sigma_1$ $(cm^2/N) \times 10^{-8}$
0.5	4.25
8	4.99
13	5.73
24	6.43
66	9.44

TABLE : 18

THE CHANGE OF BIREFRINGENCE PER STRESS DIFFERENCE FOR PMMA CONDITIONED IN n- BUTANOL

DURATION OF CONDITIONING HRS	$\lvert\Delta\rvert(\sigma_2 - \sigma_1)$ (cm^2/N) x10^{-8}
3	4.07
96	3.75
336	3.66

TABLE 19.

THE CHANGE OF BIREFRINGENCE PER STRESS DIFFERENCE FOR PMMA CONDITIONED IN METHANOL.

DURATION OF CONDITIONING HRS	$\lvert\Delta\rvert/(\sigma_2 - \sigma_1)$ $(cm^2/N) \times 10^{-8}$
3	4.16
72	4.38
336	4.97
504	6.16

TABLE 20.

THE CHANGE OF BIREFRINGENCE PER STRESS DIFFERENCE FOR PMMA CONDITIONED IN ETHYLENE GLYCOL.

DURATION OF CONDITIONING HRS.	$\lvert\Delta\rvert/(\sigma_2 - \sigma_1)$ $(cm^2/N) \times 10^{-8}$
3	4.14
48	3.93
504	3.57

TABLE : 21

THE CHANGE OF BIREFRINGENCE PER STRESS DIFFERENCE FOR PMMA CONDITIONED IN ETHANOL

DURATION OF CONDITIONING HRS	$\lvert\Delta\rvert/(\sigma_2 - \sigma_1)$ $(cm^2/N) \times 10^{-8}$
3	4.14
336	4.20
504	4.23

the polymer chains orient in response to the applied stress decreases with duration of conditioning in these two solvents. This is explicable if one assumes that there is increased stiffness of the polymer chains as a result of the desorption of residual moisture from the PMMA samples (see chapter 5 section 5.3.0). The increased rigidity of the polymer chains could be attributed to reformation of intermolecular bonds and more interaction of the strongly polar side carbomethoxy ($COOCH_3$) groups. These increase steric hinderance and so chain flexibility is reduced.

Samples conditioned in ethanol do not show the influence of the solvents on the stress-induced birefringence until after a long time of conditioning. Figure 43 and table 21 illustrate this observation. Even after three weeks conditioning, there is a very slight increase on the change of birefringence per stress difference (see Fig. 43). The birefringence varies linearly with stress difference upto about the stress difference of -4226 N/cm^2.

6.2.0 Influence of solvents on the material fringe value and stress optical coefficient of PMMA

The material fringe value and stress optical coefficient are photoelastic parameters characteristic of a given transparent material. They indicate the ease with which anisotropy is produced in the structural arrangement of a transparent material when it is subjected to mechanical stress. The material fringe value and stress optical coefficient are also functions of the wavelength of the incident light used and so their values are always stated for the particular light used. The influence of the characteristic incident light on these photoelastic parameters arises from the electric field associated with it which is responsible for molecular and electronic polarizabilities (see chapt. 3.2.0). A high value of the stress optical coefficient means the material is highly stress birefringent. Such a material would have a low material fringe value. A meterial which is less stress birefringent will have a characteristic low stress-optical coefficient and high fringe value.

The material fringe values for the various PMMA samples were determined using the relation

$$f_{\sigma} = \frac{-4F}{\Pi N}\left[\frac{1}{D-2y} + \frac{1}{D+2y}\right].$$

where F is the load, N is the fringe order, D is the diameter of a sample and y is the distance along the the line drawn as the diameter on the sample, from the centre of the disk to the point of reference (Fig. 16). F/N was obtained from the slopes of the intial linear parts of Load-fringe order plots. The stress optical coefficient C was determined using the equation

$$f_\sigma = \lambda/C$$

where λ = 5893A for the incident sodium yellow light used.

Poly(methyl methacrylate) is known to have a very low stress optical sensitivity (ability to exhibit double refraction of light when placed under stress), comparable to that of most inorganic glasses. {39} . Its reported material fringe value in tension for sodium yellow light is -1541.20 N/cm {40} . The PMMA used in this study had at room temperature a material fringe value under compression $f_\delta = 1415.39 \pm 0.40$ N/cm for sodium light of wavelength λ= 5893A. The stress optical coefficient was $(4.16 \pm 0.004) \times 10^{-8} Cm^2/N$.

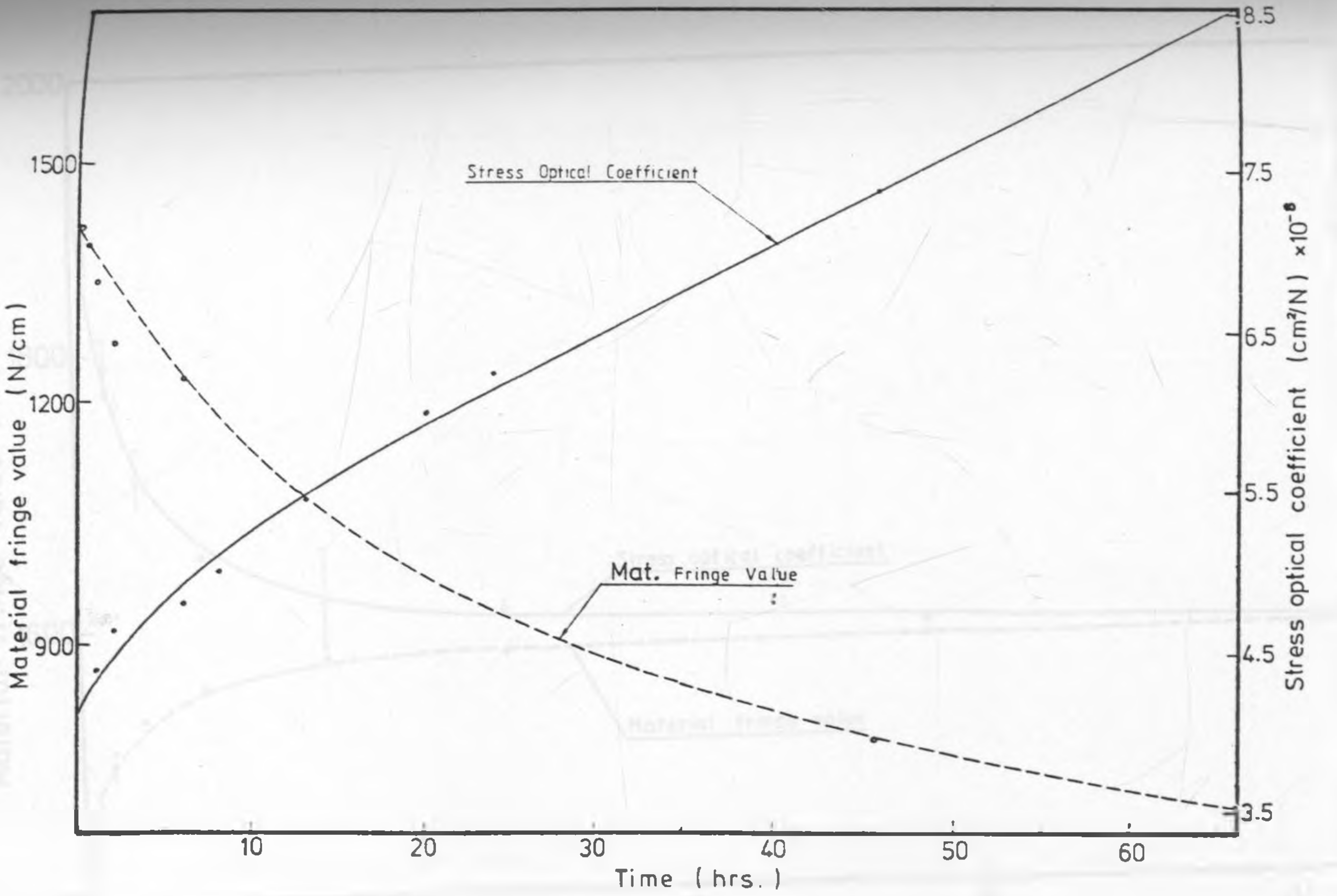


Fig. 44. Variation of the material fringe value and the Stress optical coefficient of PMMA after conditioning in acetonitrile for various durations.

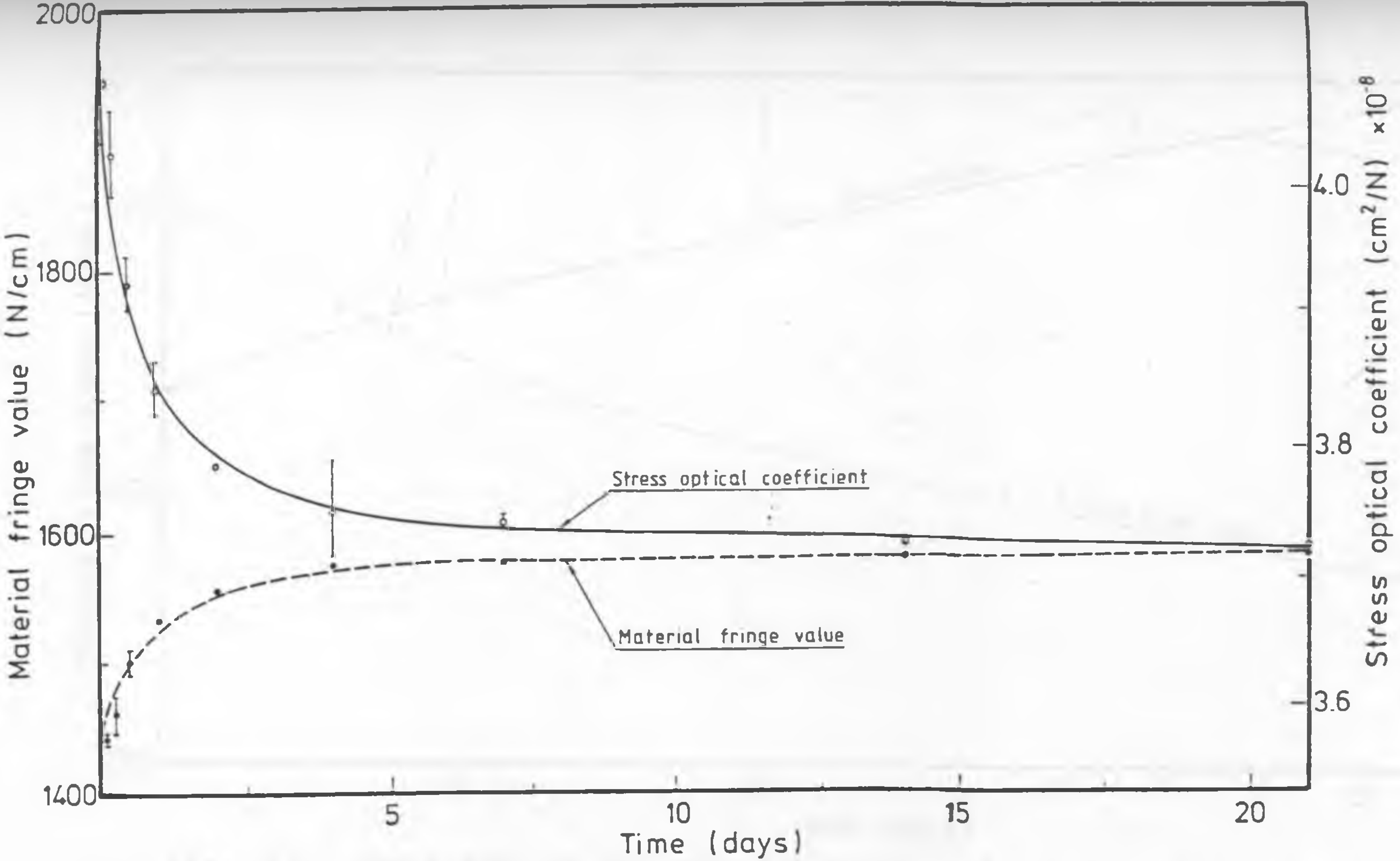


Fig. 45. Variation of the Material fringe value and the Stress optical coefficient of PMMA after conditioning in n-butanol for various durations.

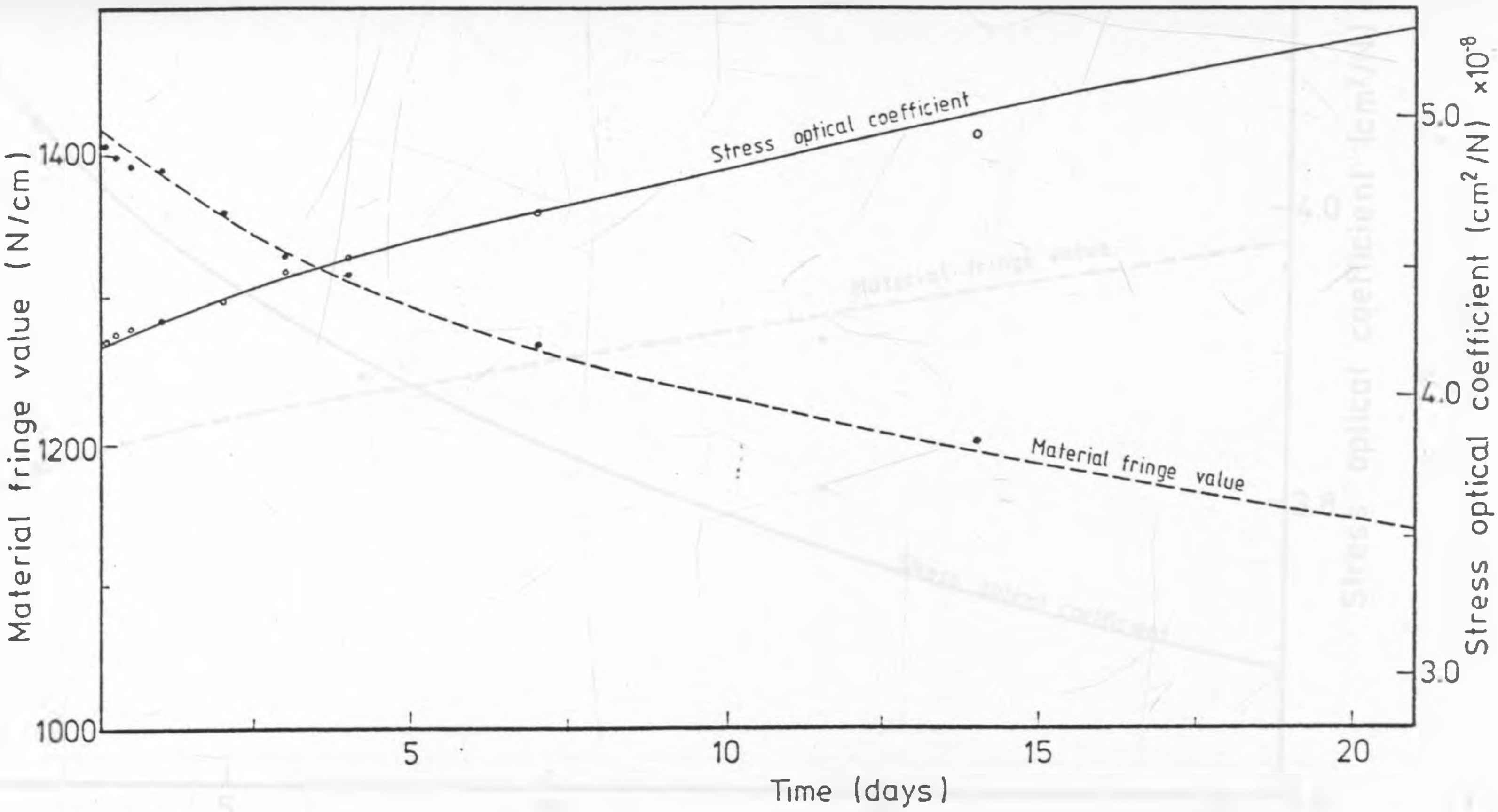


Fig. 46. Variations of the material fringe value and the Stress optical coefficient of PMMA after conditioning in methanol for various durations.

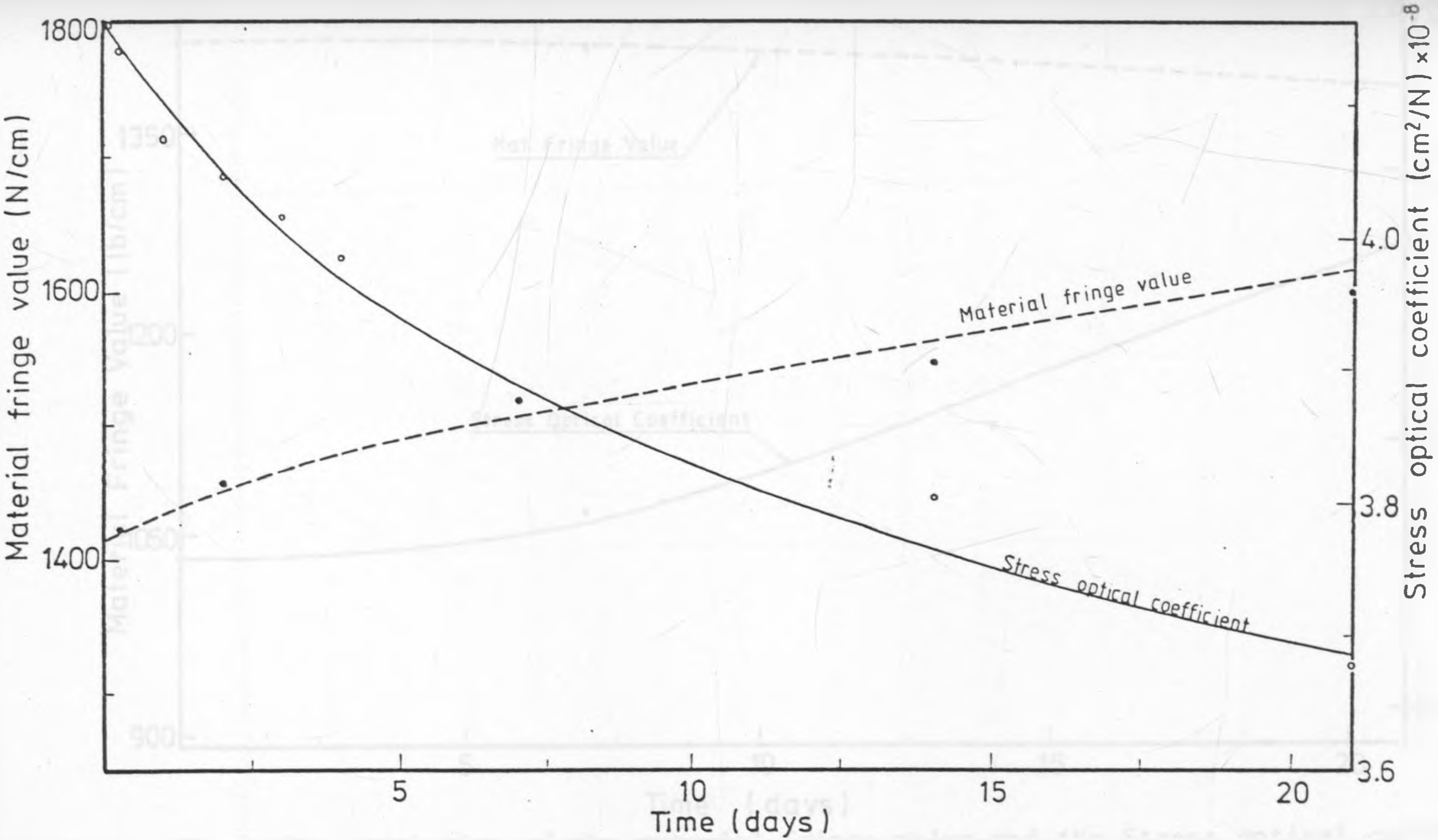


Fig. 4.7. Variation of the Material fringe value and the Stress optical coefficient of PMMA after conditioning in ethylene glycol.

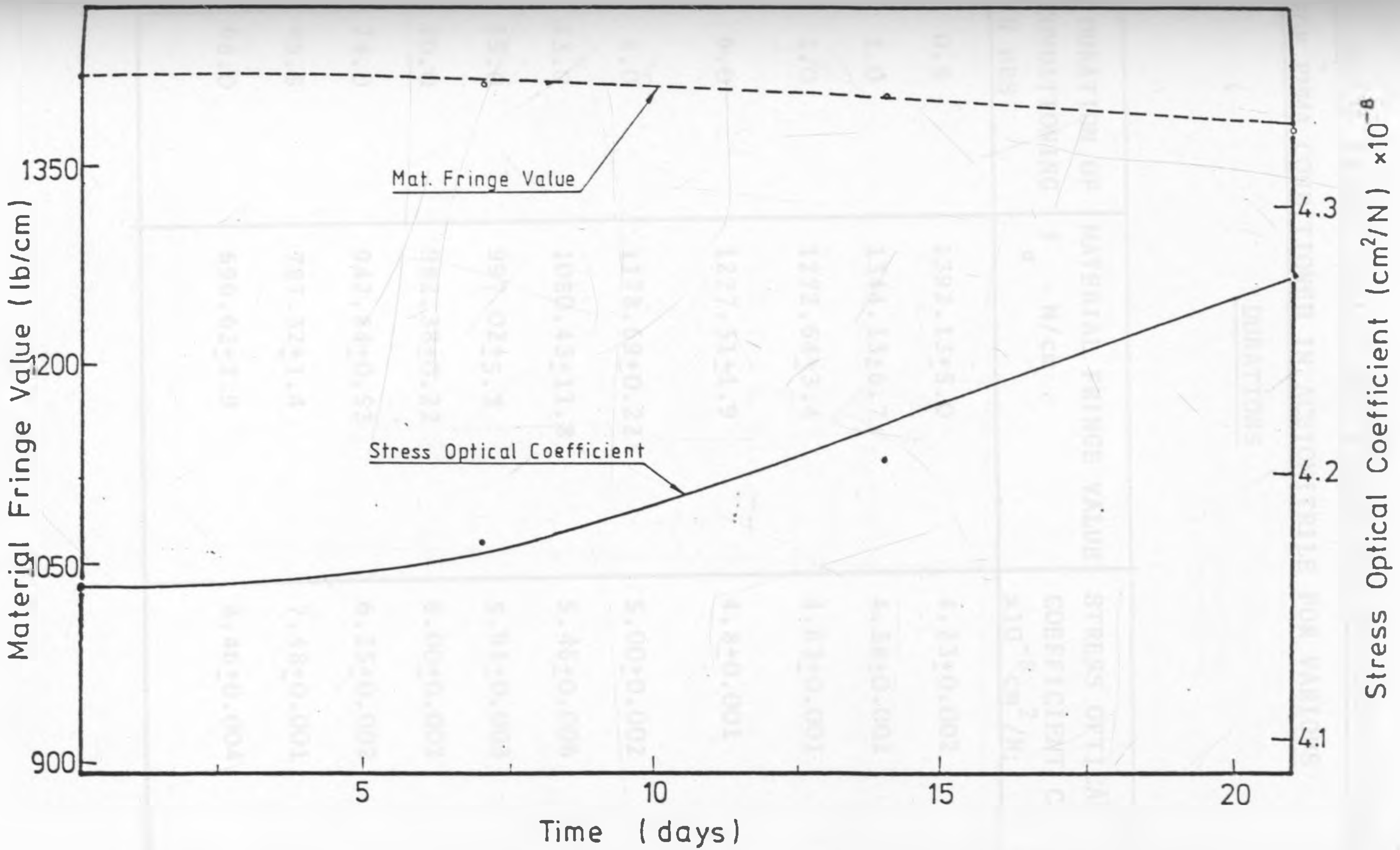


Fig. 48. Variation of the material fringe value and the Stress optical coefficient of PMMA after conditioning in ethanol for various durations.

TABLE 22

MATERIAL FRINGE VALUES AND STRESS OPTICAL COEFFICIENTS FOR PMMA CONDITIONED IN ACETONITRILE FOR VARIOUS DURATIONS

DURATION OF CONDITIONING IN HRS	MATERIAL FRINGE VALUE f_σ N/cm	STRESS OPTICAL COEFFICIENT C $\times 10^{-8} cm^2/N$;
0.5	1392.13±5.0	4.23±0.002
1.0	1344.13±6.7	4.38±0.002
2.0	1272.64±3.4	4.63±0.001
6.0	1227.31±1.9	4.8±0.001
8.0	1178.69±0.22	5.00±0.002
13.0	1080.43±11.8	5.45±0.006
15.0	997.02±5.3	5.91±0.003
20.0	982.38±0.22	6.00±0.002
24.0	942.84±0.53	6.25±0.002
45.5	787.32±1.4	7.48±0.001
66.0	696.62±2.9	8.46±0.004

TABLE 23

MATERIAL FRINGE VALUES AND STRESS OPTICAL COEFFICIENT FOR PMMA CONDITIONED IN n-BUTANOL FOR VARIOUS DURATIONS

DURATION OF CONDITIONING HRS	MATERIAL FRINGE VALUE f_σ N/cm	STRESS OPTICAL COEFFICIENT C $x10^{-8}cm^2/N$
3	1444.48 ± 0.22	4.08 ± 0.001
6	1464.23 ± 13.3	4.02 ± 0.003
12	1502.09 ± 8.9	3.92 ± 0.002
24	1533.76 ± 0.22	3.84 ± 0.002
30	1546.89 ± 13.3	3.81 ± 0.003
48	1557.52 ± 0.22	3.78 ± 0.001
72	1561.25 ± 0.36	3.77 ± 0.001
96	1572.69 ± 4.4	3.75 ± 0.004
168	1576.73 ± 0.22	3.74 ± 0.002
336	1583.01 ± 0.22	3.72 ± 0.001
504	1584.39 ± 0.22	3.72 ± 0.001

TABLE 24

MATERIAL FRINGE VALUES AND STRESS OPTICAL COEFFICIENTS FOR PMMA CONDITIONED IN METHANOL FOR VARIOUS DURATIONS

DURATION OF CONDITIONING	MATERIAL FRINGE VALUE (N/cm) f_σ N/cm	STRESS OPTICAL COEFFICIENT C $x10^{-8}(cm^2/N$
3	1408.81± 5.8	4.18 ± 0.002
6	1400.67± 0.22	4.21± 0.002
12	1396.13± 0.22	4.22± 0.002
24	1392.04± 2.7	4.23± 0.001
48	1362.99± 2.2	4.32± 0.001
72	1331.58± 1.5	4.43± 0.001
96	1318.95± 2.2	4.47± 0.001
168	1269.80± 0.40	4.64± 0.002
336	1202.45± 0.49	4.90± 0.001
504	987.68± 3.3	5.97± 0.001

TABLE 25

MATERIAL FRINGE VALUES AND STRESS OPTICAL COEFFICIENTS FOR PMMA CONDITIONED IN ETHYLENE GLYCOL FOR VARIOUS DURATIONS.

DURATION OF CONDITIONING (HRS)	MATERIAL FRINGE VALUE f_σ N/cm	STRESS OPTICAL COEFFICIENT C $\times 10^{-8}$ cm^2/N
3	1417.67 ± 0.40	4.16 ± 0.001
6	1423.62 ± 0.40	4.14 ± 0.001
12	1424.69 ± 0.09	4.13 ± 0.001
24	1447.86 ± 0.44	4.07 ± 0.001
48	1457.38 ± 0.49	4.04 ± 0.001
72	1468.82 ± 0.02	4.01 ± 0.001
96	1480.16 ± 0.02	3.98 ± 0.001
168	1519.35 ± 0.20	3.88 ± 0.002
336	1549.91 ± 0.22	3.80 ± 0.001
504	1602.98 ± 0.22	3.68 ± 0.001

TABLE 26

MATERIAL FRINGE VALUE AND STRESS OPTICAL COEFFICIENTS FOR PMMA CONDITIONED IN ETHANOL FOR VARIOUS DURATIONS

DURATION OF CONDITIONING	MATERIAL FRINGE VALUE f_σ N/cm	STRESS OPTICAL COEFFICIENT C $\times 10^{-8} cm^2/N$
UNCONDITIONED	1415.39±0.40	4.16± 0.001
3	1415.39±0.40	4.16± 0.001
6	1415.39±0.40	4.16± 0.001
12	1415.39±0.40	4.16± 0.001
168	1410.50±0.40	4.18± 0.002
336	1399.42±0.44	4.21± 0.001
504	1376.08±0.22	4.28± 0.001

The influence of solvents on the material fringe value f_σ and stress optical coefficient C for PMMA is shown in Figs. 44-48. The material fringe values and stress optical coefficients are given in tables (22-26). Figs. 44 and 46 show a decrease in the material fringe value (dotted curves), while the stress optical coefficient increases with duration of conditioning. This implies that the stress optical sensitivity of PMMA after conditioning in acetonitrile and methanol increased.

This could be explained by the fact that unconditioned PMMA has substantial free volume. The free volume is the intermolecular spaces, the size of which is determined by several factors; amongst which are the molecular size, size of pendant groups and inherent steric forces. Intermolecular forces also play a big role in determining the free volume. It is assumed that imbibed solvent occupies the intermolecular spaces and this is determined by the solvent-solute molecular interaction.

Depending on the solvent-solute interaction it is conceivable that in the cases of PMMA-acetonitrile and PMMA-methanol systems the polymer intermolecular bonding forces are weakened. The imbibed solvents tend to separate the polymer chains thus increasing the PMMA intermolecular distances. It can therefore be expected that after drying the PMMA samples to equilibrium mass, there is more free volume available to the polymer chains. Also some residual solvent remains in the polymer.

This reduces the stiffness and increases the flexibility of the polymer chains. The polar interaction between the polar pendant ester groups decreases. On application of mechanical stress, chain orientation in response to stress increases because of the increased chain deformability and mobility. The stress optical sensitivity therefore increases; hence we are actually talking of mechanically assisted molecular and molecular polarizability in preferred directions. Fig. 48 shows an effect on PMMA by ethanol similar to that produced by acetonitrile and methanol but the changes for PMMA conditioned in ethanol are small.

Figs. 45 and 47 for samples conditioned in n-butanol and ethylene glycol show that the material fringe value increases with duration of conditioning in both solvents. The stress optical coefficient decreases with duration of conditioning. Contrary to the observations for acetonitrile, methanol and ethanol, the stress optical sensitivity of PMMA decreases after conditioning in both n-butanol and ethylene glycol. This could also be attributed to increased stiffness of the molecular chains and enhanced polar interaction due to desorption of the residual moisture which has a plasticising effect. Chain deformation and mobility in response to mechanical stress is thus reduced and so is the stress optical sensitivity.

The rapid variation of the material fringe value and the stress optical coefficient of the PMMA at short durations of conditioning in n-butanol can be explained if we conceive of a fast rate of desorption of residual moisture due to a high affinity of the n-butanol for water. As this desorption tends to completetion at long durations of conditioning, the PMMA samples tend to acquire some finite equilibrium mass. The property change due to the desorption of the residual moisture then becomes minimal; hence the observed asymptotic variation of the material fringe value and stress optical coefficient of the PMMA after long periods of conditioning in n-butanol.

6.3.0 Effect of solvents on Polarizability

The polarizability per unit volume (β) of the PMMA conditioned in the solvents used in this study was calculated using the Lorentz-Lorenz formular (see equation 1 where $\beta = N_A \alpha_e$) . The molecular polarizability anisotropy ($\alpha_2 - \alpha_1$) was calculated for every solvent conditioned PMMA samples, using the relation

$$C = \frac{2\Pi}{45KT} \frac{(\bar{n}^2 + 2)}{\bar{n}} (\alpha_2 - \alpha_1) \qquad \ldots(9)$$

where C is the stress optical coefficient, k is the Boltzman constant, T is absolute temperature and $\bar{n}$ is the average refractive index.

The results of the polarizability per unit volume (β) as a function of the duration of conditioning are given in tables 27-31 for PMMA conditioned in acetonitrile, n-Butanol, methanol, ethylene glycol and ethanol respectively. It is observed that the polarizability per unit volume decreases with duration of conditioning in acetonitrile, n-butanol, methanol and ethylene glycol. This decrease could be attributed to the decrease in refractive index of the PMMA with duration of conditioning in these solvents (see tables 12-16). The refractive index is a function of the molecular structure and the density of a material.

TABLE 27

POLARIZABILITY PER UNIT VOLUME AND MOLECULAR POLARIZABILITY ANISOTROPY FOR PMMA CONDITIONED IN ACETONITRILE

DURATION OF CONDITIONING (HRS)	REFRACTIVE INDEX	POLARIZABILITY PER UNIT VOLUME $\beta \times 10^{-2} m^{-3}$	MOLECULAR POLARIZABILITY ANISOTROPY $(\alpha_2-\alpha_1) \times 10^{-32} m^3$
0.5	1.4870±0.0001	6.8634±0.0009	1.0380±0.0040
1.0	1.4855±0.0005	6.8454±0.0050	1.0761±0.0050
2.0	1.4843±0.0001	6.8309±0.0009	1.1378±0.0030
6.0	1.4828±0.0001	6.8129±0.0009	1.1811±0.0020
8.0	1.4698±0.0005	6.6556±0.0050	1.2416±0.0010

TABLE 28

POLARIZABILITY PER UNIT VOLUME AND MOLECULAR POLARIZABILITY ANISOTROPY FOR PMMA CONDITIONED IN n- BUTANOL

DURATION OF CONDITIONING (HRS)	REFRACTIVE INDEX	POLARIZABILITY PER UNIT VOLUME $\beta x10^{-2}m^{-3}$	MOLECULAR POLARIZABILITY ANISOTROPY $(\alpha_2-\alpha_1)x10^{-32}m^3$
3	1.4919±0.0001	6.9221±0.001	0.9969±0.0002
6	1.4914±0.0020	6.9161±0.021	0.9835±0.0090
12	1.4912±0.0004	6.9137±0.004	0.9589±0.0050
30	1.4911±0.0002	6.9125±0.0003	0.9315±0.007
48	1.4909±0.0009	6.910±0.009	0.9250±0.001
72	1.4907±0.0007	6.9078±0.007	0.9230±0.0010
96	1.4904±0.0005	6.9042+0.005	0.9166±0.0090

TABLE 29

POLARIZABILITY PER UNIT VOLUME AND MOLECULAR POLARIZABILITY ANISOTROPY FOR PMMA CONDITIONED IN METHANOL.

DURATION OF CONDITIONING (HRS)	REFRACTIVE INDEX	POLARIZABILITY PER UNIT VOLUME $\beta \times 10^{-2} m^{-3}$	MOLECULAR POLARIZABILITY ANISOTROPY $(\alpha_2-\alpha_1)\times 10^{-32} m^3$
3	1.4909±0.0002	6.9101±0.0020	1.0229±0.0040
6	1.4882±0.0001	6.8778±0.001	1.0310±0.0010
12	1.4880±0.0001	6.8754±0.0010	1.0344±0.0010
24	1.4865±0.0002	6.8574±0.002	1.0383±0.0020
48	1.4863±0.0004	6.8550±0.002	1.0606±0.002
72	1.4860±0.0001	6.8514±0.001	1.08617±0.001
96	1.4850±0.0003	6.8394±0.003	1.0980±0.0020

TABLE 30

POLARIZABILITY PER UNIT VOLUME AND MOLECULAR POLARIZABILITY ANISOTROPY FOR PMMA CONDITIONED IN ETHYLENE GLYCOL

DURATION OF CONDITIONING (HRS)	REFRACTIVE INDEX	POLARIZABILITY PER UNIT VOLUME $\beta \times 10^{-2}$ m^{-3}	MOLECULAR POLARIZABILITY ANISOTROPY $(\alpha_2-\alpha_1)\times10^{-32}m^3$
3	1.4916±0.0001	6.9185±0.001	1.0156±0.0006
6	1.4912±0.0004	6.9137±0.002	1.0117±0.0006
12	1.4910±0.0002	6.9113±0.002	1.0113±0.0006
24	1.4902±0.0001	6.9018±0.001	0.9959±0.0006
48	1.4900±0.0003	6.8994±0.001	0.9895±0.0006
72	1.4897±0.0001	6.8958±0.001	0.9820±0.0004
96	1.4892±0.0010	6.8898±0.005	0.9746±0.0007

TABLE 31

POLARIZABILITY PER UNIT VOLUME AND MOLECULAR POLARIZABILITY ANISOTROPY FOR PMMA CONDITIONED IN ETHANOL

DURATION OF CONDITIONING (HRS)	REFRACTIVE INDEX	POLARIZABILITY PER UNIT VOLUME $\beta \times 10^{-2}\ m^{-3}$	MOLECULAR POLARIZABILITY ANISOTROPY $(\alpha_2-\alpha_1)\times 10^{-32} m^3$
3	1.4923±0.0001	6.9269±0.001	1.0169±0.0006
6	1.4922±0.0003	6.9257±0.003	1.0169±0.0007
12	1.4917±0.0003	6.9197±0.003	1.0173±0.0007
168	1.4909±0.0004	6.9101±0.003	1.0218±0.0007
336	1.4880±0.0004	6.8754±0.002	1.0317±0.0006
504	1.4863±0.0001	6.8550±0.001	1.0506±0.0002

Imbibed solvents like acetonitrile and methanol could alter the molecular structure of PMMA and change the density hence altering the polarizability per unit volume. N-butanol and ethylene glycol desorbed moisture from the PMMA used in this study. This also could lead to structural changes of the molecular chains and so affect the polarizability. Ethanol shows slight effect in the polarizability per unit volume of PMMA even after long-conditioning.

Tables 27-31 also show values of the optical anisotropy or the molecular polarizability anisotropy $(\alpha_2 - \alpha_1)$ evaluated for every solvent conditioning. It is noted that the optical anisotropy increases with duration of conditioning of the PMMA in acetonitrile and methanol while it decreases with duration of conditioning in n-butanol and ethylene glycol. Ethanol shows little effect on the optical anisotropy. The optical anisotropy in the polymer molecular chains could be explained by the fact that, when incident light strikes a single atom the electric field associated with the light wave distorts the electron cloud of the atom and induces a dipole moment. When the atoms combine to form a molecule like in the molecular chains of PMMA, the molecules may not be isotropic because the interactions between induced

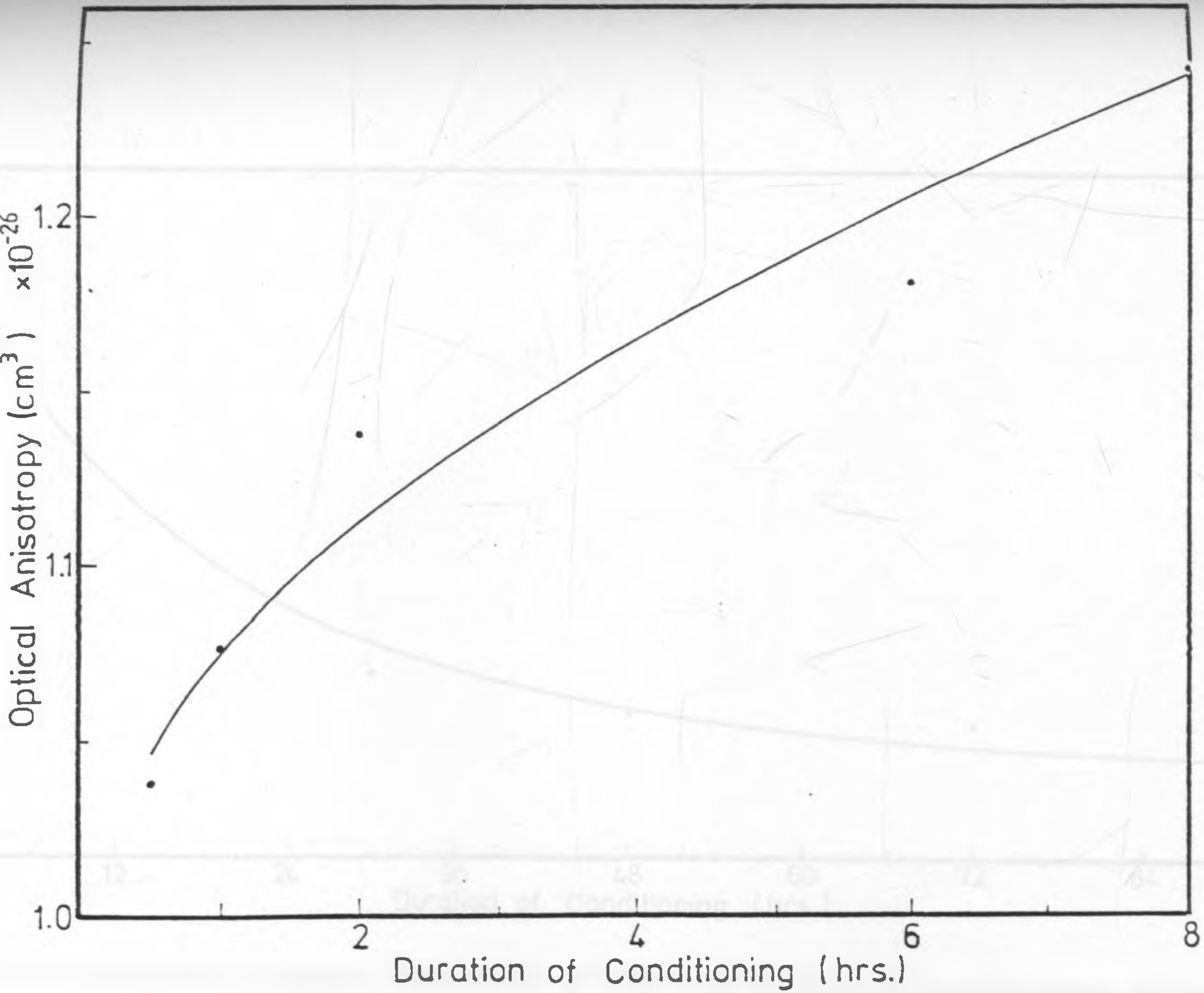


Fig. 19. Variation of optical anisotropy in PMMA with duration of conditioning in acetonitrile.

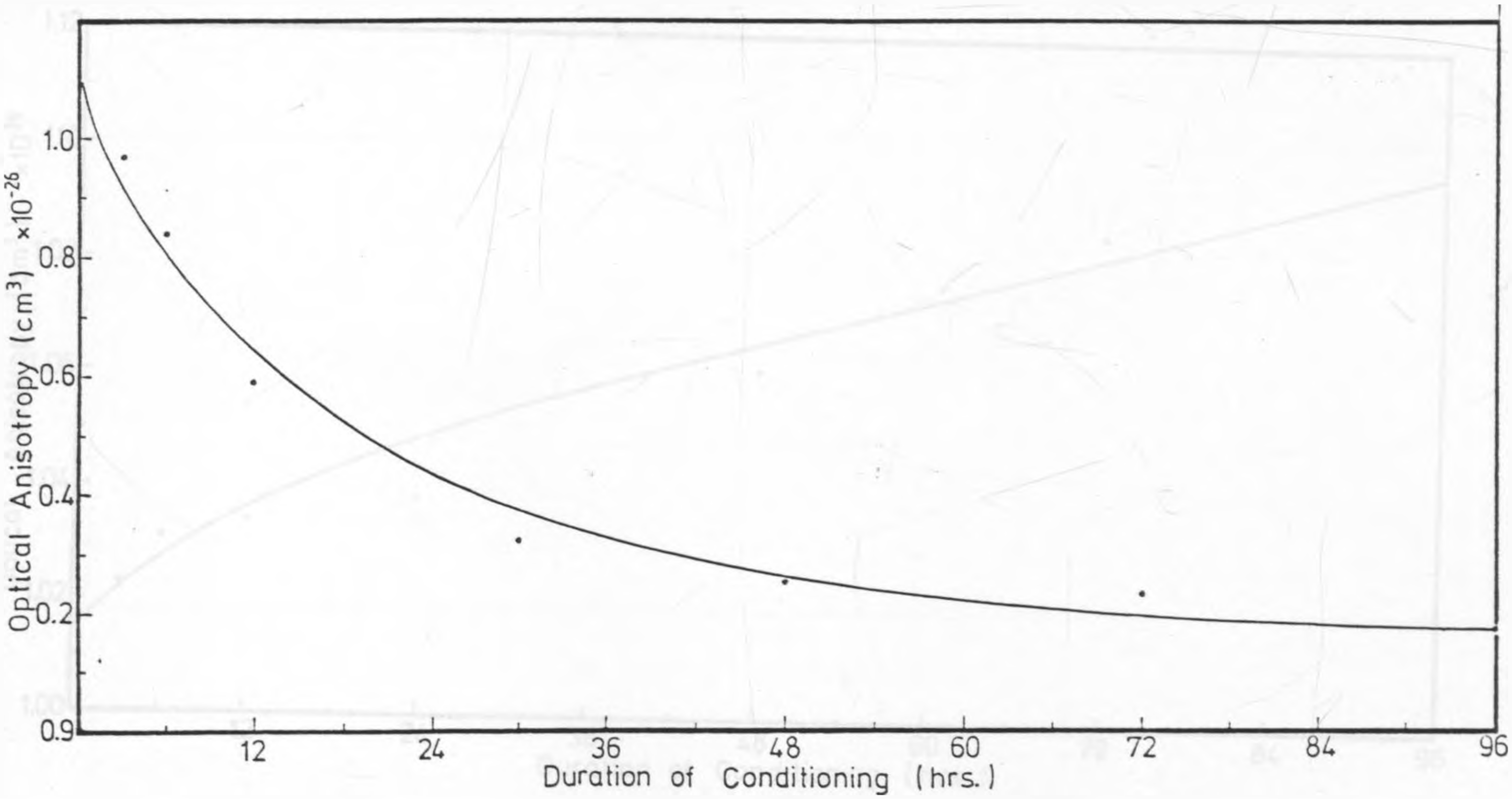


Fig. 50. Variation of optical anisotropy in PMMA with duration of conditioning in n-butanol.

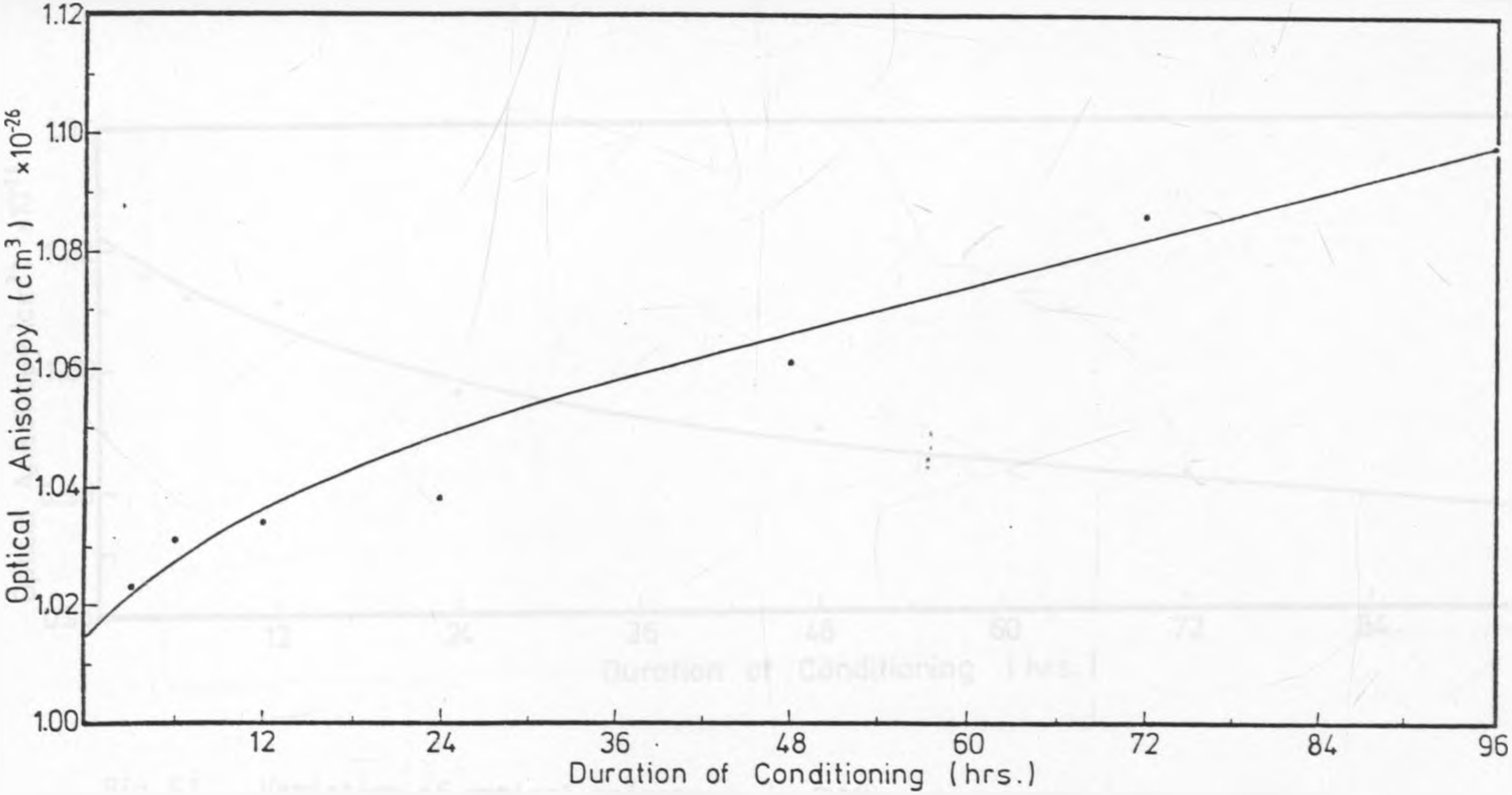


Fig. 51. Variation of optical anisotropy in PMMA with duration of conditioning in methanol.

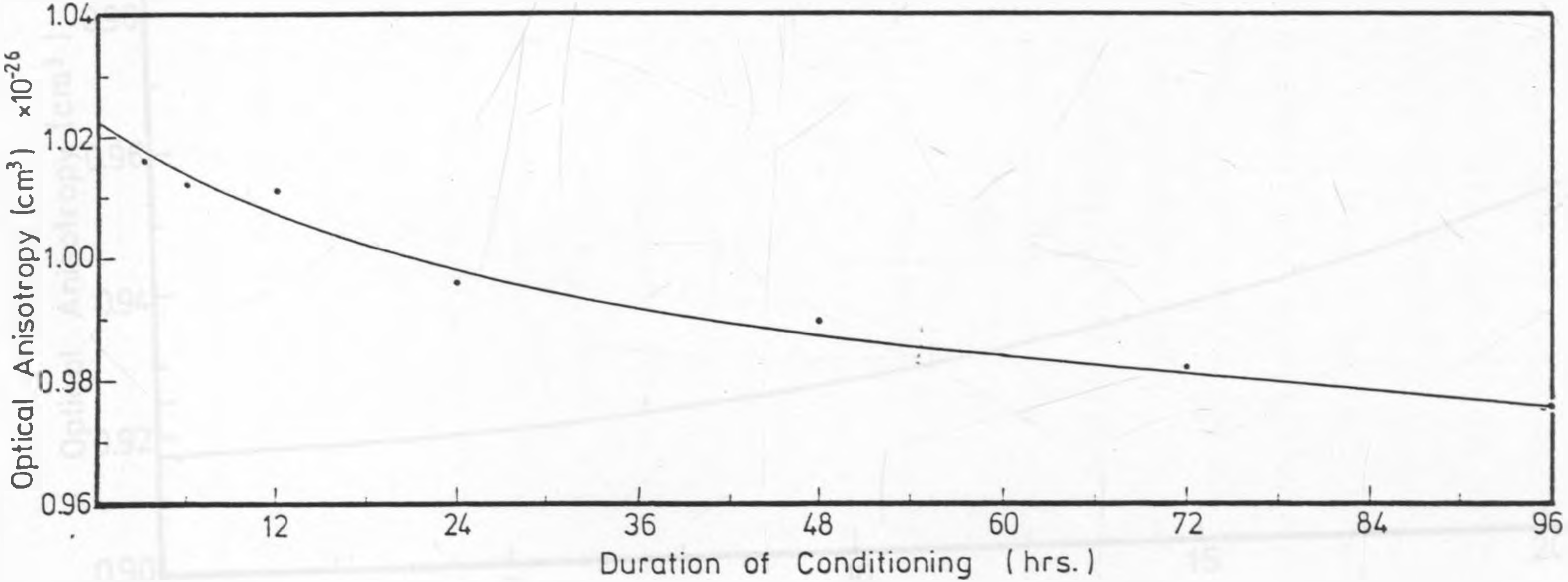


Fig. 52 . Variation of optical anisotropy in PMMA with duration of conditioning in ethylene glycol.

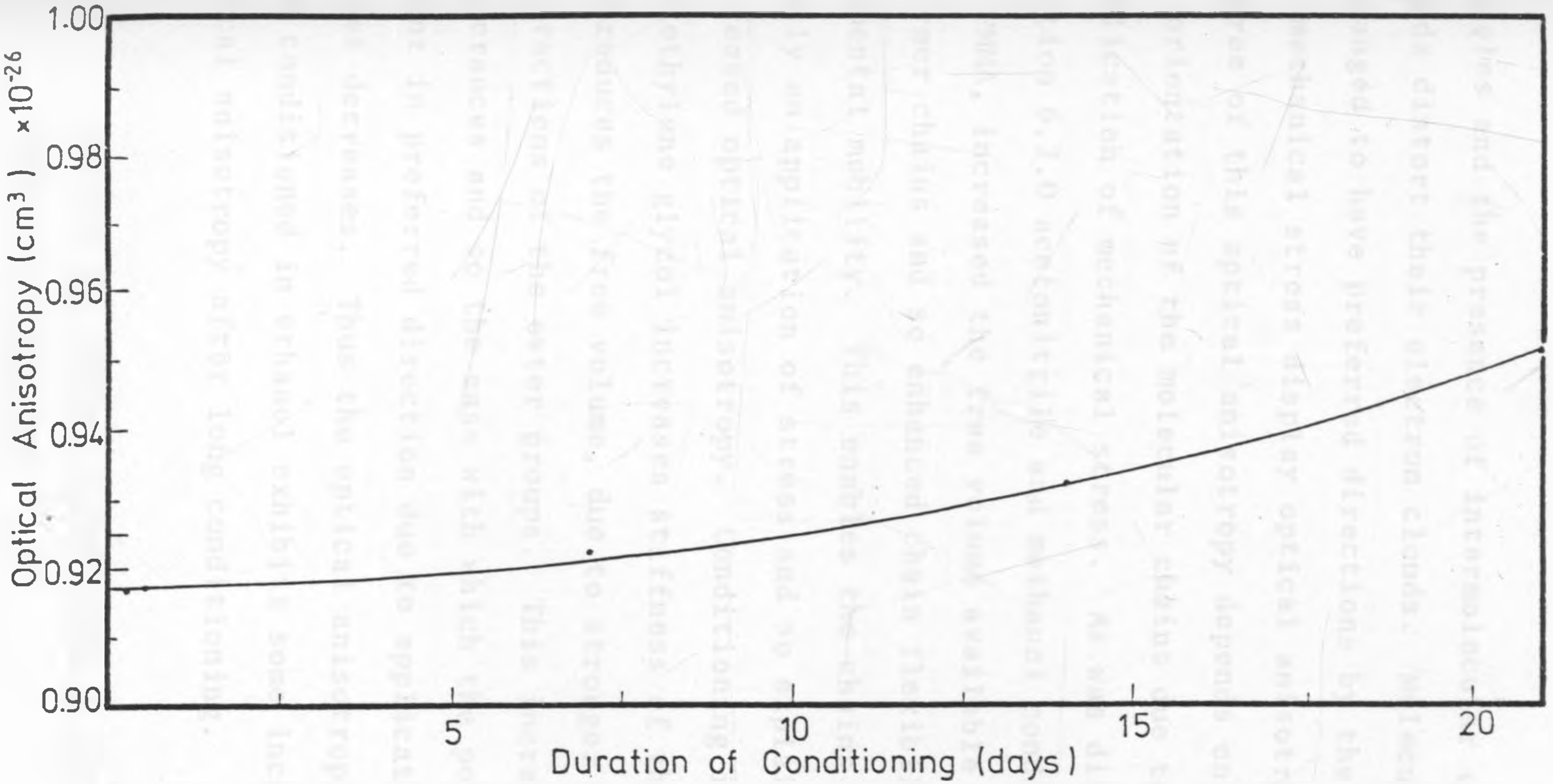


Fig. 53. Variation of optical anisotropy in PMMA with duration fo conditioning in ethanol.

dipoles and the presence of intermolecular valence bonds distort their electron clouds. Molecules arranged to have preferred directions by the application of mechanical stress display optical anisotropy. The degree of this optical anisotropy depends on the extent of orientation of the molecular chains due to the application of mechanical stress. As was discussed in section 6.2.0 acetonitrile and methanol conditioning of PMMA, increased the free volume available to the polymer chains and so enhanced chain flexibility and segmental mobility. This enables the chains to orient easily on application of stress and so explains the increased optical anisotropy. Conditioning in n-butanol and ethylene glycol increases stiffness of the chains, and reduces the free volume, due to stronger polar interactions of the ester groups. This increases steric hinderances and so the ease with which the polymer chains orient in preferred direction due to application of stress decreases. Thus the optical anisotropy decreases. PMMA conditioned in ethanol exhibits some increase in optical anisotropy after long conditioning.

6.4.0 Effects of degree of swelling on the stress optical coefficient

The percentage degree of swelling by weight of the PMMA used in this study was evaluated for acetonitrile, methanol and ethanol conditioning using the equation

$$s = \frac{(w_s - w) \times 100}{w} \qquad \ldots(33)$$

where s is the degree of swelling . w_s is the swollen weight and w is the equilibrium weight after drying. The values are given in tables 32, 33 and 34. Values of s were also obtained for n-butanol and ethylene glycol, where w_s was the weight of the PMMA sample after conditioning and w was the weight before conditioning. These results are presented in chapter 5 tables 6 and 8.

The variation of the stress optical coefficient of PMMA with the degree of swelling is given by the plots in Figs. 54-58. It is observed that the stress optical coefficient of PMMA after conditioning in acetonitrile and methanol increases with percentage degree of swelling by weight. (See Fig.54, 56). The stress optical coefficient decreases as the weight decrease when PMMA is conditioned in n-butanol and ethylene glycol. The difference in the variation of the stress optical coefficient of PMMA in these solvents is explained by the fact that, the percentage degree of swelling by weight of the PMMA conditioned in

TABLE 32.

SWELLING AND RESIDUAL SOLVENT RESULTS FOR PMMA CONDITIONED IN ACETONITRILE

DURATION OF CONDITIONING (HRS)	PERCENTAGE (RESIDUAL SOLVENT) AFTER DRYING	DEGREE OF SWELLING BY WEIGHT (%)
0.5	0.214 ± 0.003	1.037±0.060
1.0	0.372± 0.004	4.398±0.20
2.0	0.733± 0.09	6.896 ±0.400
6.0	0.974± 0.006	25.706± 0.050
8.0	1.862± 0.100	35.884± 0.700
13.0	2.410± 0.005	47.960± 0.100
15.0	4.055 ± 0.01	54.030± 0.300
20.0	5.902 ± 0.300	61.444± 2
24.0	7.648± 0.200	68.687 ±0.600
45.5	10.549± 0.400	163.261± 2
66.0	10.992± 0.200	216.07± 2

TABLE 33

SWELLING AND RESIDUAL SOLVENT RESULTS FOR PMMA CONDITIONED IN METHANOL

DURATION OF CONDITIONING HRS	PERCENTAGE RESIDUAL SOLVENT	PERCENTAGE DEGREE OF SWELLING BY WEIGHT.
3	0.03 ± 0.002	0.10 ± 0.005
6	0.07 ± 0.02	0.24 ± 0.02
12	0.35± 0.05	0.37 ± 0.03
24	1.10 ± 0.10	0.50 ± 0.02
48	1.73 ± 0.05	0.70± 0.02
72	3.63 ± 0.10	0.90 ± 0.09
96	4.63± 0.11	1.25± 0.01
168	5.77± 0.10	3.10 ± 0.05
336	6.81 ± 0.50	4.66± 0.05
504	8.67 ± 0.10	6.34 ± 0.2

TABLE 34

SWELLING AND RESIDUAL SOLVENT RESULTS FOR PMMA CONDITIONED IN ETHANOL

DURATION OF CONDITIONING (HRS)	PERCENTAGE RESIDUAL SOLVENT	PERCENTAGE DEGREE OF SWELLING BY WEIGHT
168	0.027 ± 0.001	0.120 ± 0.01
336	0.063± 0.005	0.265 ± 0.006
504	0.083 ± 0.005	0.376 ± 0.003

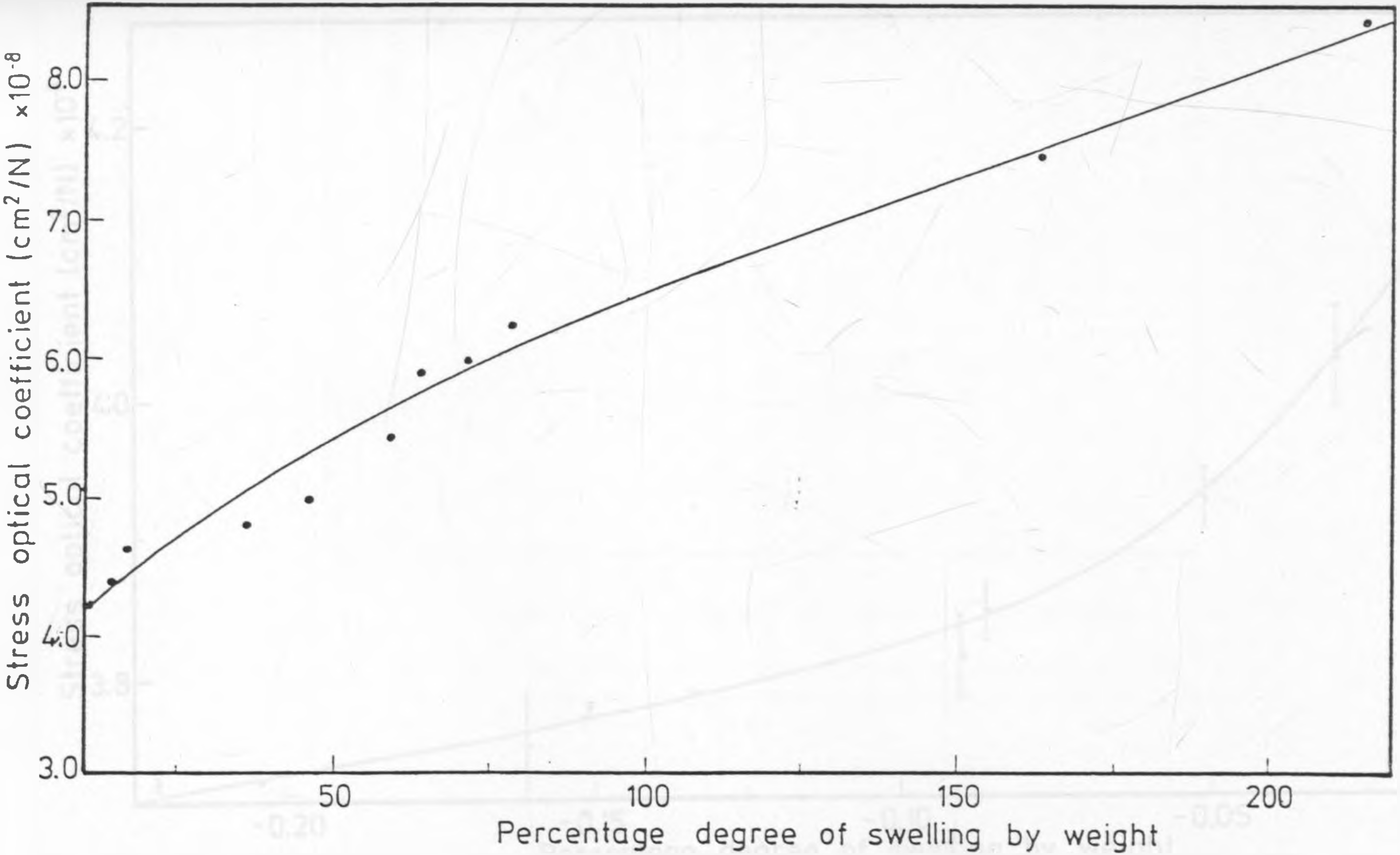


Fig. 54. Variation of Stress optical coefficient of PMMA with percentage degree of swelling by weight after conditoning in acetonitrile.

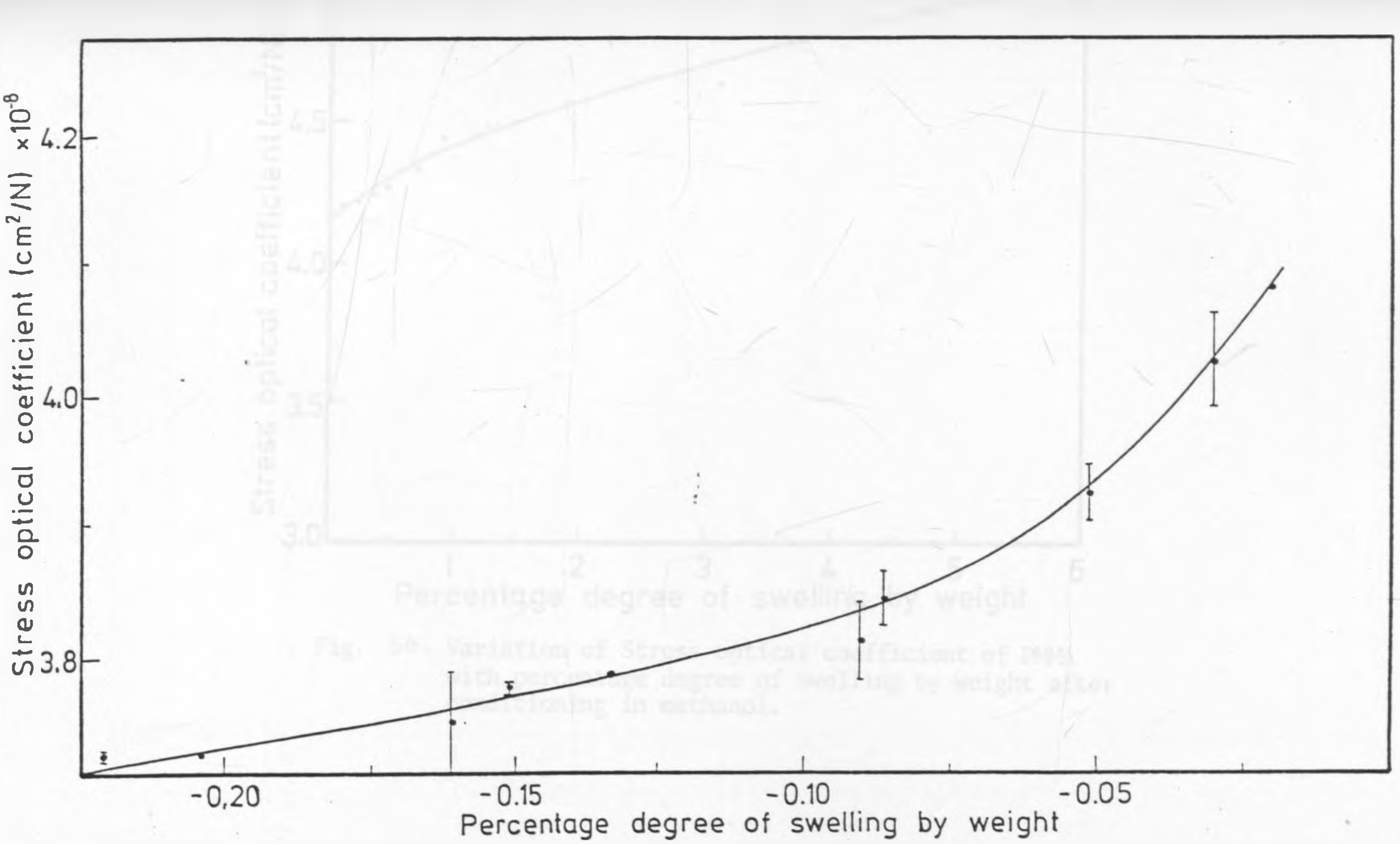


Fig. 55 . Variation of Stress optical coefficient of PMMA with percentage degree of swelling by weight after conditioning in n-butanol.

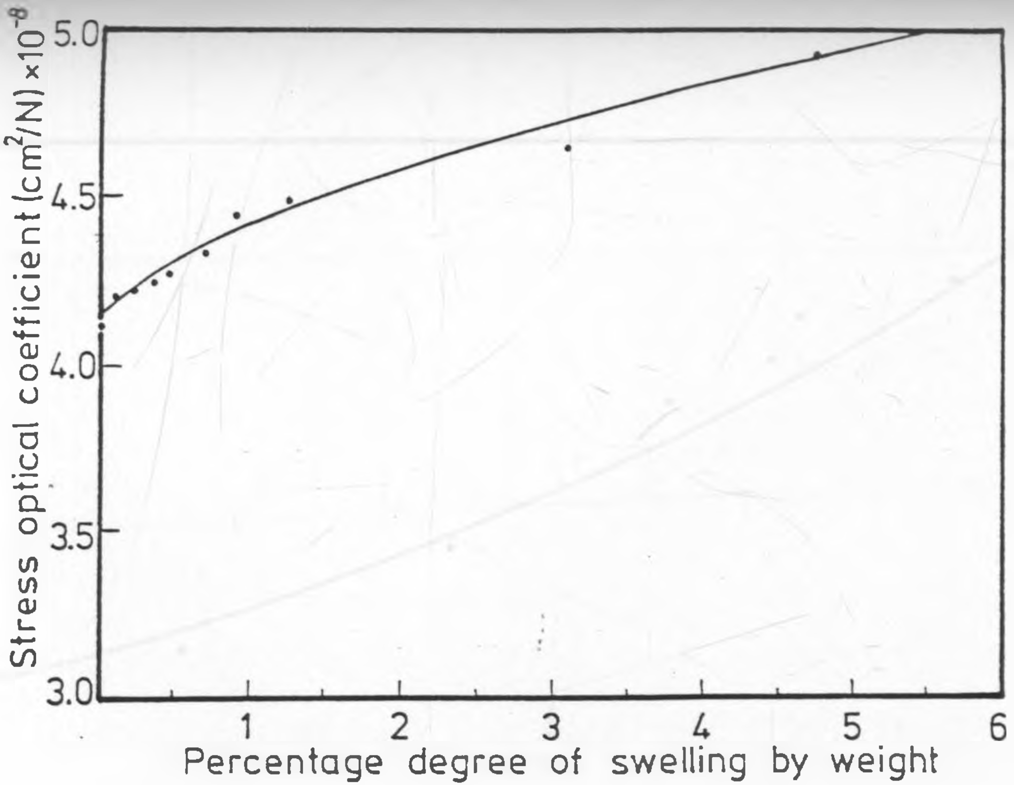


Fig. 56. Variation of Stress optical coefficient of PMMA with percentage degree of swelling by weight after conditioning in methanol.

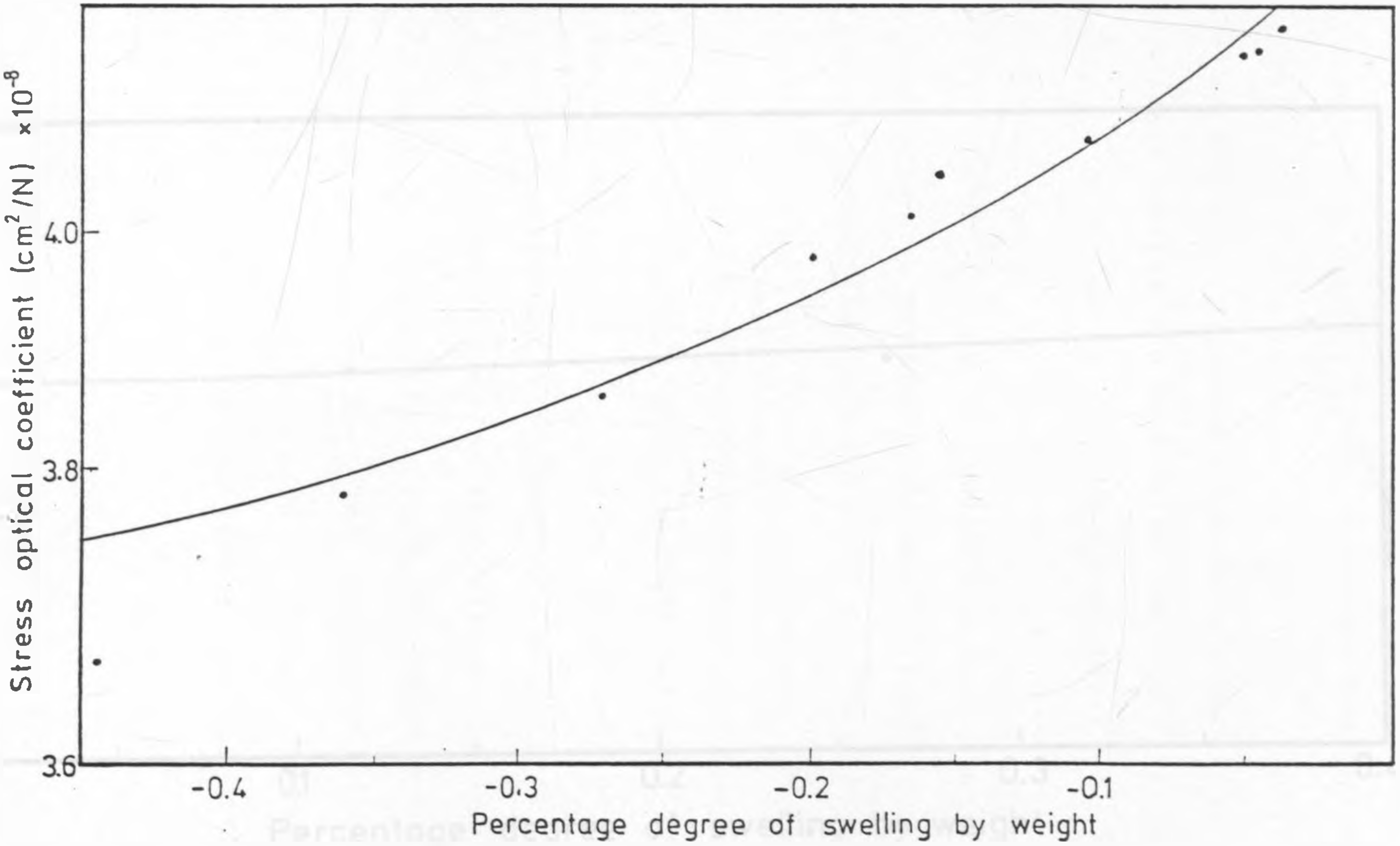


Fig. 57. Variation of Stress optical coefficient of PMMA with percentage degree of swelling by weight after conditioning in ethylene glycol.

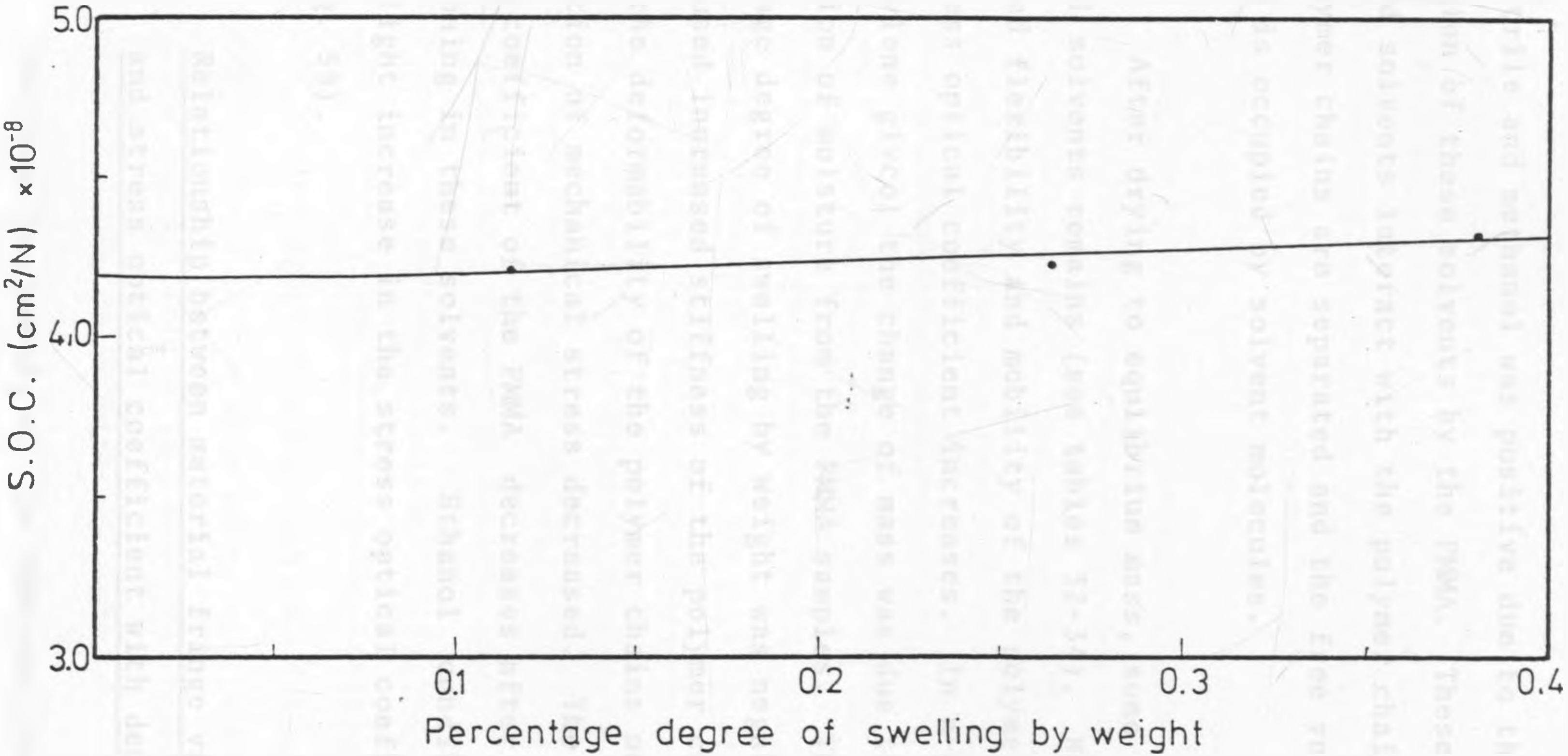


Fig. 58. Variation of Stress optical coefficient of PMMA with percentage degree of swelling by weight after conditioning in ethanol.

acetonitrile and methanol was positive due to the absorption of these solvents by the PMMA. These absorbed solvents interact with the polymer chains. The polymer chains are separated and the free volume created is occupied by solvent molecules.

After drying to equlibrium mass, some residual solvents remains (see tables 32-34). With increased flexibility and mobility of the polymer chains, the stress optical coefficient increases. In n-butanol and ethylene glycol the change of mass was due to desorption of moisture from the PMMA samples. The percentage degree of swelling by weight was negative. This caused increased stiffness of the polymer chains and so the deformability of the polymer chains on application of mechanical stress decreased. The stress optical coefficient of the PMMA decreases after conditioning in these solvents. Ethanol conditioning shows slight increase in the stress optical coefficient (see Fig. 58).

6.5.0 Relationship between material fringe value, and stress optical coefficient with density.

Decrease in density of the PMMA was observed after conditioning in the solvents used in this study and after drying samples to equilibrium mass. This change was more pronounced after conditoning PMMA in acetonitrile and methanol. The variation of density as a function of duration of conditioning in these two solvents is given in chapter 5 section 5.4.0. The PMMA samples didn't regain their original mass and volume even after drying to equilibrium. The increased equilibrium mass was attributed to presence of residual solvent, (see tables 32-34). The decrease in density for the PMMA samples conditioned in n-butanol and ethylene glycol is associated with the decrease in mass. Due to the regidity of the samples the changes of volume were not significant. From Figs. 59 and 60 , it is shown that the stress optical coefficient decreases linearly with increase in density. The material fringe value increases with density (see Fig. 60, 61). These observations imply that high density PMMA would have a lower stress optical sensitivity than less dense PMMA. This could be due to the restricted chain movement in the dense polymer because of increased steric hinderances than in the less dense one. The tendency for the polymer chains to orient in response to mechanical stress decreases with increase in density of the polymer.

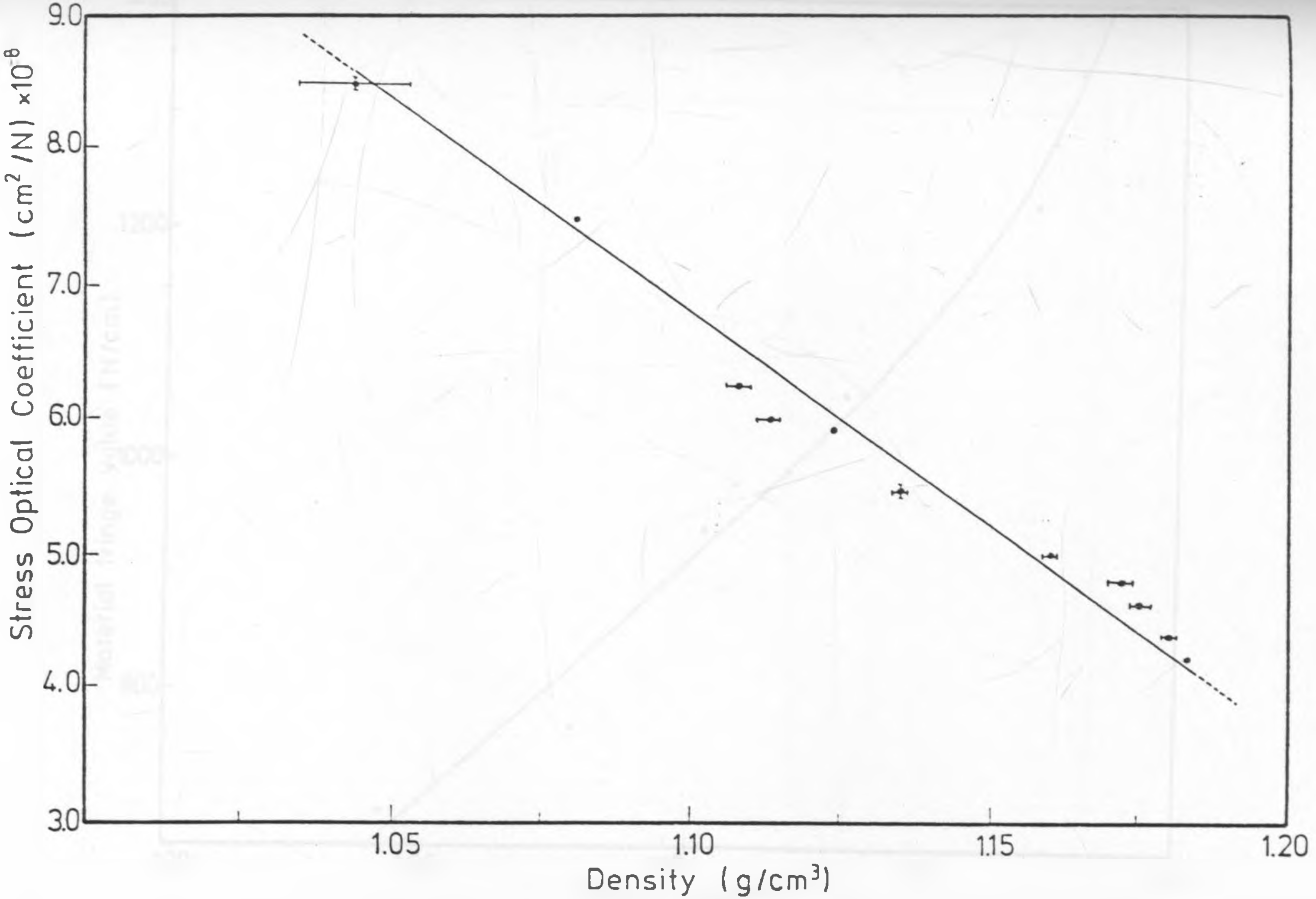


Fig. 59. Stress optical coefficient-density relation for PMMA after conditioning in acetonitrile.

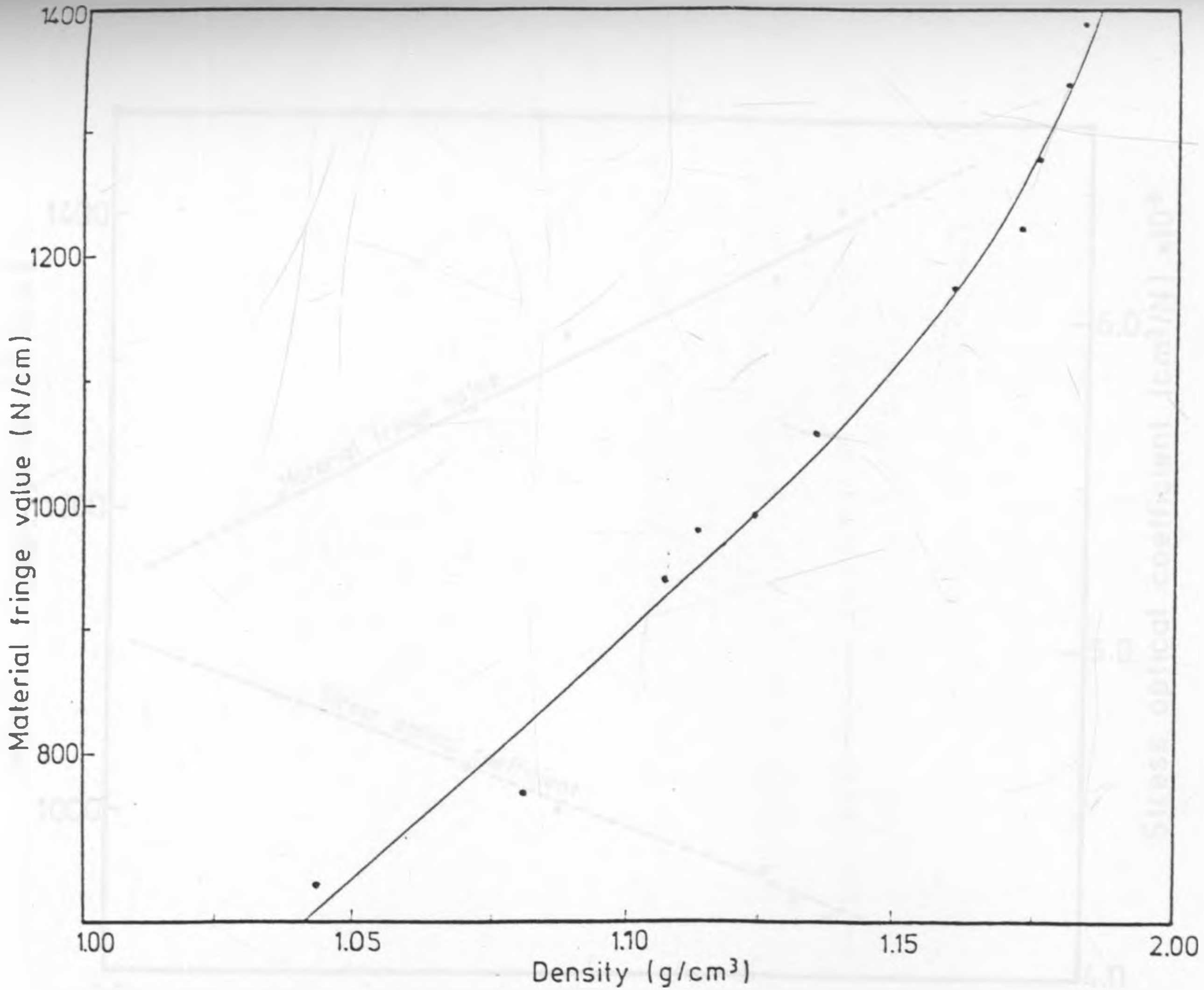


Fig. 60. Material fringe value–Density relation for PMMA after conditioning in acetonitrile.

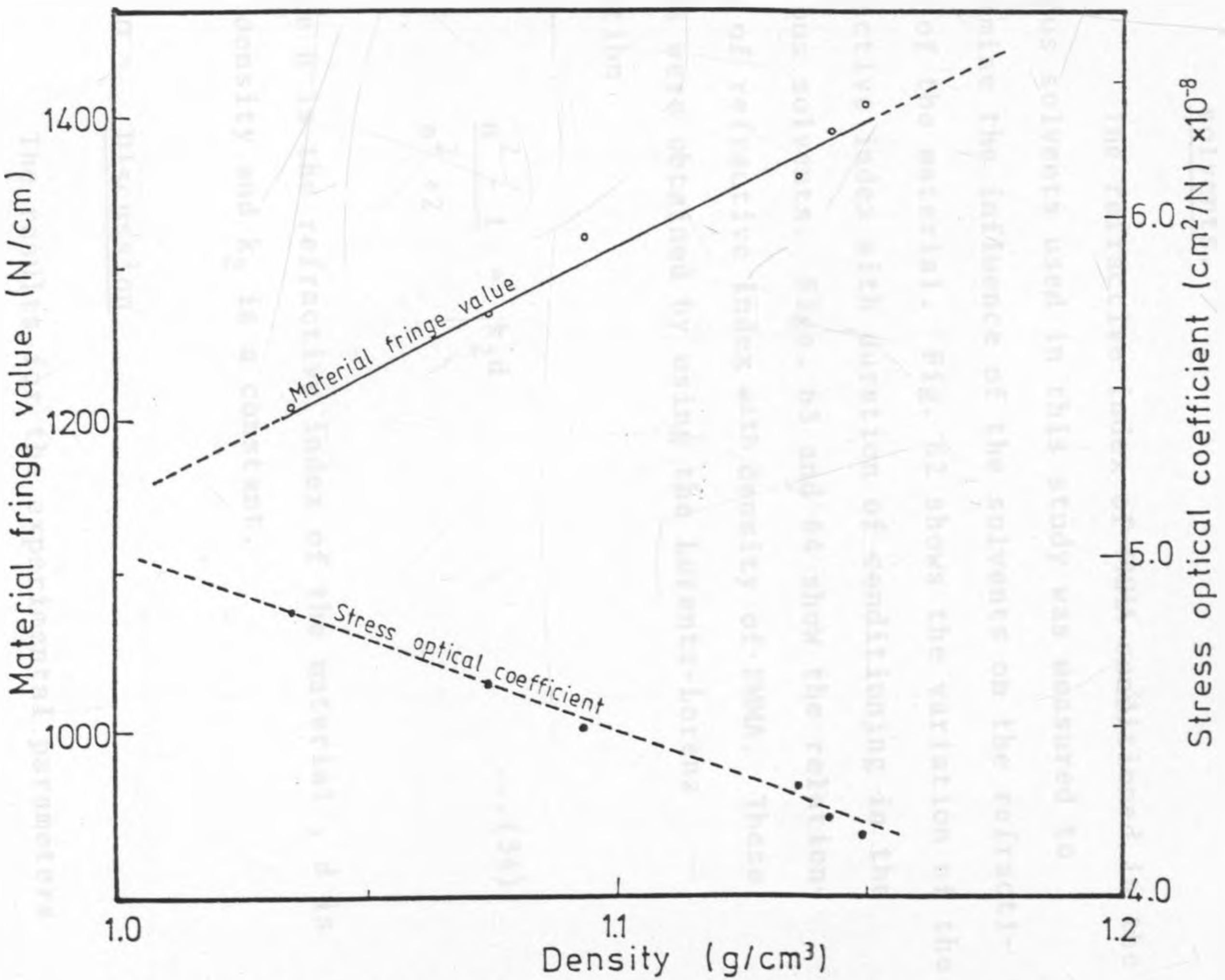


Fig. 61. Material fringe value-Density and stress optical coefficient-Density relationship for PMMA conditioned in methanol.

6.6.0 Variation of refractive index of PMMA with duration of conditioning in various solvents.

The refractive index of PMMA conditioned in the various solvents used in this study was measured to determine the influence of the solvents on the refractivity of the material. Fig. 62 shows the variation of the refractive index with duration of conditioning in the various solvents. Figs. 63 and 64 show the relationship of refractive index with density of PMMA. These plots were obtained by using the Lorentz-Lorenz equation

$$\frac{n^2 - 1}{n^2 + 2} = k_2 d \qquad \ldots(34)$$

where n is the refractive index of the material , d is the density and k_2 is a constant.

6.7.0 Discussion

The results for the experimental parameters considered in this study show a great deal of influence of solvent conditioning on the PMMA properties. The birefringence stress difference plots (Figs. 39-43) are linear through the origin, and the stress level at which the PMMA samples deviate from proportionality

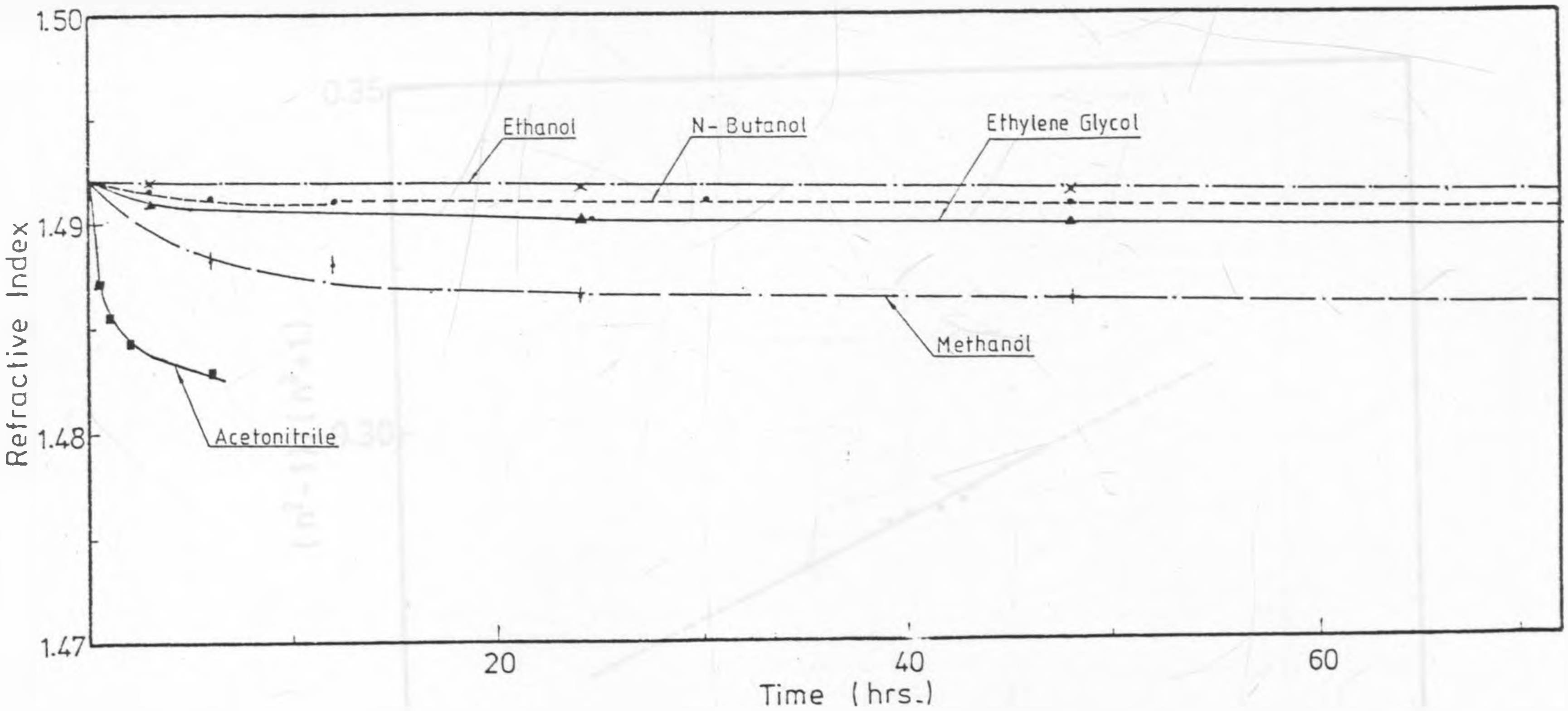


Fig. 62. Variation of refractive index of PMMA with duration of conditioning in various solvents.

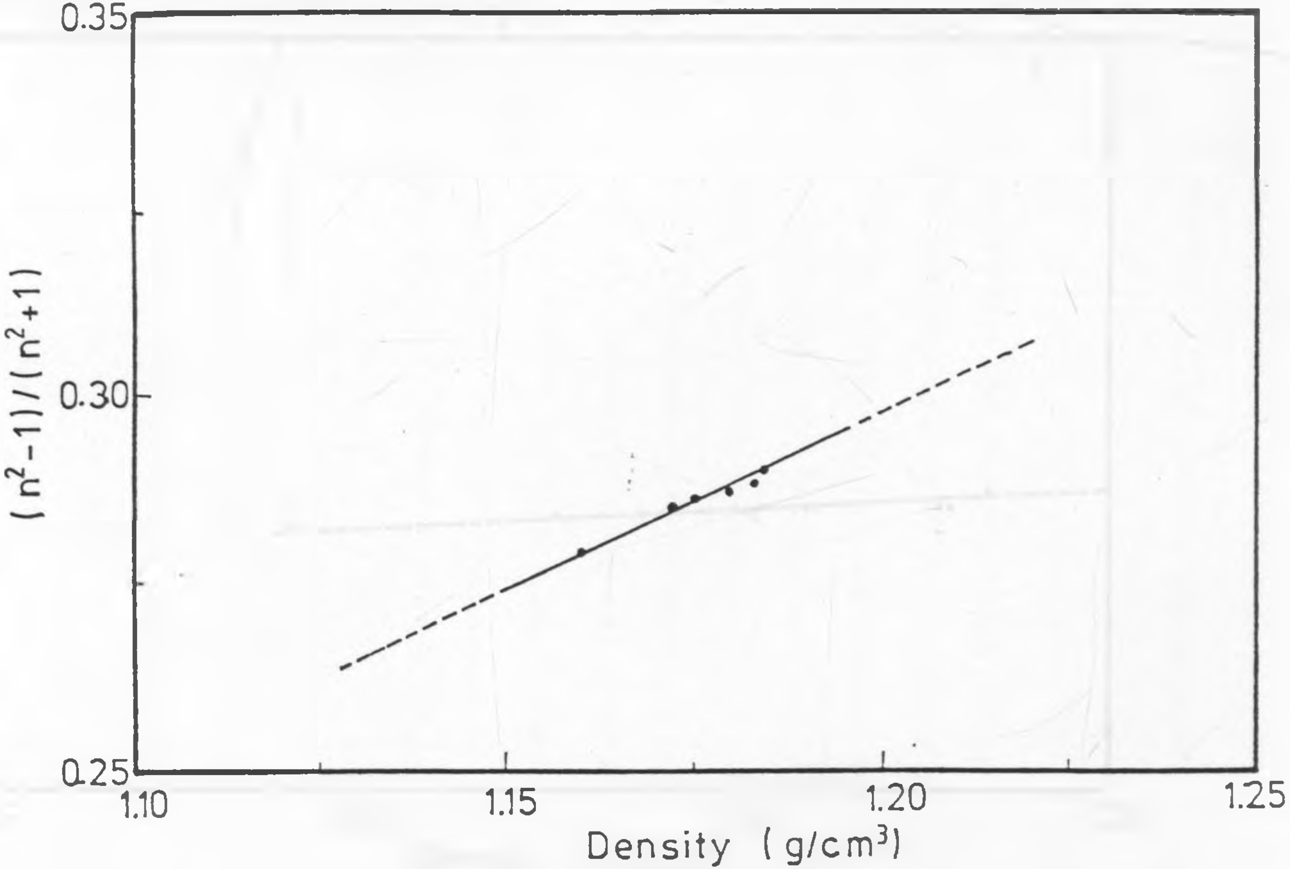


Fig. 63. Refractive index-density relation as fitted using the Lorentz-Lorenz equation for PMMA conditioned in acetonitrile.

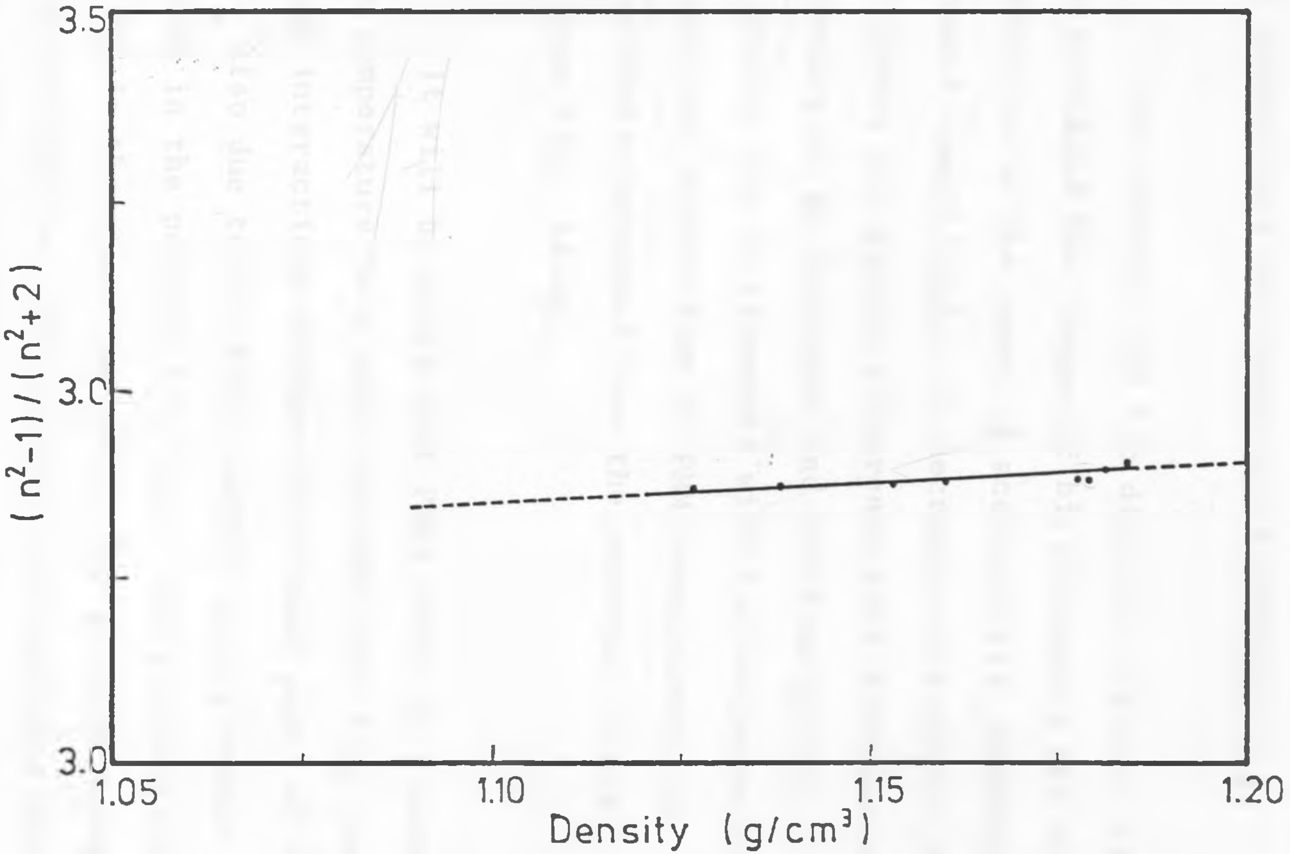


Fig. 64. Refractive index-density relation as fitted using the Lorentz-Lorenz equation for PMMA conditioned in methanol.

of birefringence with stress difference, as shown in the region of upturn of the birefringence plots depended on the solvent and the duration of conditioning.

The solvents had two distinct effects: they either increased the change of birefringence per stress difference as in the cases of acetonitrile, methanol and ethanol conditioning, or decreased the change of birefringence per stress difference with duration of conditioning as in n-butanol and ethylene glycol. These results are in agreement with the variation of stress-optical coefficient of PMMA conditioned in these solvents; obtained from the material fringe values (see Figs. 44-48).

It will be noted that PMMA which is glassy at room temperature is a polar polymer with long range potential interactions between individual parts of the chains. Also due to the bulky methyl groups steric hindrances in the polymer are high. The flexibility of the chains is therefore low and so the polymer shows low stress birefringence. The results from acetonitrile and methanol conditioning show increased stress-optical sensitivity with duration of conditioning. These results suggest an increase in chain flexibility and segmental mobility. Absorption of these solvents into the polymer tended to separate the polymer chains as the solvent molecules distributed themselves through the polymer. The intermolecular bonding forces between the polymer chains were weakened because of chain scissions and because of the bonding at solvent locations being shared by solvent molecules.

This preference of polymer segment for solvent molecules as neighbours increased the effective dimensions of the chains. The solvents thus perturbed the polymer molecules and the relationship between the perturbed-chain and unperturbed-chain dimensions {41} is desgnated as

$$<r^2> = \alpha^2 <r_o^2>. \qquad ...(35)$$

where $<r^2>$ is the actual mean square end to end distance of a polymer chain, $<r_o^2>$ is the unperturbed (unswollen) chain mean square end to end distance and α is the expansion coefficient.

In good solvents, extended or more open polymer conformations are favoured for high solvation. Strong forces develop between polymer and solvent molecules. The polymer chains are relatively expanded increasing the total volume occupied by a single chain.

The effective covolume (or excluded volume) of a pair of chain segments therefore would be increased beyond that of the actual excluded volume of the individual segments. The expansion coefficient α would be greater than unity.

Acetonitrile and methanol were medium solvents to PMMA. Sufficiently open polymer chain conformations were provided which allowed polymer-solvent interactions but without interfering to any great extent with the polymer-polymer interchain attractions. The effective covolume of the polymer segment was unaffected by these solvents and so the excluded-volume effects were not as much as in good solvents. The expansion coefficient α exceeds unity but less so than in the case of good solvents.

The separation of the polymer chains by solvent molecules reduced the cohesive energy density of the polymer and also reduced the steric hindrances associated with attached side methyl groups. The expansion of the chains as a consequence of swelling forced them out of their equilibrium conformations. After drying the PMMA samples to equilibrium mass, the chains assumed different conformations due to their elastic reactions. Still with some free volume available to the chains and the presence of residual solvents in dried PMMA samples, the activation energy required to initiate rotational motion of the chains was reduced. The ease with which the chains would orient or assume preferred conformational states (spatial arrangement), when the samples were subjected to mechanical stresses increased.

The results for PMMA conditioned in ethanol (Fig. 36) did not show any significant change in mass until after 7 days conditioning. Consequently no changes in the birefringence per stress difference (stress optical coefficient) and changes in material fringe value were noted for PMMA conditioned in ethanol for these durations.

It can be inferred from these observations that during these periods, there was little interaction between the polymer and the solvent molecules. The polymer molecules tended to coil up as much as possible, minimizing the number of contacts with solvent molecules.

This can be explained in terms of the energy of mixing that is related to the intermolecular forces between similar and dissimilar molecules. The energy of mixing that accompanies the formation of contact between polymer and solvent molecules is given by

$$\Delta\varepsilon = \tfrac{1}{2}\,\varepsilon_{11} + \tfrac{1}{2}\varepsilon_{22} - \varepsilon_{12} \qquad ...(36)$$

where ε_{11} is the energy of interaction between polymer molecules (Solute-solute chemical potential), ε_{22} is the energy of interaction between solvent molecules (solvent-chemical potential) and ε_{12} is the energy of the polymer-solvent moleculer (solvent-solute chemical potential). The observations for the PMMA - ethanol system suggest that $\varepsilon_{12} << \varepsilon_{11}$ and ε_{22}; hence the solvent did not affect the conformational states of the polymer chains.

This period where no changes were observed could be the reportedly "incubation period" for the PMMA-ethanol system at room temperature {42} . Changes were evident after 7, 14 and 21 days of conditioning. In these cases there was an increase in the stress induced birefringence and the stress optical coefficient. This result is attributed to easy orientation of the chains when the polymer is subjected to a state of stress.

The results for PMMA conditioned in n-butanol and ethylene glycol however show a decrease in the stress optical sensitivity with duration of conditioning

TABLE 35

CHANGE OF MASS FOR SAMPLES CONDITIONED IN ETHYLENE GLYCOL

SAMPLE	MASS BEFORE CONDITIONING (g)	MASS AFTER 24 HR CONDITIONING IN ETHYLENE GLYCOL (g)	MASS, TWO DAYS AFTER REMOVAL FROM SOLVENT (g)	MASS, THREE DAYS AFTER REMOVAL FROM SOLVENT (g)
1	7.3100	7.3058	7.3073	7.3074
2	7.3046	7.3013	7.3021	7.3022
3	7.2990	7.2944	7.2965	7.2965

(Figs. 45 - 47). These results imply that there is increased chain stiffness, strong interchain interaction and more steric hinderances.

The unplastising effect due to desorption of residual moisture to which these observations were attributed (see section 6.1.0.), was checked by monitoring the masses of three PMMA samples immediately after removing them from ethylene glycol in which they had been conditioned for 24 hours. The results for the masses checked for three days are given in table 35. They show that the masses of the samples after removal from the solvent were lower than the original masses. They however kept on increasing for the three days but the original masses were never regained. The regained mass was due to moisture absorbed from the surrounding while the unregained mass could have been due to lost monomer units, which also could have a plasticising effect.

The desorption of the residual moisture by these solvents tended to increase the polymer-polymer interchain interactions and more compact configurations could have been more favoured than the extended ones. The effect of excluded volume were compensated for by the increased relative preference for compact structure which in turn reduced the orientation tendency of the chains on application of stress. The unplasticisation effect due to the removal of moisture is in agreement with results of Moore and Flick {18} who showed that high water concentrations in PMMA increased chain orientation when the polymer was stressed. PMMA is known to be a hydrophilic polymer which can absorb moisture to an equilibrium concentration the level of which depends on the humidity. The diffusion of water in solvents like isopropanol and n-butanol has been reported in some literature {43}.

The results on the polarizability anisotropy in PMMA (Figs 49-53) show a variation with duration of conditioning similar to that of stress optical coefficient in the various solvent conditioned samples. In acetonitrile, methanol and ethanol conditioned PMMA samples, the polarizability anisotropy increased with duration of conditioning, suggesting an increase in the orientational component of the polarizability anisotropy, due to the applied stress. The polarizability anisotropy however decreased with duration of conditioning in n-butanol and ethylene glycol. This property of the polymer depends on conformation of the chains. It comprizes of the electronic, atomic and orientation polarization anisotropies. The orientation component can be composed of several orientational segments ranging from small side chains to whole molecular motions. All these components are a function of the stress field applied, as this may result to different conformational states. The increased flexibility of polymer chains and free volume in PMMA conditioned in acetonitrile, methanol and ethanol, explain the increased orientational component of the polarizability anisotropy induced by the application of stress. Further contribution to the polarizability anisotropy which increased with duration of conditioning in these solvents, is due to the presence of residual solvents which would affect the electronic and atomic components of the polarizability anisotropy. The results for n -butanol and ethylene glycol can be attributed to the decrease of the orientational component of the polarizability anisotropy with duration of conditioning . This would be so because the increased rigidity of the polymer chains due to strong polymer-polymer molecule interactions decreases the ease with which the chains orient in response to applied mechanical stress.

It was found from the results that the refractive index of the PMMA showed a decrease with duration of conditioning in all the solvents. Refraactive index is also a conformation dependent property. Solvent conditioning of the PMMA samples generally affected its equilibrium conformation properties (i.e bond angles, bond lengths and hindrances to chain backbone rotations). This in turn affected the end-to-end distances of the polymer chains and the dipole moments. As a consquence of this, the relative permittivity and hence the refractive index of the PMMA was altered.

The observations on the changes of the refractive index of the PMMA samples could also be explained in terms of the decrease in the electronic polarizability per unit volume as a result of solvent conditioning of the polymer samples. Other factors which contribute to these changes are the presence of residual solvents with different refractive indices from that of the polymer and the decrease in the density of the PMMA samples. A low density PMMA would affect the velocity of an incident light wave to a lesser extent than a more dense one.

The results on the variation of stress optical coefficient with density of PMMA shown in Figs. 56-58 suggest that more loosely packed PMMA chains with little intermolecular interaction would orient easily when the polymer is subjected to stress.

Generally, it should be mentioned that the extent of the influence of the solvents on the PMMA properties depended on the polymer solvent interaction for each system. The effect of a specific solvent on the PMMA could be identified by the solubility parameter which according to Hildebrand {44} is defined as the square root of the cohesive energy density.

$$\delta = (\Delta E_i^{v}/V_i)^{\frac{1}{2}} \qquad \ldots(37)$$

where δ is the solubility parameter, ΔE_i^{v}; is the molar energy of vaporization and V_i is the molar volume of the solvent.

Accordingly, a good solvent would be that with a solubility parameter δ_1 comparable to that of the polymer δ_2. This relation is particularly true in the absence of strong hydrogen bonding in the solvent. It is generally approximated that solubility can be expected if $|\delta_1 - \delta_2|$ is less than 3.5 - 4.1 $(J/cm^3)^{\frac{1}{2}}$ {45}.

From the results, it was observed that

acetonitrile showed the greatest influence on the stress-optical properties of PMMA. Acetonitrile has a solubility parameter $\delta_1 = 24.3\ (J/cm^3)^{\frac{1}{2}}$ and has low hydrogen bonding tendency. PMMA has a solubility parameter δ_2 ranging from 18.6 to 19.4 $(J/cm^3)^{\frac{1}{2}}$. The $|\delta_1 - \delta_2|$ for acetonitrile- PMMA system ranges from 4.9 to 5.7 $(J/cm^3)^{\frac{1}{2}}$. This difference in the solubility parameters was above the range where solubility would occur but allowed for polymer-solvent interactions which did not interfere greatly with the polymer-polymer interactions, i.e. the polymer chemical potential ϵ_{11} was close to the polymer-solvent chemical potential ϵ_{12}. The strong interaction between acetonitrile and PMMA molecules can be attributed to the interaction between the electro-negative nitrile group (CN) in the solvent and polar carbo-methoxy ($COOCH_3$) group in the polymer.

However, the solubility parameter and the hydrogen bonding index were not sufficient solvent properties to be used to predict the influence of a particular solvent on the studied PMMA properties. In particular this did not apply in the case of methanol, n-butanol, ethanol and ethylene glycol conditioning. Inconsistencies were noted when the PMMA properties and the PMMA - solvent interactions were correlated in terms of the solubility parameter. For example acetonitrile and nitromethane are both low hydrogen bonded solvents but acetonitrile is lower than nitromethane {δ_1 = 25.9 $(j/cm^3)^{\frac{1}{2}}$} in the solubility parameter scale. PMMA which has a solubility parameter much close to acetonitrile disolves readily in nitromethane. Similarly it is also observed that Dimethyl formamide {δ_1 = 24.7 - $(J/mc^3)^{\frac{1}{2}}$} is a strongly hydrogen bonded solvent which is higher in the solubility parameter scale than acetonitrile but PMMA disolves readily in dimethyl formamide while it swells in acetonitrile.

N-butanol {δ_1 = 23.2$(J/cm^3)^{\frac{1}{2}}$} is lower than methanol {δ_1 = 29.6 $(J/cm^3)^{\frac{1}{2}}$} in terms of solubility parameter, and both solvents are strongly hydrogen bonded. The PMMA -solvent interaction would have been expected to be more in n-butanol with δ_1 closer to PMMA than in methanol. The reverse was however observed.

Similar inconsistencies in relating PMMA - solvent interactions with the solubility parameter were noted in ethanol-PMMA and Ethylene glycol-PMMA systems. These inconsistencies have been explained by the fact that the solubility parameter concept involves the resolution of the composite influences of Van der Walls, Polar and dydrogen bonding forces. It would therefore be essential to consider the influences of these separate parameters together with properties like solvent molecular size and solvent viscosity in polymer-solvent systems since they may have important contributions to the specific polymer-solvent interactions.

6.8.0 Conclusions

1. The results of stress induced birefringence in PMMA samples conditioned in acetonitrile, n-butanol, methanol, ethylene glycol and ethanol indicate that the birefringence varied linearly with stress difference through the origin, and the stress-difference level at which deviation from proportionality of birefringence with stress-difference depended on the solvent in which PMMA samples were conditioned and the duration of conditioning. PMMA samples conditioned in acetonitrile and methanol showed deviation from proportionality at stress levels which decreased with duration of conditioning.

2. The change of birefringence per stress difference increased with duration of conditioning in

acetonitrile methanol and ethanol while it decreased with duration of conditioning in n-butanol and ethylene glycol. These results show that solvents had an effect on the correlation between the mechanical and optical properties of the polymer as shown by the birefringence stress difference plots for PMMA samples conditioned in the solvents for various durations.

3. Results of the stress optical coefficients for PMMA, which were obtained from material fringe values show an increase with duration of conditioning of the polymer in acetonitrile, methanol and ethanol; with samples conditioned in ethanol showing the least effect. The results indicate an enhancement of orientation of the polymer chains and hence an increase in the stress-optical sensitivity. Samples of PMMA conditioned in n-butanol and ethylene glycol show a decrease of the stress optical coefficient with duration of conditioning. This is an indication that the ease with which the polymer chains orient in response to stress decreases after conditioning the samples in these solvents.

4. Refractive index values measured for all solvent conditioned PMMA samples decreased with duration of conditioning. Large changes were observed in samples conditioned in acetonitrile and methanol.

5. The results also show that the optical anisotropy $\alpha_2 - \alpha_1$ increased with duration of conditioning in acetonitrile, methanol and ethanol. These indicate that the structural disymmetry induced by stress and hence the orientational component of the optical anisotropy increased with duration of conditioning in these solvents.

The values of optical anisotropy however decreased with duration of conditioning in n-butanol and ethylene glycol.

6. The density of the PMMA decreased after conditioning in all the solvents used.

7. The density and refractive index results for PMMA conditioned in acetonitrile and methanol show a relationship that is in agreement with the Lorentz-Lorenz relation.

8. The results obtained for PMMA samples conditioned in acetonitrile and methanol show that low density PMMA would have a high stress-optical sensitivity than more dense PMMA. This indicates that loosely packed polymer chains will orient easily since they have little steric hindrances.

9. The optical sign for all solvent conditioned PMMA samples was positive under compression.

6.9.0 Recommendations

It was the aim of this study to explore further on the deformational and orientation behaviour of PMMA and how this behaviour would be influenced by environmental and mechanical stresses. This information was to be obtained through birefringence studies of poly(methyl methacrylate) conditioned in various solvents. The present results presented here indicate how the stress optical properties of the polymer would be affected by environmnetal factors like atmospheric contaminants and industrial chemicals; information which should be important for both scientific and manufacturing purposes.

There was however no consistent relationship on the variation of the studied PMMA properties with solvent properties like cohesive energy density and hydrogen bonding tendency. The following areas are therefore recommended for future work.

1. A study of the influence of solvent polarity on the

stress optical properties of glassy polymers, like PMMA.

2. A study of the influence of solvents on stress-optical properties of PMMA at temperature above room temperature. Raising the temperature of the solvent lowers its viscosity and affects the solubility parameter. This may have a different effect on the polymer-solvent interaction and hence on the stress optical properties.

3. A study on the mechanical and optical properties of preoriented PMMA gels using good solvents to PMMA

4. Since the polarizability anisotropy of PMMA has been observed to increase with conditioning in some solvents, a study could be carried out to look at the influence of preorientation of PMMA gels on the switching mechanism of the polymer. Similar studies could also be done on other polymers.

5. A study on the electrooptic properties of PMMA, obtained from measurements of orientation birefringence of the polymer solution induced by an electric field would give further helpful information.

6. A study to investigate the exact interaction mechanisms through which the solvents stated here do affect the PMMA birefringence would be an appropriate outgrowth of this study.

REFERENCES

1. Mascia, L. The role of Additives in plastics, Edward Arnold publishing company, London, England, 1974.

2. Kwei, T.K., 'Macromolecules in solution', Chap.4 in Bovey F.A. and Winslow F.H. (ed), macromolecules: An introduction to Polymer Science, Academic press Inc. New York, San Francisco, London, 1979.

3. Miller, M.L. The Structure of Polymers, Reninhold Publishing corporation 1966.

4. Deanin, R.D., Polymer Structure Properties and Applications, Cahners, Boston, Mass, 1972.

5. Kawasalei, et al., Makromol. Chem; 36, 260 (1960); 42, 165 (1960).

6. Gall, W.G., and McCrum, N.G., J. Polym. Sci. 50, 489 (1961).

7. Shen, M.C., and Strong, J.D., 'Low-Temperature Internal Friction Study of Diluents in some Polymethacrylates', J. Appl. Phs. 38, 4197 (1967).

8. Janacek, J., J. Macromol. Sci. Phys. B2, 497 (1968).

9. Ward, I.M., (ed), Structure and Properties of oriented Polymers, Applied Science Publishers, London, 1975.

10. Andrews, R.D., 'Measurement of orientation in Polystyrene monofilaments by means of double refraction', J. Appl. Phys. 25 , 1223 (1954).

11. Pinnok, P.R., and Ward, J.M., 'Study of Stress-Optical behaviour of Polyethylene Terephthalate', Trans. Faraday Soc. 62, 1308 (1966).

12. Andrews, R.D. and Kazama, Y., 'Birefringence Effects in Unplasticized and Plasticized PVC'., J. Appl. Phys. 39, 4891 (1968).

13. Kolsky, H., and Shearman, A.C., 'Photoelastic investigations of structural changes in Plastic materials' Proc. Phys. Soc. (London) 55, 383 (1943).

14. Robinson, H.A. Ruggy, R., Slantz, E, 'Elasto-Viscous and Stress-Optical Properties of commercial Polymerized Poly(methyl methacrylate) as a function of temperature,' J. Appl. Phys. 15, 343 (1944).

15. Tsvetkov, V.N. and Patrova, A., 'The Birefringence of Poly(methyl methacrylate) in several solvents of different index of refraction', J. Phys. Chem.

16. Lamble, J.H., and Dahmouch, E.S., 'Photoelastic properties of Plasticised Poly(methyl methacrylate) in the glassy state', Brit. J. Appl. Phys. 9 , 388 (1958).

17. Jenkel, E. , and Heusch, R., 'Study of the effects of Solvents and Plasticisers on the glass transition in Polystyrene and Poly(methyl methacrylate)', Kolloid-Z 89 , 130 (1953).

18. Moorre, R.S., and Flick, J.R., 'Influence of water concentration on the Mechanical and Rheo-optical properties of Poly(methyl methacrylate)" Water in Polymers by Rowland, S.P., American Chemical Society Washington, D.C. 1980.

19. Kuhn, W., and Grun, F. Kolloid-Z 101 , 247 (1942)

20. Treloar, L.R.G., The Physics of Rubber elasticity, 2nd ed., Oxford University Press, Inc., 1958.

21. Gurnee, E.F., 'Theory of Orientation and Double refraction in Polymers', J. Appl. Phys. 25 1232 (1954).

22. Stein, R.S., 'Optical Studies of the Stress-induced crystallization of Polymers', Polym. Eng. Sci. 16 , 152 (1976).

23. Budynes, R.G., Advanced Strength and Applied Stress analysis, McGraw-Hill Book Company 1977.

24. Forziati, A.F., Optical methods, Chap. III in Gordon, M.K., (ed)., Analytical Chemistry of Polymers Part II, Interscience Div. John Wiley and Sons, New York 1962.

25. Born. M., Optik, Julius Springer Verlag, Berlin 1933.

26. Kuske, A., Robertson, G., 'Photoelastic stress Analysis', John Wiley and Sons, Inc., New York. 1974.

27. Corker, E.G., and Filon, L.N.G., 'Treatise on Photoelasticity,'Cambridge University Press, New York, 1931.

28. Mindilin, R.D., Review of the Photoelastic methods of Stress Analysis, J. Appl. Phys. 10., 222-241, 273-294, (1939).

29. Collins, E.A., and Bares, J., Experiments in Polymer Science, John Wiley and Sons. Inc. New York 1973.

30. O'konski, C.T., 'Photoelasticity p. 590 in, Bikales, N.M.; Conrod, J.; Ruks A.; Perlaman, J., (ed).,

Encyclopedia of Polymer Science and technology Vol. 9, Interscience Div. John Wiley and sons, New York 1968

31. Frotcht, M.M. Photoelasticity, Vol. 2, John Wiley and Sons Inc. New York 1948.

32. Jessop, H.T. 'The optics of a Polariscope', J. Sci. Instr. 25 , 124 (1948).

33. Dally, W.J. and Riley, E.W. Experimental stress analysis, McGraw-Hill Inc. 1978.

34. Jessop H.T., 'On the Tardy and Senarmont Methods of Measuring Fractional Relative Retardations', Brit. J. Appl. Phys. 4, 138-141 (1953).

35. Moore, S.R., and Gieniewski, C., 'Rheo-Optical Properties of ABS Polymers and their component materials' J. Appl. Phys. 41, 4367 (1970).

36. Gurnee, F.E.; Patterson, T.L., and Andrews, D.R., 'Apparatus for making simultaneous stress and Birefringence measurements on Polymers', J. Appl. Phys. 26, 1106 (1955).

37. Bovey F.A. and Tiers, G.V.D., J. Polym. Sci. 44 173 (1960).

38. Shah, V., Handbook of Plastics testing technology, A Wiley Interscience Publication, John Wiley and Sons, New York 1984.

39. Andrews, R.D., 'Linear Polymers' in Houwink, R. and deDecker, H.K., (ed) Elasticity Plasticity and Structure of Matter, Cambridge at the University Press 1971.

40. Jessop, H.T., and Harris, F.C., 'Photoelasticity: Principles and Methods', Dover Publications, Inc., New York, 1950.

41. Rodriguez, F., 'Principles of Polymer systems' McGraw-Hill Book Company, New York 1970.

42. Junichiro, M. and Shigeki, T. J. Mate. Sci. 21 2114-2118 (1986).

43. Randall M.; Longtin, B. and Weber, H. "The Diffusion of Water into normal Butyl alcohol at 30^{o}C, J. Phy. Chem. 45 , 343 (1941).

44. Hildebrand, J.H., and Scott, R.L., The Solubility of none electrolytes,, 3rd end., Reinhold Publishing Corporation, New York, 1950.

45. Beerbower, A., and Dickey, J.P., "Advanced Methods of predicting Elastomer/Fluids Interactions", Am. Soc. Lubr. Eng. Trans. 12, 1-20 (1969).

46. Ross, L., and Birley, A.W., 'Optical Properties of Polymer Materials and their measurements' J. Phys. D: Appl. Phys. 6, 795(1973).

47. Ziabicki, A., 'Molecular Theories of the Rheological Behaviour of Condensed Polymer systems', International Congress of Rheology 7th gathering Sweden 1976, Proccedings of 7th Structural Congress in Rheology, Chalmers University of Technology, Gothenburg Sweden. August 23rd - August 27th 1976.

48. Kolsky, H., 'Stress-Birefringence in Polystyrene', Nature, 166, 235-236 (1950).

49. Brydson, J.A., 'Plastics Materials' (3rd ed.), London, Newsness-Butterworths, 1975.

50. Seymour, R., Plastics Vs. Corrossives, John Wiley and Sons, New York 1982.

51. Krevalen, D.W. Van, Properties of Polymers: Their estimation correlation with chemical structure, Elsevier Scientific Publishing Company,

Amsterdam-Oxford-New York 1976.

52. Koelble, D.H., Free Volume and Polymer Rheology, Chap. 6, in Eirich, F.R., (ed) '<u>Rheology</u>: <u>Theory and Applications</u>', Academic Press, New York and London 1969.

53. Saunders, D.W., 'The Photoelastic Properties of Cross-Linked Amorphous Polymers, Part 1 and 2', Trans. Faraday Soc. <u>52</u> , 1414 -1431 (1956).

54. Flory, P.J., <u>Principles of Polymer Chemistry Chap. 13</u> , Cornell University Press Ithaca, New York 1953.

55. Williams, J.G., <u>Stress Analysis of Polymers</u>, 2nd (revised) edition, Ellis Horwood Ltd., New York Chichester - Brisbane-Torinto, 1980.

56. Read, B.E. 'Dynamic Birefringence of PMMA', J. Polym. Sci., Part C, <u>16</u>, 1887 (1967).

57. Kajiyama, T., Stein, R.S., and Macnight, W.J., 'Birefringence Studies of the Relaxation of

Ethylene-Methacrylic acidCopolymers and their salts', J. Appl. Phys. 41, 4361 (1970).

58. Spence J., 'Optical Anisotropy and the Structure of Cellulosic Sheet Materials, J. Phy. Chem. 43, 865 (1941).

59. Mcloughim, J.R. and Tobolsky, A.V., 'The Visco-elastic behaviour of PMMA', J. Colloid Sci. VII, 1952.

60. Shibayama, K., Tanaka, T., and Kodana, M., 'Effects of Diluents and cross linking on secondary Mechanical Dispersion of Polyalkyl Methacrylates', Proceedings of the fifth international Congress on Rheology Vol. 3, p. 451 edited by Shigeharu Onogi, University of Tokyo. Press Tokyo, University Park Press, Baltmore, Maryland, and Manchester, England 1970.

61. Tsai, W.; Chen, C.C., and Saver, J.A., 'Environmental effects of Silicone oils on mechanical properties of low and high molecular weight' PMMA, J. Mate Sci. 19, 3967 (1984)

62. Nakamura, K. et. al., 'Mechanical properties of slightly plasticised Poly(Vinyl Chloride), Proccedings of the fifth international Congress on Rheology' Vol. 3, p. 409. Edited by Shigeharu Onogi Universities of Tokyo, University Park Press, Baltmore, Maryland, and Manchester, England 1970.

63. Urbanski, W.C., et al. Handbook of analysis of syn thetic polymers and plastics, John Wiley and sons Inc. New York 1977.

64. Wahlstrom, E.E., Optical Crystallography, John Wiley and Sons, New York, 1951.

APPENDICES

APPENDIX A.1.

LOAD- FRINGE ORDER DATA FOR PMMA CONDITIONED IN ACETONITRILE FOR VARIOUS DURATIONS

TABLE A.1.1

Duration...0.5 hrs

LOAD (N)	FRINGE ORDER
266.90	0.3592
400.36	0.5315
533.81	0.6944
667.26	0.8556
800.71	1.0222
934.16	1.1944
1067.62	1.3611
1201.07	15278
1334.52	1.7611
1467.97	1.9722
1601.42	2.1917

TABLE A.1.2

Duration...1 hr.

LOAD (N)	FRINGE ORDER
266.90	0.3722
400.36	0.5481
533.81	0.7250
667.26	0.8833
800.71	1.0500
934.16	1.2205
1067.62	1.4196
1201.07	16438
1334.52	1.8379
1467.97	2.0695
1601.42	2.2639

TABLE A.1.3

Duration .. 2 hrs.

LOAD (N)	FRINGE ORDER
266.90	0.3986
400.36	0.5611
533.81	0.7500
667.26	0.9194
800.71	1.1117
934.16	1.3278
1067.62	1.4722
1201.07	1.6944
1334.52	1.8778
1467.97	2.1389
1601.42	2.3472

TABLE A.1.4

Duration---6 hrs

LOAD(N)	FRINGE ORDER
240.21	0.3556
266.90	0.4153
320.28	0.4924
373.67	0.5556
400.36	0.6077
427.05	0.6380
533.81	0.6944
587.19	0.7833
640.57	0.8593
667.26	0.9708
693.95	1.0132
747.33	1.0833
800.71	1.1625
850.09	1.2393
907.47	1.3333
934.16	1.3833
960.85	1.4444
1014.23	1.5000
1067.62	1.6084
1121.00	1.6938
1174.37	1.7500
1201.07	1.8611
1227.76	1.9167
1281.14	2.0278
1334.52	2.1667

TABLE A.1.5

Duration ---8 hrs

LOAD(N)	FRINGE ORDER
240.21	0.3685
266.90	0.4306
320.28	0.5056
373.67	0.5740
400.36	0.6111
427.05	0.6528
480.43	0.7166
533.81	0.8028
587.19	0.8806
640.57	0.9639
667.26	1.0278
693.95	1.0417
747.33	1.1264
800.71	1.1917
842.11	1.2500
907.47	1.3389
934.16	1.3889
960.85	1.4444
1014.23	1.5348
1067.62	1.6111
1121.00	1.7570
1174.37	1.8264
1201.07	1.8764
1281.14	2.0417

TABLE A.1.6

Duration --13 hours

LOAD (N)	FRINGE ORDER
160.14	0.2778
186.83	0.3167
213.52	0.3611
240.21	0.3982
266.90	0.4375
293.59	0.4907
320.28	0.5417
346.98	0.5852
373.67	0.6334
400.36	0.6737
427.05	0.7361
453.74	0.7959
480.43	0.8444
507.12	0.9181
533.81	0.9722
587.19	1.080
640.57	1.2083
693.95	1.3472
747.33	1.4861
800.71	1.6306

TABLE A.1.7

Duration --- 15 hours

LOAD (N)	FRINGE ORDER
160.14	0.2824
186.83	0.3361
213.52	0.3778
240.21	0.4306
266.90	0.4722
293.59	0.5139
320.28	0.5556
346.98	0.6222
373.67	0.6556
400.36	0.7055
427.05	0.7639
453.74	0.8056
480.43	0.8611
507.12	0.9167
533.81	0.9861
560.50	1.0333
587.19	1.0694
613.88	1.1667
640.57	1.2333
667.26	1.3056
693.95	1.4167
720.64	1.4722
747.33	1.5556
774.02	1.6667
800.71	1.7222
827.40	1.8056

TABLE A.1.8

DURATION ---20 hrs

LOAD (N)	FRINGE ORDER
160.14	0.2926
186.83	0.3458
213.52	0.3800
240.21	0.4391
266.90	0.4851
293.59	0.5232
320.28	0.5611
373.67	0.6895
400.36	0.7389
427.05	0.8000
453.74	0.8472
480.43	0.9083
533.81	1.0500
587.19	1.1181
640.57	1.2500
667.27	1.3333
693.95	1.4796
747.33	1.6018
800.71	1.8195

TABLE A.1.9

Duration--- 24 hrs.

LOAD (N)	FRINGE ORDER
160.14	0.3111
186.83	0.3542
213.52	0.3834
240.21	0.4444
266.90	0.5070
320.28	0.6270
346.98	0.7023
373.67	0.7222
400.36	0.7778
427.05	0.8278
453.74	0.8833
480.43	0.9722
507.12	1.0278
533.81	1.1000
567.19	1.1944
640.57	1.3333
667.26	1.4444
693.95	1.5000
720.64	1.6389
747.33	1.7778
774.02	1.8889
800.71	2.1111

TABLE A.1.10

Duration---45 hrs

LOAD (N)	FRINGE ORDER
133.45	0.2778
146.80	0.3194
160.14	0.3574
173.49	0.3898
186.83	0.4278
200.18	0.4685
213.52	0.5120
226.87	0.5556
240.21	0.5944
253.56	0.6398
266.90	0.6815
280.25	0.7259
293.59	0.7630
306.94	0.8148
320.28	0.8685
333.63	0.9333
346.98	0.9722
360.32	1.0542
373.67	1.1370
387.01	1.2065
400.36	1.3037
413.70	1.3889
427.05	1.5000
453.74	1.6148
480.43	1.7556
507.12	1.9537
533.81	2.1806

TABLE A.1.11

Duration 66 hrs

LOAD(N)	FRINGE ORDER
133.45	0.3611
146.80	0.3889
160.14	0.4444
173.49	0.5000
186.83	0.5500
200.18	0.5833
213.52	0.6090
226.87	0.6408
240.21	0.6963
253.56	0.7500
266.90	0.8042
280.25	0.8750
293.59	0.9056
306.94	0.9685
320.28	1.0417
333.63	1.1113
346.98	1.1833
360.32	1.3056
373.67	1.3611
387.01	1.4444
400.36	1.6389
413.70	1.7778
427.05	1.9167
453.74	2.1250
480.42	2.4444

APPENDIX A.2

LOAD- FRINGE ORDER DATA FOR PMMA CONDITIONED IN N-BUTANOL FOR VARIOUS DURATIONS

TABLE A.2.1.
Duration .. 3 hrs

LOAD (N)	FRINGE ORDER
266.90	0.3056
400.36	0.4709
533.81	0.6528
66.26	0.8148
800.71	0.9667
934.16	1.1407
1067.62	1.2815
1201.08	1.4775
1334.52	1.6944
1467.97	1.9187
1601.42	2.1737

TABLE A.2.2.
Duration.. 6hrs

LOAD (N)	FRINGE ORDER
266.90	0.3000
400.36	0.4639
533.81	0.6333
667.26	0.8074
800.71	0.9583
934.16	1.1389
1067.62	1.2500
1201.08	1.4722
1334.52	1.6926
1467.97	1.8982
1601.42	2.1426

TABLE A.2.3.
Duration .. 12 hrs.

LOAD (N)	FRINGE ORDER
266.90	0.2972
400.36	0.4570
533.81	0.6181
667.26	0.7806
800.71	0.9403
934.16	1.1250
1067.62	1.2361
1201.08	1.4556
1334.52	1.6695
1467.97	1.8778
1601.42	2.1204

TABLE A.2.4

Duration...24 hrs

LOAD (N)	FRINGE ORDER
266.90	0.2917
400.36	0.4463
533.81	0.6111
667.26	0.7639
800.71	0.9306
934.16	1.0833
1067.62	1.2315
1201.08	1.4130.
1334.52	1.6407
1467.97	1.8241
1601.42	2.0833

TABLE A.2.

Duration .

LOAD (N)
266.90
400.36
533.81
667.26
800.71
934.16
1067.62
1201.08
1334.52
1467.97
1601.42

5

.30 hrs

FRINGE ORDER
0.2903
0.4389
0.6100
0.7625
0.9278
1.0750
1.2250
1.4084
1.6042
1.7695
1.0324

TABLE A.2.6

Duration ..48

LOAD (N)	FRINGE ORDER
266.90	0.2796
400.36	0.4278
533.81	0.5953
667.26	0.7552
800.71	0.9028
934.16	1.0556
1067.62	1.2056
1201.08	1.3611
1334.52	1.5296
1467.97	1.7000
1601.42	1.9204

TABLE A.2.7
Duration ..96 hrs

LOAD (N)	FRINGE ORDER
266.90	0.2620
400.36	0.4250
533.81	0.5944
667.26	0.7528
800.71	0.8944
934.16	1.0496
1067.62	1.1944
1201.08	1.3600
1334.52	1.5212
1467.97	1.7150
1601.42	1.9144

TABLE A.2.8
Duration 336 hrs

LOAD (N)	FRINGE ORDER
266.90	0.2556
400.36	0.4148
533.81	0.5833
667.26	0.7481
800.71	0.8814
934.16	1.0407
1067.62	1.1685
1201.08	1.3593
1334.52	1.5185
1467.97	1.7000
1601.42	1.9093

TABLE A.2.9
Duration 504 hrs

LOAD (N)	FRINGE ORDER
266.90	0.2544
400.36	0.4120
533.81	0.5722
667.26	0.7417
800.71	0.8028
934.16	1.0389
1067.62	1.1680
1201.08	1.3611
1334.52	1.5000
1467.97	1.7222
1601.42	1.9084

APPENDIX A.3

LOAD-FRINGE ORDER DATA FOR PMMA CONDITIONED IN METHANOL FOR VARIOUS DURATIONS

A.3.1 Duration .. 3 hrs		A.3.2 Duration .. 6 hrs		A.3.3. Duration ..12 hrs	
LO (N)	FO	EO (N)	FO	LO	FO
266.90	0.3352	266.90	0.3380	266.90	0.3435
400.36	0.5037	400.36	0.5074	400.36	0.5111
533.81	0.6694	533.81	0.6722	533.81	0.6778
667.26	0.8380	667.26	0.8403	667.26	0.8435
800.71	1.0056	800.71	1.0120	800.71	1.0139
934.16	1.1713	934.16	1.1778	934.16	1.1820
1067.62	1.3352	1067.62	1.3481	1067.62	1.3556
1201.08	1.5148	1201.08	1.5287	1201.08	1.5398
1334.52	1.6787	1334.52	1.7167	1334.52	1.7398
1467.97	1.9945	1467.97	2.0111	1467.97	2.0158
1601.42	2.1574	1601.42	2.1806	1601.42	2.1889

A.3.4

Duration .. 24 hrs

LO (N)	FO
266.90	0.3491
400.36	0.5259
533.81	0.6805
667.26	0.8463
800.71	1.0222
934.16	1.1917
1067.62	1.3583
1201.08	1.5455
1334.52	1.7639
1467.97	2.0000
1601.42	2.2222

A.3.5.

Duration..

LO (N)
266.90
400.36
533.81
667.26
800.71
934.16
1067.62
1201.08
1334.52
1467.97
1601.42

72 hrs

FO
0.3574
0.5361
0.7000
0.8667
1.0574
1.2130
1.4176
1.6723
1.8611
2.0852
2.3333

A.3.6

Duration ..96 hrs

LO (N)	FO
266.90	0.3602
400.36	0.5503
533.81	0.7194
667.26	0.8926
800.71	1.0796
934.16	1.3556
1014.23	1.4167
1067.62	1.5889
1201.08	1.7917
1334.52	2.0000

A.3.7.

Duration..168 hrs

LO (N)	FO
213.52	0.2778
266.90	0.3710
320.28	0.4167
373.67	0.5417
400.36	0.6056
427.05	0.6639
480.43	0.7472
533.81	0.8320
587.19	0.9139
640.57	1.0264
667.26	1.0972

A.3.8

Duration .

LO (N)
133.45
160.14
186.83
213.52
240.21
266.90
293.59
320.28
346.98
373.67
400.36
427.05
453.74
480.43
507.12
533.81

.336 hrs

FO
0.2222
0.2500
0.2898
0.3403
0.3611
0.3889
0.4222
0.4620
0.5046
0.5528
0.6074
0.6778
0.7268
0.7991
0.8787
0.9083

A.3.9

Duration...504 hrs

LO (N)	FO
133.45	0.2500
160.14	0.2900
186.83	0.3398
213.52	0.3889
240.21	0.4389
266.90	0.4880
293.59	0.5398
320.28	0.5963
346.98	0.6547
373.67	0.7194
400.36	0.7852
427.05	0.8458
453.74	0.9084
480.43	1.0019
507.12	1.0547
533.81	1.1417

APPENDIX A.4

LOAD - FRINGE ORDER DATA FOR PMMA CONDITIONED IN ETHYLENE GLYCOL FOR VARIOUS DURATIONS

TABLE A.4.1

Duration .. 3 hrs

LO (N)	FO
266.90	0.3278
400.36	0.4944
533.81	0.6620
667.26	0.8306
800.71	0.9926
934.16	1.1611
1067.62	1.3278
1201.08	1.4972
1334.52	1.7324
1467.97	2.0084
1601.42	2.2083

TABLE A.4.2

Duration.. 6 hrs

LO (N)	FO
266.90	0.3203
400.36	0.4875
533.81	0.6556
667.26	0.8236
800.71	0.9861
934.16	1.1556
1067.62	1.3208
1201.08	1.4956
1334.52	1.7200
1467.97	1.9931
1601.42	2.1944

TABLE A.4.3.

Duration.. 24 hrs

LO (N)	FO
266.90	0.3093
400.36	0.4759
533.81	0.6463
667.26	0.8070
800.71	0.9704
934.16	1.1500
1067.62	1.3074
1201.08	1.4759
1334.52	1.7111
1467.97	1.9722
1601.42	2.1547

TABLE A.4.4

Duration..48 hrs

LO (N)	FO
266.90	0.3019
400.36	0.4658
533.81	0.6361
667.26	0.7964
800.71	0.9611
934.16	1.1343
1067.62	1.2281
1201.08	1.4685
1334.52	1.6963
1467.97	1.9139
1601.42	2.0833

TABLE A.4.

Duration 7

LO (N)
266.90
400.36
533.81
667.26
800.71
934.16
1067.62
1201.08
1334.52
1467.97
1601.42

5.

2 hrs

FO
0.2991
0.4611
0.6324
0.7935
0.9547
1.1241
1.2908
1.4592
1.6843
1.9037
2.1259

TABLE A.4.6

Duration 96 hrs

LO (N)	FO
266.90	0.2917
400.36	0.4556
533.81	0.6259
667.26	0.7889
800.71	0.9500
934.16	1.1167
1067.62	1.2778
1201.08	1.4398
1334.52	1.6398
1467.97	1.8889
1601.42	2.1111

TABLE A.4.7

Duration ..168 hrs

LO (N)	FRINGE ORDER
266.90	0.2861
400.36	0.4444
533.81	0.6153
667.26	0.7667
800.71	0.9417
934.16	1.0972
1067.62	1.2667
1201.08	1.4222
1334.52	1.6111
1467.97	1.8861
1601.42	2.0833

TABLE A.4.

Duration .

LO (N)
266.90
400.36
533.81
667.26
800.71
934.16
1067.62
1201.08
1334.52
1467.97
1601.41

.8

..336 hrs

FRINGE ORDER
0.2833
0.4389
0.6111
0.7611
0.9306
1.0847
1.2556
1.4111
1.5944
1.8787
2.0426

TABLE A.4.9

Duration.. 504 hrs

LO (N)	FRINGE ORDER
266.90	0.2750
400.36	0.4176
533.81	0.5787
667.26	0.7268
800.71	0.8852
934.16	1.0396
1067.62	1.1944
1201.08	1.3333
1334.52	1.4907
1467.97	1.6778
1601.41	1.8889

APPENDIX A.5

LOAD - FRINGE ORDER DATA FOR PMMA CONDITIONED IN ETHANOL FOR VARIOUS DURATIONS

TABLE A.5.1

Duration ..3 hrs

LOAD (N)	FRINGE ORDER
266.90	0.3333
400.36	0.5000
533.81	0.6667
667.26	0.8333
800.71	1.000
934.16	1.1667
1067.62	1.3333
1201.08	1.5028
1334.52	1.7259
1467.97	1.9944
1601.42	2.1611

TABLE A.5.2

Duration .. 6hrs

LOAD (N)	FRINGE ORDER
266.90	0.3333
400.36	0.5000
533.81	0.6667
667.26	0.8333
800.71	1.0000
934.16	1.1667
1067.62	1.3333
1201.08	1.5000
1334.52	1.7296
1467.97	1.9944
1601.42	2.1667

TABLE A.5.3

Duration ..12 hrs

LOAD (N)	FRINGE ORDER
266.90	0.3333
400.36	0.5000
533.81	0.6639
667.26	0.8306
800.71	1.000
934.16	1.1667
1067.62	1.3333
1201.08	1.4982
1334.52	1.7222
1467.97	1.9945
1601.42	2.1654

TABLE A.5.4
Duration .. 48 hrs

LOAD (N)	FRINGE ORDER
266.90	0.3278
400.36	0.5000
533.81	0.6667
667.26	0.8306
800.71	0.9889
934.16	1.1668
1067.62	1.3333
1201.08	1.5056
1334.32	1.7083
1467.97	1.9778
1601.42	2.1630

TABLE A.5.
Duration .

LOAD (N)
266.90
400.36
533.81
667.26
800.71
934.16
1067.62
1201.08
1334.32
1467.97
1601.42

5
..72 hrs

FRINGE ORDER
0.3305
0.5021
0.6672
0.8331
1.0021
1.1668
1.3340
1.5048
1.6806
1.9768
2.1625

TABLE A.5.6
Duration ...96 hrs

LOAD (N)	FRINGE ORDER
266.90	0.3340
400.36	0.5045
533.81	0.6678
667.26	0.8306
800.71	0.9972
934.16	1.1679
1067.62	1.3056
1201.08	1.5082
1334.32	1.6778
1467.97	1.9306
1601.42	2.1655

TABLE A.5.7

Duration ..168 hrs

LOAD (N)	FRINGE ORDER
266.90	0.3361
400.36	0.5100
533.81	0.6719
667.26	0.8389
800.71	1.0084
934.16	1.1708
1067.62	1.3287
1201.08	1.5111
1334.52	1.7472
1467.97	1.9654
1601.42	2.1667

TABLE A.5.8

Duration 336 hrs

LOAD (N)	FRINGE
266.90	0.3389
400.36	0.5111
533.81	0.6778
667.26	0.8417
800.71	1.0111
934.16	1.1778
1067.62	1.3444
1201.08	1.5139
1334.52	1.7528
1467.97	1.9722
1601.42	2.1778

ORDER

TABLE A.5.9

Duration 504 hrs

LOAD (N)	FRINGE ORDER
266.90	0.3444
400.36	0.5181
533.81	0.6870
667.26	0.8453
800.71	1.0222
934.16	1.1861
1067.62	1.3500
1201.08	1.5306
1334.52	1.7611
1467.97	1.9778
1601.42	2.1889