THE ACTION OF POLAR ADSORBATES ON NYLON 66

by

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ABSTRACT

The present investigation deals with two broad aspects of fibre research: both directed towards the elucidation of the role of the polar groups in polyamides and polypeptides.

(1) The study of the interaction of certain disaggregating polar reagents like lithium bromide, lithium perchlorate and magnesium perchlorate with nylon 66.

(2) The study of changes in sorption of water, when polyamide (nylon 66) and polypeptide (silk) fibres are subjected to a tensile deformation.

The effect of polar reagents on the dimensions and tensile characteristics suggests a possibility of interaction at the polar group.

The changes in X-ray diffraction patterns reveal a significant decrease in the β form, and an annealing effect. The interaction is confined to the polycrystalline regions, and the reagents

do not produce setting of nylon. It is suggested that β form appears towards the edges of the crystallites.

The N.M.R. and the infra-red study of N-ethyl acetamide (model compound) suggests a possibility of an interaction between the polar reagent and the CONH groups.

Nylon films treated with polar reagents show a new absorption peak at 3390 cm^{-1}, which changes on deuteration to 2518 cm^{-1}. It has been shown that this is a new NH peak and that it may have slight parallel dichroism.

An ion-dipole interaction mechanism has been suggested which favours the possibility of co-ordination of ions with the lone pair electron of the nitrogen atom.

The changes in regain of nylon with strain, at different humidities (13, 35, 52, 66 and 93% r.h.) have been measured. Regain increases with increased strain, but, except at 13% r.h., the changes have been found to be independent of humidity. It is interesting to note that the changes in regain are quite appreciable (about 1.0% moisture regain for 8% strain), and are in agreement with those calculated from stress relaxation of nylon at different humidities. The calculated changes in volume from the known value of Poisson's ratio for nylon agrees fairly well with the observed change in regain. The changes in regain of silk under strain vary with the changes in surrounding humidity. At 65% r.h. the changes are comparable to those for nylon 66. The results have been interpreted in terms of stress relaxation mechanism.

The longitudinal swelling of nylon has been measured under a constant load of 2.4g/denier. On substituting suitable values from the above experiments in the thermodynamic equation a reasonable agreement between the calculated and the experimental values of the reversible modulus for nylon 66 has been found.

It has been postulated that the interaction of water with nylon is confined to the rotational energy levels of the system. This postulate has been extended to various observed phenomena as follows.

(a) The change in α'- loss modulus peak for nylon as a result of increase in temperature or humidity, involves two different molecular mechanisms.

(b) The similarity between stress relaxation behaviour of different fibres in water has been attributed to a possibility of interaction of water with the rotational energy levels of various fibrous systems; regardless of the presence of specific interchain interactions in some hydrophilic fibres.

(c) An alternative explanation for the sigmoid shape of the curves of rigidity modulus against humidity for nylon has been proposed: this is in conformity with the spectral evidence that there are no free NH groups in nylon 66.

(d) A possible mechanism for setting of nylon 66 has been suggested, and it has been shown that the weakening of inter-chain interaction alone is not sufficient to impart desirable dimensional stability.

A hypothetical system has been proposed which explains that the relative movement of segments is not the sole contributor to stress relaxation, and that the main chains may play an important role.

PUBLICATION

Some aspects of the work described in this thesis have been included in the following article

"ACTION OF POLAR REAGENTS ON NYLON 66"

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by G. Sarda
N. Peacock

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CHAPTER I

INTRODUCTION

The interdependence of intuitive search[1] and knowledge of the interaction of polar reagents[2] with polar groups in amides has been an important consideration in the elucidation of subtle intricacies of macromolecular structure. To this end a fairly radical attempt is made in the hope of co-ordinating available infra-red methods, essentially empirical as applied to high polymers, and intrinsically empirical thermodynamic methods.

The present investigation confines itself to the interaction of disaggregating polar reagents with the peptide group. It may be noted that the selection of specific disaggregating reagents is important since use of degrading reagents would defeat the very purpose of this study. Whereas for infra-red methods polar reagents are used to induce an ion-dipole interaction (chemical treatments), the thermodynamic approach is based on induced deformation (physical changes) which leads to sorption at polar sites.

MOLECULAR FORCES IN NYLON 66

The word nylon[3] has no etymological significance, and is a generic term for all the synthetic linear polyamides obtained either from the condensation of a di-amine and a di-carboxylic acid or by polymerisation of any ω-amino acid. In the case of nylon 66, hexamethylene di-amine and adipic acid are used.

$$H_2N\ (CH_2)_6NH_2 + HOOC(CH_2)_4COOH\ =$$
$$-\ NH(CH_2)_6NHOC(CH_2)_4CONH\ -$$

There seem to be two possible types of molecular interaction in polyamides[4]: a non-specific one associated with the packing of polyethylenic segments, and a specific one associated with peptide linkages. It may be noted that the amide (CONH) group is an important structural feature which also appears in polypeptides.

NON-SPECIFIC INTERACTIONS

These[5] are Van der Waals' type of attraction forces, and are weakest among all the different types of force. They are quantum mechanical in origin,[6] are directional, but being transient attain an overall spherical symmetry with time; therefore, on an average they are non-directional and lead to the closest packing of molecules. The contribution of these forces to polymer structure has yet to be found.

SPECIFIC INTERACTIONS

1. Hydrogen bonding:

A hydrogen bond[7] exists between a functional group A–H and an atom or a group of atoms B in the same or different molecules, when

(a) there is evidence of bond formation,

(b) there is evidence that this bond linking A–H and B, specifically involves the hydrogen atom already bonded to A.

The proton donating power of A–H will depend on the electron affinity of atom A, and on the tendency of B to attract electrons. Crystallographic studies have shown that the A–B distance is appreciably smaller than the sum of the known Van der Waals' radii, and in a A–H..B system this may be attributed to the presence of hydrogen bonding.

In general the N–H..O bond[8] is linear (to within about 10 degrees), and the nitrogen-oxygen distance is 2.79 ± 0.12 A. The energy of the hydrogen bond seems not to depend greatly on the angle at the oxygen atom, but there is evidence that maximum stability results from having all the four atoms of N–H..O–C aligned.

Nagakura[9, 10] concluded from U.V. studies that hydrogen bonding is not solely electrostatic in mechanism, and that quantum mechanical delocalisation mechanism also contributes. Even in an asymmetric hydrogen bond a weak covalent link is formed between H and B atoms. Cannon[6] has gone further to say that the properties and the energy of hydrogen bond are determined more by the quantum contribution than by the electrostatic interaction.

2. Dipolar interactions

These are purely electrostatic attractions between "$^{+}$NCO^{-}" dipoles which lie along molecular chains. These, since dipoles are related directly to the geometry of the molecules, will be directional forces, and will lead to orientation-dependent interactions: i.e. they develop a maximum interaction energy for a specific relative orientation of the molecule. In a tri-atomic system[11] A-H..B the total interaction energy E is built up from the acceptor-donor interaction energy E_a, and that of dipole-dipole interaction E_g, i.e.:

$$E = E_a + E_g \quad \ldots\ldots\ldots\ldots (1)$$

The system may well exist where directional dipole-dipole interaction between molecules may reinforce or oppose any quantum interaction. When water molecules associate, the dipoles align so that the electrostatic interaction reinforces the hydrogen bond quantum interaction. On the other hand, in an amide the dipole-dipole interaction between the OCN dipoles opposes the tendency for hydrogen bond formation. In the secondary amides and polyamides where the CONH group is in the trans form, the dipole interaction being the stronger attraction controls the association of the CONH groups.

RESONANCE IN AMIDES[8]

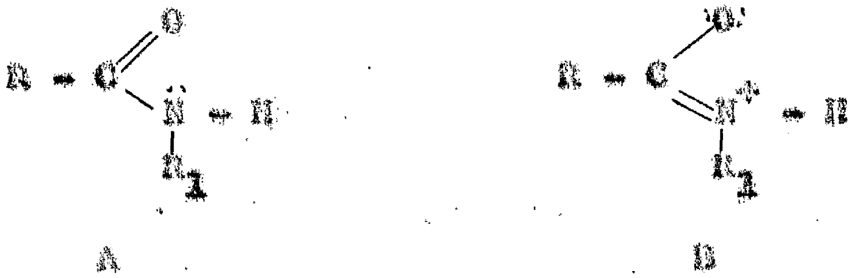


Fig. 1.

The SP^2 hybridization[12] results in two principle resonance structures of the amide group, as shown in Fig. 1; which are not equivalent and it is expected that A contributes somewhat more than B to the resonance hybrid. The resonance energy is about 21 K.cal/mole. The appearance of structure B is completely inhibited by addition of a proton to the nitrogen atom. Under normal conditions the C-N bond length is 1.32 A, which is less than the normal single bond distance between C and N atoms, and the contribution of the two structures is evaluated at 60% for (A) and 40% for (B).

POLAR REAGENTS

A molecule in which the centres of positive and negative charges are not coincident in space is said to be polarised. When two different kinds of atoms unite to form a di-atomic molecule, the product is usually polar;

however, the intrinsic tendency of separation of the charge centres depends on the relative position of atom in the periodic-table. The hydration of the ions or the solvation effects enhance the polar character of the reagent in solutions.

SURVEY OF PHYSICAL METHODS USED FOR STUDYING MOLECULAR STRUCTURE.

Methods of investigating the molecular structure of long chain polymers[13] are somewhat limited both in scope and number. The physical methods that have proved most valuable depend upon the interactions between matter and radiation of one kind or another. When there is a transfer of energy, the effects are studied by spectroscopic techniques, and when there is no transfer of energy between radiation and molecules, the phenomenon of diffraction is studied, e.g. by X-ray methods.

X-RAY DIFFRACTION

The ultimate product of X-ray diffraction technique could be an account of the electron density distribution over the molecule, a distribution averaged in time and space over a vast number of individual molecules in the crystals, but this is excessively complex. By a simple analysis based on Bragg's law it gives some information about relative position of atoms in crystalline regions and fairly accurate deduction of probable conformation of molecular chains in high polymers. The quantitative analysis of the intensity distribution of the diffraction spots can be used in the assessment of the crystallite size and the orientation of crystallites.

SPECTROSCOPIC METHODS

The spectroscopic method is more radical. Its immediate findings are transitions between pairs of energy levels: these levels depend on the eigen values of the appropriate wave function. Since these methods look towards the wave function, they constitute the most fundamental experimental approach to the investigation of molecular structure.

PHOTON AS A PROBE INTO THE MOLECULAR STRUCTURE

The discrete quantised energy states of a molecule are given as under:[14]

1. The energy levels of electrons (10^{-11} ergs),
2. the vibrational energy levels of nuclei in their relative displacements (10^{-13} ergs),
3. the rotational energy levels of the molecule as a whole (10^{-16} ergs),
4. additional energy levels arising out of an interaction of applied electric or magnetic field with the rotational motion of molecule as a whole or with the spin of electrons and nuclei.

There is a probability of transition from one state to another if the correct amount of energy is supplied. One way of supplying energy is by means of electromagnetic radiation, which behaves as if it were composed of discrete particles of energy called photons. Energy of photons is given by the equation:

$$E = hc/\lambda \quad \ldots\ldots\ldots\ldots \quad (2)$$

E = energy of photon,
h = Planck's constant (6.624×10^{-27} erg. seconds),
c = velocity of light in vacuo.,
λ = wavelength of the radiation.

For instance, infra-red radiation (2-$15\ \mu$) will provide photons which can induce transitions in the vibrational energy levels.

INFRA-RED SPECTROSCOPY

Infra-red spectroscopy has achieved ~~the~~ most significant results in the investigation of molecular structure, but it has various limitations. The most significant among them is that the infra-red technique in case of high polymers is empirical;[15] since it takes advantage of the fact that, when a light atom like hydrogen vibrates against a heavy system, the mass of the latter does not affect the characteristic vibration frequency of the light atom; or in other words the assignment of various bands is based on their similarity to those observed in the case of simple molecules.

The frequency at which an atom can vibrate is determined by its mass, and the strength of the forces holding it in place (the ratio of force to displacement is called force-constant). The major force arises from the valence bond, but the characteristic frequency varies in a systematic way with environment of the bond or group within the molecule, because of inductive and mesomeric effects and steric strains or hindrances, and shifts in frequency may occur due to association between molecules.

DEUTERIUM SUBSTITUTION

The method of isotopic substitution has been much used to simplify the solution of molecular vibrational problems. As vibration frequency depends on the mass of vibrating atoms, one would expect a significant lowering of frequency of A-H system on deuterium exchange. The ratio of the frequencies[16] can be estimated roughly from the classical theory of a harmonic oscillator:

$$\frac{\nu D}{\nu H} = \sqrt{\frac{MH}{MD}} = \sqrt{\frac{1}{2}} \quad \ldots\ldots\ldots \quad (3)$$

where M = mass of the vibrating atom.

USE OF POLARISED INFRA-RED RADIATION

In a uniaxial structure such as a fibre, the maximum amount of information from polarised absorption spectra can be obtained from two settings of the polariser:

parallel and perpendicular to the special axis. The ratio of the optical densities measured with electric vector parallel and perpendicular to the axis is called the dichroic ratio.

NUCLEAR MAGNETIC RESONANCE[17]

This is a recent development and its application to the study of high polymers has various limitations. It differs from the infra-red methods as under:

1. N.M.R. technique is based on the magnetic properties of certain light nuclei which are related to their rotational properties. The splitting of the energy levels depends on the applied magnetic field (Zeeman effect) and the effective magnetic field experienced by each nucleus[18] (say a proton in A-H..B system), will depend on the amount of electronic shielding e.g. diamagnetic shielding will oppose Zeeman splitting.
2. According to Heisenberg's uncertainty principle, the natural width of a spectral line[19] is proportional to the reciprocal of the average time a system spends in the excited state. At higher frequencies in the infra-red region, the natural line width is seldom if ever the limit of resolution; however, at the radio-frequencies employed in N.M.R. technique, it is possible to reach this limit. In order to avoid saturation of the signal[20] a reasonable population difference must be maintained

between excited and unexcited states, and this offers certain limitations to the supply of external energy which is used to induce transitions between different states.

3. High resolution N.M.R. is a powerful technique to detect chemical shifts and study the effective interaction at amide protons. However, the use of viscous solutions which retard rotation, the presence of traces of paramagnetic impurities, quadrupole effects[20] and sp^2 hybridization may cause serious broadening of the bands.

ASSIGNMENTS OF ABSORPTION FREQUENCY BANDS IN NYLON 66

The infra-red spectrum of nylon 66 in the 2 - 15 μ region has been observed many times,[20 - 26] and most of the strong bands in the interval 2 μ - 7 μ have been assigned with reasonable certainty. Glatt[27] examined the overtone region (0.8 μ - 2.5 μ) of nylon 6.10 (polyhexamethylene sebacamide), and made a number of assignments.

The bands at 3300, 1640, and 1550 cm^{-1} are characteristic of the CONH group and Sutherland[28] and Bamford et al[29] have summarized the earlier views on these. There is little dispute that the 3300 cm^{-1} band represents the NH stretching mode but there is some controversy over the assignment of the other bands (see Table 1). The situation was greatly clarified by Fraser and Price[30] who postulated that the π - P electron interaction in the group makes the

TABLE I.

Assignment of CONH group frequencies.[31]

Mode of vibration	Frequency (cm^{-1})	
NH stretching	3300	s
Amide I+II (combination mode)	3200	m (shoulder)
2 (AmideII) -overtone	3080	w
Amide I-OCN asymmetric stretching	1650	s
Amide II (symmetric vOCN +δNH)	1550	s
Amide III (symmetric vOCN +δNH)	1270	s
Amide IV-OCN deformation	620	m
Amide V - NH out of plane deformation	690	s
*Amide VI C=O " " " "	550-600	m.

* Amide V and VI may be coupled since Amide VI shifts on deuteration.

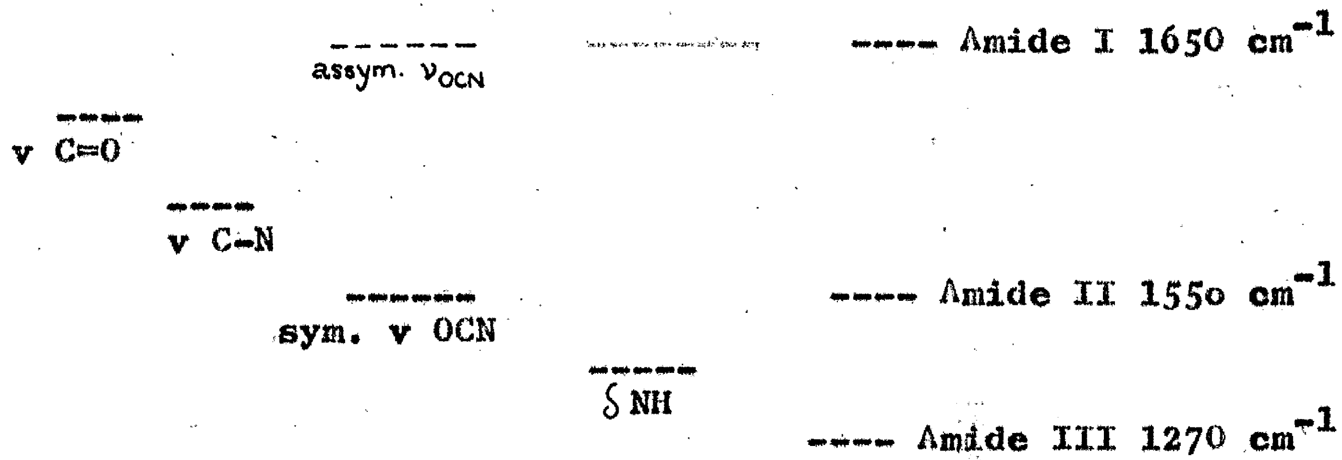


Fig. 2. Coupling in CONH group

v = stretching frequency

δ = deformation frequency

force constants of the CO and CN bonds approximately equal and mechanical coupling of their vibrations occurs. The complex coupling is pictorially summarised in Fig. 2. The above assignment is confirmed by the frequency shifts which occur on deuteration.

There is still some controversy over the weak band at 3080 cm^{-1}, which may be the first overtone of amide II[26] or be a frequency associated with intra-chain hydrogen bonding.[32] The presence of hydrogen bonds[33] materially changes the position of various bands e.g. free NH between 3570–3450 cm^{-1} changes to 3330–3050 cm^{-1}.

CHAIN CONFIGURATION

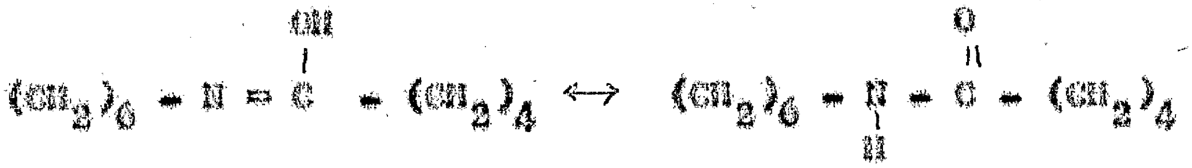
The work of Astbury and his school,[34] especially on the properties of wool, introduced the idea that a polypeptide chain could assume, according to circumstances, either an extended or a regularly folded configuration. It may be noted that whereas intermolecular hydrogen bonding favours an extended configuration, intra-molecular hydrogen bonding invariably leads to a folded configuration. The first indication that the synthetic polypeptide might be in a folded configuration was obtained from the infra-red spectrum of an oriented film of poly-methyl L-glutamate (using polarised radiation). Though several more or less complicated structural models have been proposed, Pauling's α- helix[35] has proved to be the most satisfactory one with certain reservations.

The work of Elliott and Malcolm[36] on solutions of silk in dichloroacetic acid and tri-fluoracetic acid reveals the importance of the solvent in determining the stability of a particular mode of chain configuration. It appears likely that molecules which are in the α-helix form in solution would tend to preserve their configuration when the solution is evaporated.

There is some indication[37] regarding the folding (80 A long folds) of polyamide chains, and at this stage a folded configuration cannot be ruled out. Such folding may account for the negative birefringence which has sometimes been observed in undrawn or slightly drawn nylon. It is interesting to note that recently Ford[38] has discovered isotropic segments in silk filaments, and has suggested that the rheological behaviour of these segments is comparable to multiple necking effect in nylon.[39]

MULTIPLICITY OF NH BANDS

Various authors have given different explanations to account for the observed multiplicity of the NH frequency in compounds containing CONH groups. Sutherland[40] suggested that 3 μ and 6 μ bands in nylon 66 might be due to the presence of OH and CN bonds, and that the occurrence of enolic groupings as under may not be ruled out.



$$(CH_2)_6 - N = \overset{\overset{OH}{|}}{C} - (CH_2)_4 \longleftrightarrow (CH_2)_6 - \underset{\underset{H}{|}}{N} - \overset{\overset{O}{\|}}{C} - (CH_2)_4$$

A possibility of the effect of electronic influences[41] on NH bonds resulting in abnormal stretching frequencies has been emphasised, and it is suggested that the presence of fine structure[19] on the high frequency side of CO and NH bands may be due to a new type of hydrogen bond arising from some other structural features yet to be elucidated. Holliday has reported that the 3300 cm^{-1} peak in nylon is a composite band with an unresolved shoulder at 3200 cm^{-1}. Some authors[42] have concluded that the multiplicity of NH stretching frequency which occurs in polyamides, can be produced by a system of coupled oscillators of the form:

$$\ldots HN - C = O \ldots\ldots H - N - C = O \ldots\ldots H - N \ldots$$

It has been shown that the bands associated with the NH stretching mode form a complex system in synthetic polypeptides, and there are certainly more than two peaks. Tsuboi[43] has considered the multiplicity of NH bands in terms of varied stereochemical configuration and compared cis and trans forms. The hydrogen bonded cis configuration is associated with a band in the region of 3170-3240 cm^{-1}, whilst the corresponding trans-form gives an absorption band in the region of 3290-3360 cm^{-1}. In addition the mode of hydrogen bonding (intermolecular or intramolecular) depending upon the configuration of individual molecular chains (extended or folded), depicts itself in a small but distinct frequency shift in the strong NH stretching mode of the order of 8 cm^{-1}.

A considerable amount of information[44] is available about the infra-red spectra of secondary amides in solution. Dilution results in a decrease in the intensity of the 3300 cm^{-1} band and a new peak appears at 3450 cm^{-1}. Cannon[45] has studied various interacting systems and concluded that the C=O group in amides readily interacts with the proton donating molecule to form a hydrogen bond, but the nitrogen atom of the amide group appears to be relatively inert. Also the carbonyl frequency for nylon is lowered on N-alkyl substitution, though the absence of hydrogen would lead one to expect the frequency to rise to a value close to that of an unassociated amide. These facts support the view that the polarity of the amide group is due to delocalisation of the lone pair of electrons at the nitrogen atom.

It is interesting to note that the alkyl groups of the main chains may well contribute to the complexity of spectral absorption. The hydrogen atom of the CHR group[46-48] may form a bridge to a carbonyl oxygen atom, since there is good evidence of CH..O bridges in comparable structures. Alkyl groups[49] are known to be readily polarisable, i.e. they can provide or accept electrons according to the particular group to which they are attached. It is possible therefore that in alkyl substituted amides, the fractional positive charge on the nitrogen atom is shared by the alkyl group, which would help the delocalisation of electrons at the nitrogen atom and result in a lowering of the carbonyl frequency as mentioned above.

More recently one finds a considerable amount of work being carried out to investigate the mechanism of interaction of polar reagents at the polar groups in nylon 66. Larose[50] has concluded from the effect of hydrogen chloride sorption on NH bands in nylon that interaction occurs at CONH groups and suggests that there are two types of hydrogen bonds in nylon, of which only one is affected. A quantitative estimation[51] of intensity of the NH band at 3300 cm^{-1} reveals that sorption of phenol and formic acid give rise to a new NH band at 3380 cm^{-1}, although saturation with aqueous vapour has no effect on the intensity of the original NH band at 3300 cm^{-1}.

Branby and King[52] have studied the effect of antimony tri-chloride on nylon and found that the 3300 cm^{-1} band is gradually replaced by a new band at 3375 cm^{-1}. They have suggested that the metallic ion forms a co-ordinate link with the CO groups in nylon. Nylon treated with iodine-potassium iodide aqueous solution,[53] reveals a new peak at 3355 cm^{-1} and this evidence favours an interaction at CO groups. A similar interaction mechanism has been concluded by Mandelkern et al,[54] who have studied the effect of lithium perchlorate on monomeric amides, and found that the 3300 cm^{-1} band is completely replaced by a new band at 3400 cm^{-1}.

Thus all the suggested mechanisms depict a general trend that the interaction occurs at CO groups, and that the nitrogen atom plays a relatively inert role. However, none of these is conclusive, and at this stage, it is difficult to visualize a general interaction mechanism which deals with the action of various reagents on related polymers.

ACTION OF POLAR REAGENTS

Certain salts e.g. lithium bromide[55] have an enormous activity coefficient (molal basis) in concentrated solutions. The dispersive power increases as the cationic size decreases and the anionic size increases: the cationic size plays the more important part. Lithium being the most polar ion is surrounded in solution by a hydration shell, variously estimated at from six to twenty molecules of water. The smaller size and larger ionizing potential of lithium tends to ally it with the elements of second group in the periodic table, particularly with magnesium. Aqueous solutions of lithium bromide or magnesium perchlorate (10 M) dissolve silk on heating, and the optical rotation indicates that silk in lithium bromide solution may be in a folded form.

Mandelkern et al[56] have worked on the dimensional changes in wool fibres treated with aqueous lithium bromide solution. The authors suggest that the shrinkage is due to the melting of crystallites. The modulus of elasticity[57] at room temperature of an α-keratin fibre immersed in aqueous lithium bromide solution decreases as the concentration of lithium bromide is increased.

Alexander[58] has studied the effect of aqueous solutions of lithium bromide on nylon and other fibres, and attributed the difference between the effect of the reagent on nylon and silk, to the presence of strong intermolecular interactions along the intervening polyethylenic segments in nylon 66.

Branby and King[52] have reported that both nylon and silk are soluble in molten antimony trichloride without apparent degradation of the molecular chains. The authors concluded that the hydrogen bonds are broken in both the amorphous and crystalline regions. On the other hand reagents like phenol and formic acid penetrate only the amorphous regions in nylon. King[59] has investigated the effect of water and formic acid on the dielectric and elastic characteristics of nylon. A close co-relation between the results was found and the changes have been attributed to the ease of rotation of polar groups.

The action of iodine solution on nylon 66[60] results in a strong meridional reflection at 8.3 Å, which suggests that the polymer is chemically modified, with iodine arranged regularly in three dimensions. Larose[61] has described profound changes in the structure of nylon due to the effect of hydrogen chloride. The new 14.4 A identity period reflects considerable shortening of the monomer chain length. Based on the work of Baker and Fuller[62] this author suggested bending of the chains to create room for bulky hydrogen chloride molecules. The X-ray pattern of nylon after desorption resembled that of untreated nylon.

FINE STRUCTURE OF FIBRES

In the past various theories (Micelle theory, continuous structure theory, fringed micelle theory, etc.) have been proposed regarding the molecular structure of fibres. However, none of these is self-contained to explain all the varied phenomena observed in high polymers. In general the presence of crystalline and non-crystalline regions (often referred to as amorphous or disordered regions) is reported, but it may be noted that there is no evidence regarding a complete irregular arrangement of molecules in non-crystalline regions, and a possibility of some order in these regions may not be ruled out. Recently Hearle[63] has proposed a form of structure which combines the most important features of a fibrillar structure with those of the fringed micelle theory. According to this the crystalline regions are regarded as continuous fringed fibrils composed of molecules diverging from the fibril at different positions along its length.

THERMODYNAMIC APPROACH

It is possible to apply the laws of thermodynamics to systems comprising textile fibres since the latter tend to attain equilibrium with the surrounding vapour pressure, although the irreversible nature of induced deformations in fibres offers some limitations.[64] In spite of the fact that the system is studied in bulk, the laws of statistical mechanics allow one to attribute the results to the basic building units of the system. The change in free energy is defined by the equation:

$$dF = dU - TdS \quad .... (4)$$

dF = change in free energy,
dU = change in internal energy,
dS = change in entropy of the system, and
T = absolute temperature.

In classical thermodynamics entropy is defined in an abstract manner as a thermodynamic variable of the system under consideration. However, in statistical mechanics[65] it is defined as a measure of the probability of a particular arrangement of the elementary particles.

A system capable of doing work possesses free energy and is characterised by spontaneity of change to a more stable system.[66] In the system of fibre-water vapour the free energy change e.g. on extension of the fibre isothermally, plays an important part in determining equilibrium. Some of the phenomena to which thermodynamic analysis may be applied are discussed below.

1.a. Phenomenon of sorption

Sorption[67] may be defined as the process in which vapour molecules are attached to sites in solids. Moisture sorption occurs mainly in the non-crystalline regions of the polymer, and it has been reported[68] that the amount of water absorbed at a given temperature and humidity is proportional to the amorphous fraction. Sharing of one water molecule by 2 - 3 sorption sites is known as co-operative sorption.[69] Various authors have reported theoretical deductions, based on the concept of multi-layer sorption in polymers; to explain the observed sorption isotherms. Quite a different approach to moisture sorption has been developed by Barkas[70], starting from the analogy between swelling and osmotic phenomenon. Water molecules penetrate the regions of high polymer concentration and the polymer swells until the stress generated by deformation of the polymer is sufficient to prevent more water from flowing in to the polymer phase. Consequently the moisture sorption will be very dependent on the stresses developed in the fibre owing to internal or external effects, and thermodynamic relations similar to those applicable in osmosis can be applied to sorption and swelling.

1.b. Visco-elastic behaviour in high polymers

Fibre stress-strain curves generally depict three marked regions:

1. The initial Hookean region;
2. The middle linear part of the curve, and finally,
3. a plastic flow or gliding of the segments prior to rupture.

Generally an entropic force of retraction, depending on the nature of intermolecular interactions, plays an important role in the initial Hookean region. The relative contribution to stress arising from entropy changes and the changes in internal energy can be found by the use of the equation:

$$P = (dU/dl)_T - T(dS/dl)_T \qquad \ldots\ldots\ldots (5)$$

P = stress in the material

dl = change in length.

The presence of a large number of specific molecular interactions, as compared with non-specific interactions (found in elastomers like rubber), results in a decrease in the entropy retraction force, and enhances the effective contribution due to changes in internal energy. The linear middle part of the curve (in case of nylon 66 after the first yield point) generally depicts stress due to changes in the internal energy of the system. The plastic flow is due to the sliding of chain molecules past one another and water serves as a "lubricant" in gliding.

A deformation causes a certain mutual displacement[71] of interaction sites; the latter determine the cohesive energy within the system. The initial configuration of interaction sites and the new configuration due to deformation may be visualized in terms of 'relaxed' and 'un-relaxed' states in the system. From the reported values for Poisson's ratio in case of fibrous polymers, one would expect an increase in volume as a result of longitudinal deformation. For a given deformation, with lapse of time increased thermal agitation, associated with the increase in volume, results in an increase in non-specific interaction due to a more compact alignment of the polyethylenic segments. Extra sorption on 'unrelaxed' sites may result in dissipation of stored stress energy in the 'un-relaxed' sites. This gradual decrease in stress with time is known as stress relaxation.

3. Significance of the Study of Changes in regain with Strain.

Changes in regain (extra sorption on 'un-relaxed' sites as mentioned above) with strain have been studied in order to throw more light on the nature of polar interaction, stress relaxation due to extra sorption, and the probable application of the laws of thermodynamics to visco-elastic materials. Apart from this the practical significance of the present work arises from our cognisance of the varying degrees of tensions involved in the processing of textile materials.

REVIEW OF SORPTION IN NYLON AND SILK

Ellis and Bath[72] have shown by infra-red spectra that the imino groups of the peptide bond are involved in the absorption of water by gelatin. However, in certain of the elastic nylons[73] where all the hydrogen atoms of the imino group have been replaced by alkyl radicals, there is still an appreciable water sorption which presumably is due to the CO groups. Senhoi[74] suggests that sorption takes place at CO groups in nylon.

Pauling[75] reported that nylon contains 890 moles of carbonyl and imido groups each per 10^5g., but holds only 100 moles of water per 10^5g. in primary sorption. The observed sorption of water by nylon indicates that about 6% of the carbonyl and imido groups fail to join together, presumably because of configurational accident, and that each of these groups then attracts water molecules. It has been reported that the amount of water sorbed at a given temperature and humidity is proportional to the amorphous fraction. Speakman[76] concluded from sorption data that the drawing of nylon results mainly in alignment of disoriented micelles rather than the formation of the micelles by the alignment of molecules. An extensive study of sorption in proteins was carried out by Bull.[77] This author has reported that the affinity for water in the low vapour pressure region (1 - 4% regain) is much the same for all the proteins. The average value for the free energy change per gram of water absorbed at 25°C is 50.6 calories. The implicit significance of this observation lies in a possibility of formulating a general sorption mechanism for related polymers.

It is interesting to compare nylon 66 with silk as regards their sorption characteristics. The presence of long intervening polyethylenic segments in nylon 66 affects the general electron configuration along the main chains and effectively lowers the accessibility of the structure to sorption. Though water does not penetrate the crystalline regions in either nylon[78] or silk,[79] it may be noted that in the latter case a greater accessibility enhances the possibility of sorption on the surfaces of fine submicroscopic crystals. In fact it has been shown experimentally[3] that the degree of crystallinity of silk does not affect the water sorption markedly. Silk has a few sorption sites[80] other than the peptide groups and physical modifications have negligible effect on sorption.

VARIATION IN SORPTION WITH STRAIN

Adsorption by solids under infinitesimal strain has been considered by various workers.[81-83] Hill[84] has discussed the case of adsorption by a fibre under a finite strain from an axial load. A thermodynamic relationship between moisture sorption and applied stress for fibres has been reported,[85] with particular emphasis on the merits and demerits of the thermodynamic approach to such system. In dealing with swelling of wood, Barkas[86] showed by means of thermodynamics that the moisture absorption of wood under stress is related to the magnitude of stress. For vulcanized rubber swollen with liquid hydrocarbons it has been established both experimentally[87, 88] and theoretically[89] that tensile stress leads to an increase in the equilibrium absorption. However, White and Stam[90] reported that the equilibrium water content of the human hair decreases with the application of a tensile stress, and the results have been shown to be inconsistent with general thermodynamics. This provided an impetus to re-examine the possibility of application of laws of thermodynamics to systems, which, unlike rubber, show large changes in internal energy with strain. Treloar found that at a constant humidity the moisture regain of horse hair,[91] and viscose rayon[92] are dependent on the applied stress: the extra sorption increases with the increase in the applied stress in conformity with the thermodynamic prediction. Gleeson[93] has described a suitable specimen holder for finding changes in regain with strain gravimetrically. This author has reported that the changes in regain for viscose filaments are in accordance with Treloar's thermodynamics. Algie[94] examined the change in resistance with time after application of various strains at 90% r.h. and 20°C for keratin fibres. The observed decrease in resistance has been attributed to an expected increase in moisture content in accordance with Treloar's thermodynamic equation.

It is interesting to note that the longitudinal swelling[95] and not the lateral swelling of the material governs the changes of tension in fibres in an atmosphere of fluctuating humidity. Meredith and Hsu[96] have reported that the values for extra sorption obtained from a rigorous theoretical analysis of their results for stress relaxation of nylon 66, are comparable with those calculated thermodynamically from the results of longitudinal swelling of nylon 66.

CHAPTER II

INTRODUCTION

Since some polar reagents such as lithium bromide dissolve a polypeptide like silk, and cause supercontraction of wool, it was thought that a study of their effect on nylon 66 might throw some light on the molecular structure in polyamides.

Initial trials were made using lithium bromide solutions only, and at a later stage the effects of magnesium perchlorate and lithium perchlorate solutions were also studied in view of a close similarity between the ionic radii and the characteristic properties of their cations. (In view of the large size of the anions, their influence is considered negligible). The various experimental stages are summarised as follows.

1. Initially it was thought desirable to find out the nature of the effect of polar reagents on physical properties of nylon 66 e.g. dimensional changes and tensile characteristics.
2. To establish the nature of above interaction, a detailed spectral investigation had to be carried out. A model compound and nylon (both unmodified and modified by treatments with hydrochloric acid) were examined with

infra-red radiation. The modified nylon was used in order to find out the effect of acid treatment, on the interaction of polar reagents with nylon. The spectral changes were confirmed by studying the viscous solutions in organic acids of nylon treated with polar reagents, and also by using a deuterium exchange technique. These data were further supplemented by evidence from X-ray diffraction studies. It may be noted that studies in the U.V. region had to be abandoned mainly because of the obscure nature of broad ~~continuum~~ absorption bands.

3. The effect of reagents on Orlon polyacrylonitrile fibres was studied; since Orlon contains nitrile groups in which the "lone pair" electrons of the nitrogen atom play a decisive role in various phenomena.

4. Some auxilliary experiments were done which involved the use of reagents like molten antimony trichloride, which is known to co-ordinate at the CO groups in nylon 66.

MATERIALS

Experiments were made on

1. 210 denier multifilament nylon 66 yarn (B.N.S. Ltd.),
2. nylon 66 films (I.C.I. Ltd.) about 10μ thick, partially oriented by hand drawing,
3. polyacrylonitrile films made from solutions of Orlon in dimethyl formamide.

CHEMICALS

1. <u>Polar reagents</u>:

Aqueous solutions of lithium bromide, magnesium perchlorate and lithium perchlorate (laboratory reagents) are expressed as parts solute/parts of solvent (Table 2). The reagents were dissolved in distilled water at 80°C and the filtered solutions were examined for hydrogen ion concentration on a Pye pH meter.

TABLE 2.

Solution	Solute g.	Solvent c.c.	pH of solution
1. Lithium bromide	100	100	6.0
2. Magnesium perchlorate	100	100	5.5
3. Lithium perchlorate	50	100	10.0

Addition of 0.5% sodium thiosulphate crystals to lithium bromide solution was made to avoid oxidation of the bromide ion.[97]

2. Pure N-ethyl acetamide, dichloroacetic acid and formic acid (98%) of Analar quality were used.

3. Deuterium oxide (98% pure, I.C.I. Ltd.) was used to carry out deuterium exchange by exposing nylon films to deuterium oxide vapour in an enclosure at 20°C.

DIMENSIONAL CHANGES

The transverse swelling of filaments was viewed under a microscope. The changes in length were measured on 20 cm. filaments mounted on two brass washers, one of which was suspended from a hook. Their length was measured with a ruler in air at 65% r.h. and then they were immersed in a solution of polar reagent contained in a measuring cylinder, removed after 24 hours and measured immediately.

Table (3) shows percentage transverse and longitudinal changes (calculated as percentage of initial dimensions at 65% r.h.) in the nylon filaments treated with the polar reagents at 20°C and 70°C for 24 hours. It may be noted that the filaments treated with magnesium perchlorate at 70°C, showed a further shrinkage of about 5% on washing with distilled water, which amounts to a total shrinkage of 18-20% for the treated and subsequently washed filament.

TABLE 3.

	20°C		70°C	
Treatment	A%	B%	A%	B%
1. Distilled water	No significant change	2	4	10
2. Lithium bromide		0	8	11
3. Lithium perchlorate		10	10	13
4. Magnesium perchlorate	1	11	15	22

A = Longitudinal shrinkage B = Transverse swelling

It is apparent from the above changes that magnesium perchlorate has a more severe effect on nylon, as compared with that due to water and solutions of lithium salts. It seems from the results, that some retraction of molecular chains takes place as a result of interaction with polar reagents. These reagents have a less significant effect on nylon, as compared with that on silk, and this may be attributed to the presence of large polyethylenic segments intervening between the polar groups in nylon 66: this is in agreement with Alexander's views.[58]

CHANGES IN TENSILE CHARACTERISTICS

The single filament strength tests were carried out on a Cambridge extensometer, using a constant rate of loading.

The tests were carried out on untreated and treated filaments (6 denier) as under.

(a) Filaments which had been conditioned at 65% r.h., were tested inside a Gallenkamp humidity oven maintained at 65% r.h. and 20°C.

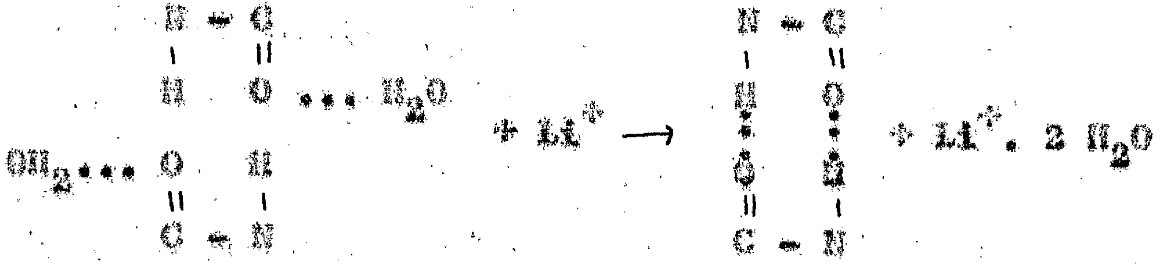
(b) Filaments which had been immersed in distilled water for 24 h. were tested in distilled water at 20°C.

(c) Filaments which had been treated in aqueous solutions of polar reagents, at 20°C and 70°C for 24 h., were tested in appropriate solutions at 20°C.

(d) Filaments which had been treated with polar reagents as above, were washed free from reagents and tested in distilled water at 20°C.

The test length used was 2 in. in all the experiments except for filaments treated with magnesium perchlorate at 70°C, when it was 1 inch. The rate of loading was 7.2 g./denier/min. for all the filaments except for those treated with magnesium perchlorate at 70°C, when it was at 3.5 g./denier/min. All the experimental points shown in the graph were the mean of six replica tests for all the filaments; the coefficient of variation in the reported values for different filaments treated under the same condition, was found to be less than 10 per cent, except for filaments treated with magnesium perchlorate at 70°C.

The results are shown in graphs 3, 4, and 5, and the observed values for the breaking load and extension at break are given in Table (4). At 20°C, the shape of the stress-strain curve resembles that at zero humidity, and the observed decrease in the breaking extension may be attributed to the elimination of gliding of the segments. Possibly the polar ions play the role of drying agent in situ, by attracting all the moisture sorbed on the polar groups in nylon, to their own hydration shells. Arguing from the generally accepted theories of the influence of moisture on hydrogen bonds in nylon, a possible mechanism involved in the process of dehydration may be visualised as follows.



$$\begin{array}{rccl} & N & - & C \\ & | & & \| \\ & H & & O \cdots H_2O \\ OH_2\cdots & O & & H \\ & \| & & | \\ & C & - & N \end{array} + Li^+ \longrightarrow \begin{array}{ccc} N & - & C \\ | & & \| \\ H & & O \\ \vdots & & \vdots \\ O & & H \\ \| & & | \\ C & - & N \end{array} + Li^+ . \ 2\ H_2O$$

However, in view of subsequent experimental results an alternative theory may be put forward and this is discussed later in this work (see page 60).

It is evident from the graphs that magnesium perchlorate has the most severe effect on the tensile characteristics of nylon filaments: even at 20°C, there is a decrease in the initial modulus, which may be attributed to an increase

TABLE 4. The effect of polar reagents on tensile strength of nylon 66.

			20°C						70°C					
Treatments	65% r.h.	Dis. water	A		B		C		A		B		C XX	
		T	T	TW	T	TW	T	TW	T	TW	T	TW	T	TW
Breaking load g/denier	7.4	6.9	7.0	6.9	5.0	5.9	4.1	5.3	5.3	6.4	5.3	5.5	1.6	2.8
Breaking extension %	16	22	11	17	17	23	11	17	17	35	32	35	72	115

A. Lithium bromide. B. Lithium perchlorate. C. Magnesium perchlorate.

T ... Treated. TW ... Treated and Washed.

Rate of loading .. 7.2 g./denier/min.

XX Rate of loading 3.5 g./denier/min.

Coefficient of variation $<$ 10 per cent except for XX.

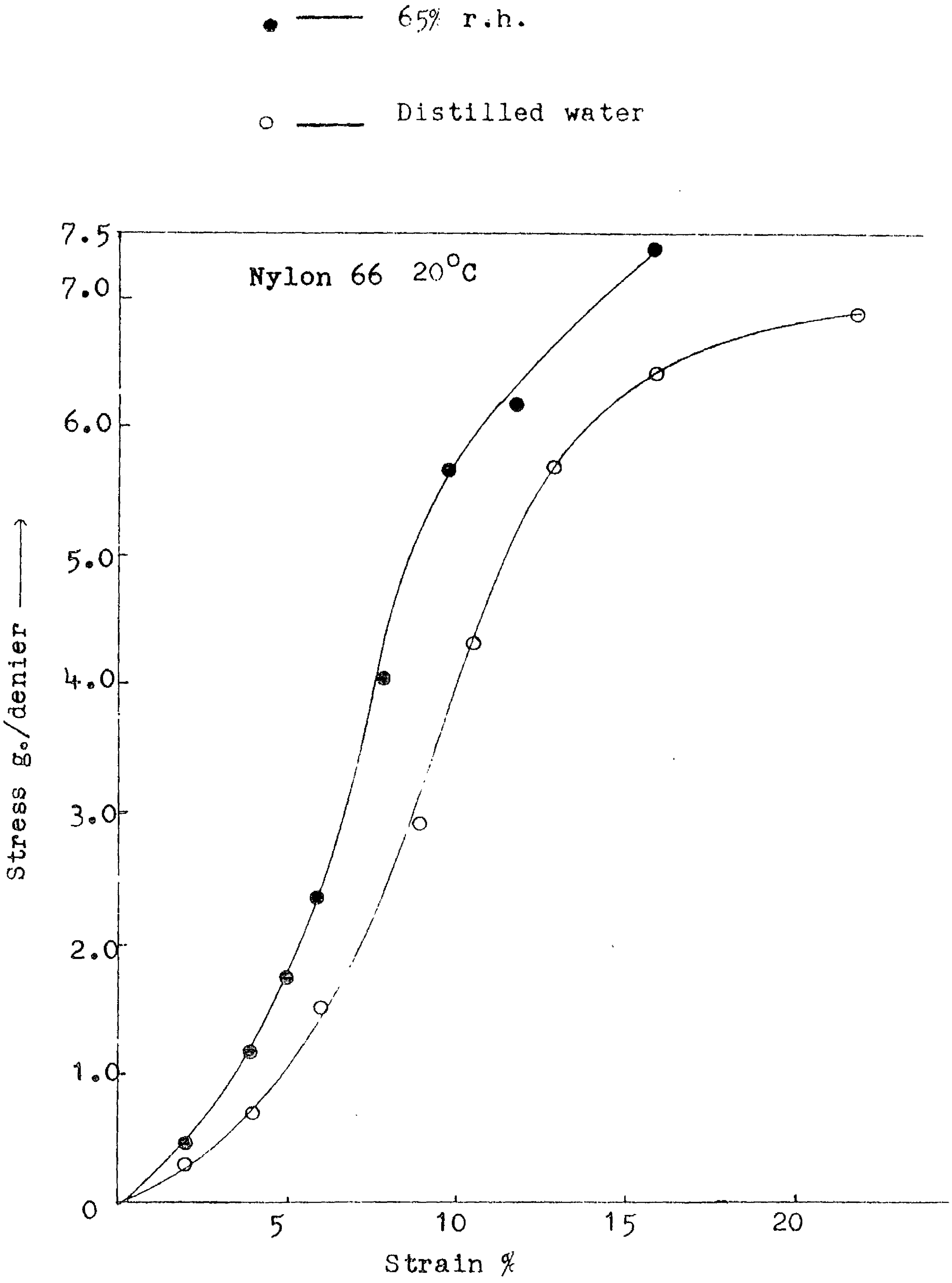


Fig. 3. Stress-strain curves for nylon 66, at 65% r.h. and in distilled water.

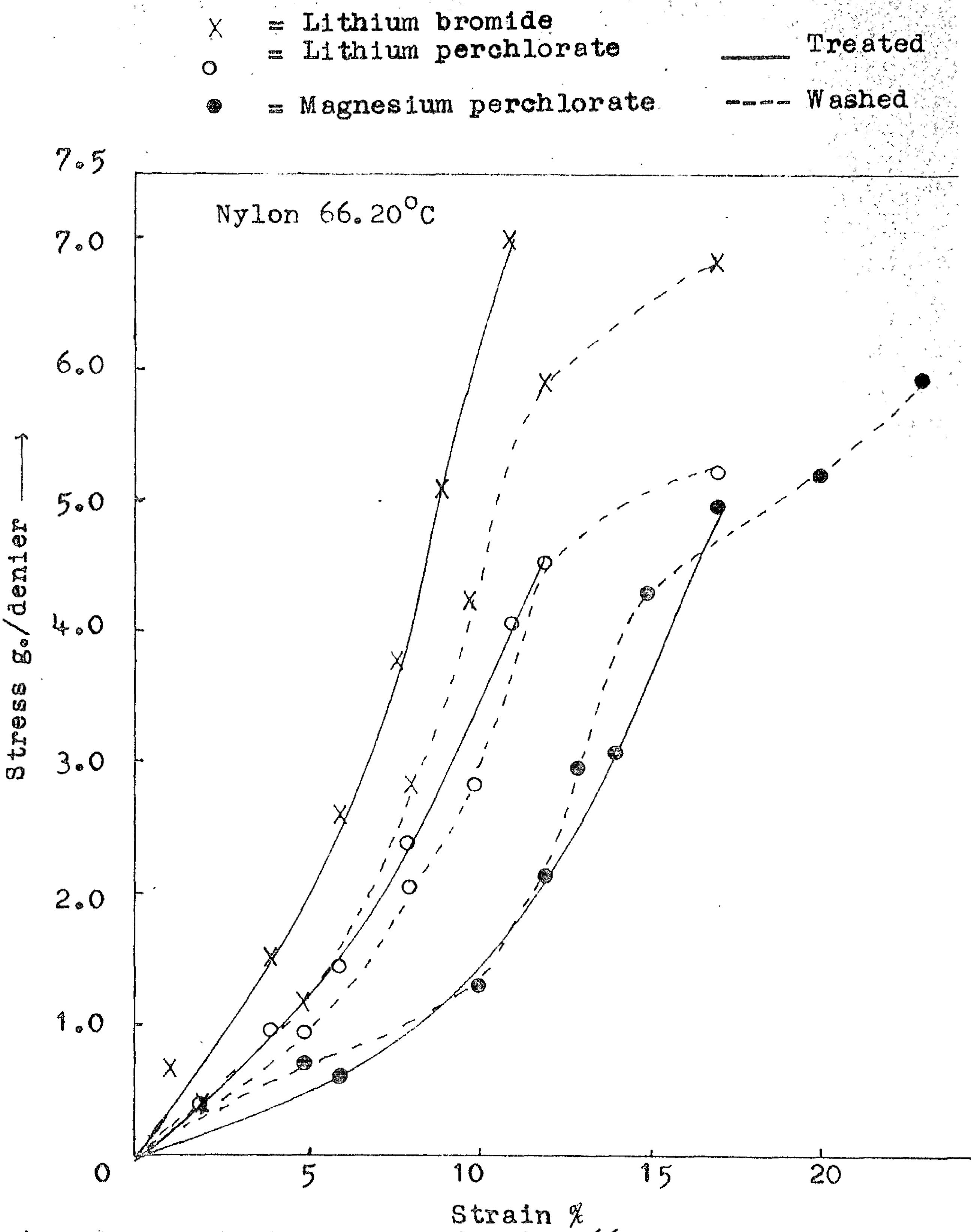


Fig.4. Stress-strain curves of nylon 66 treated with polar reagents, at 20°C.

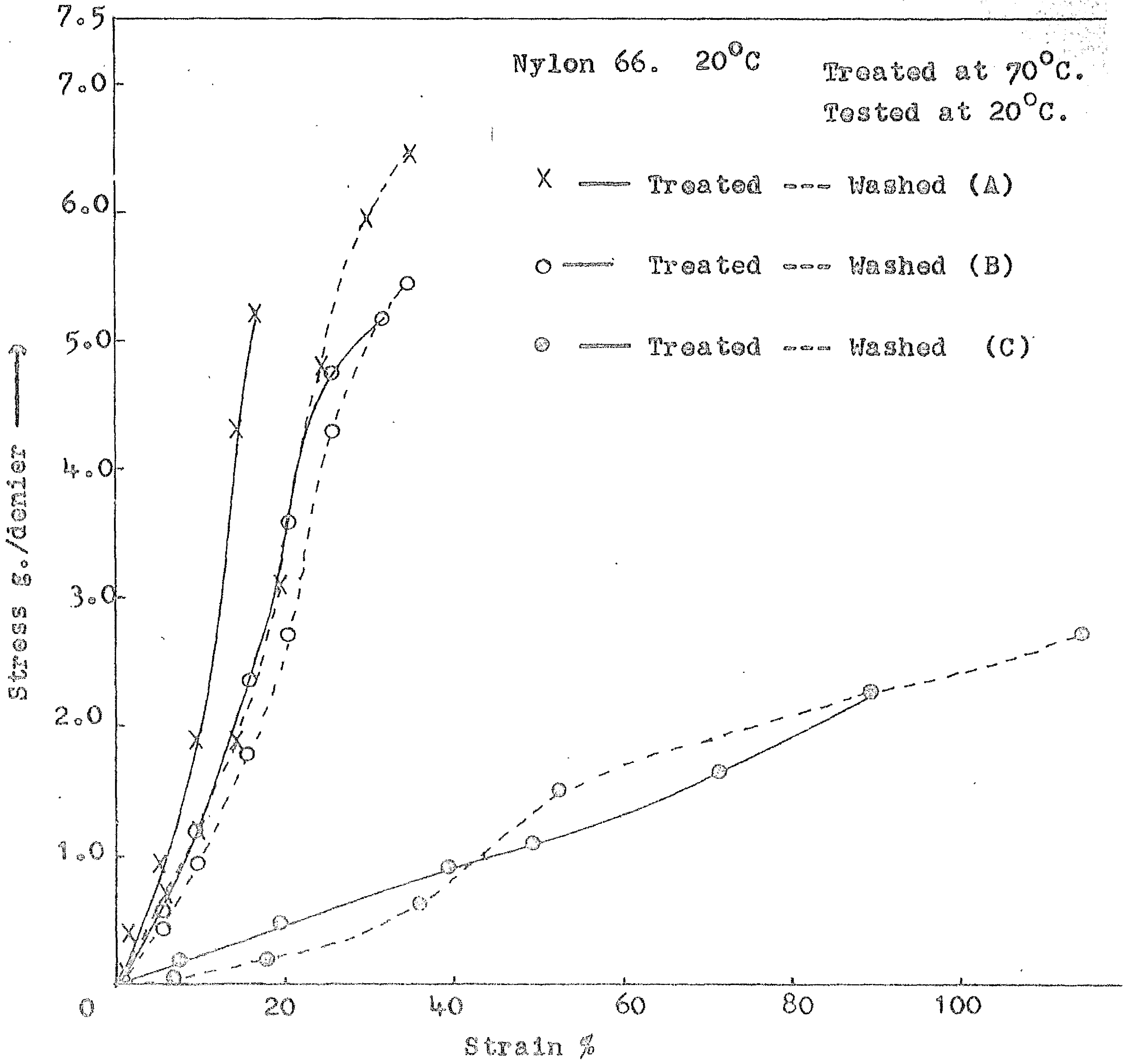


Fig.5. Stress-strain curves for nylon 66 treated with polar reagents at 70°C.

(A) Lithium bromide (B) Lithium perchlorate

(C) Magnesium perchlorate.

in the rotational freedom of the chains. At 70°C, whereas lithium salts do not produce any marked changes, the filaments treated with magnesium perchlorate show a remarkable extensibility, which would indicate an absence of strong interaction at the polar groups, and a large increase in the entropy effects in the system. On the other hand, such a drastic effect may be due to the degradation of molecular chains, and therefore a possibility of degradation and disaggregation of chains occurring simultaneously, may not be ruled out. However, it will be shown at a later stage (see page 45) that the spectral evidence does not support a possibility of degradation of molecular chains. It is interesting to note that the washing of the filaments free from reagents tends to restore the original tensile characteristics of the untreated nylon, particularly the restoration of the tail of the curve. However, filaments treated with magnesium perchlorate at 70°C retain a large amount of permanent change, even after washing, and it is not clear as to what mechanism is responsible for such a drastic irreversible change. One would expect that changes in X-ray diffraction pattern may throw some light on this, and the matter will be discussed at a later stage.

X-RAY DIFFRACTION

X-ray diffraction photographs of nylon 66 filaments were taken using Ni-filtered CuK$_\alpha$ radiation of wavelength

1.54 A, from a Philips sealed off tube run at 40 kV and 15 mA. The X-ray beam was collimated by a lead glass capillary tube 5 cm. long and having an internal diameter of 0.3 mm. The specimen was mounted in the form of a parallel bundle of filaments, in a special stainless steel holder on the end of the collimator: the specimen holder had a moveable jaw which enabled the sample to be stretched. The X-ray film was held in a cassette mounted on rails running parallel to the collimator. The front of the cassette was covered with a thin aluminium foil (40 μ thick), and at the centre of the foil a lead stop was stuck with Durofix, in order to absorb the primary un-diffracted X-ray beam. The specimen to flat film distance was 3.0 cm : this distance was calibrated by placing a thin silver foil in the bundle of filaments and measuring the diameter of the silver diffraction rings.

The various experiments carried out were as follows.

(1) The X-ray photographs of untreated nylon 66 filaments were taken.

(2) To find out the exact nature of prominent equatorial streaks, one half of the front of the cassette was covered with 16 layers of thin aluminium foil (40 μ thick). The bundle of nylon filaments was exposed to X-rays, and photograph was carefully examined.

It was found that though the shielding due to thick layers of aluminium foils reduced considerably the intensity of characteristic reflections, very little change was noticed in the intensity of equatorial streaks i.e. these are due to white radiation.

(3) Nylon filaments treated with solution of lithium bromide, and magnesium perchlorate at 20°, 50°, 80° and 100°C for 24 hours were examined for changes in diffraction pattern. The filaments were kept slack throughout the treatments.

(4) Finally the filaments treated with the above reagents at 100°C were washed free from reagents, dried at 60°C for 12 hours and then diffraction patterns were obtained.

(5) The filaments which had initially been stretched 5% were treated in a similar way to that described in (3) and (4), using magnesium perchlorate at 80°C: the fibres were kept at their stretched length throughout the experiment.

A visual examination of diffraction photographs of treated and untreated nylon reveals that polar reagents do not penetrate the α-crystalline regions. The visible changes are noted as follows.

1. With increase in temperature of the treatment and on subsequent washing, the length of the equatorial arcs increased suggesting an increased dis-orientation of crystallites: this effect was not however very great even for the washed fibres and the final dis-orientation was

estimated visually at 15°. An apparent sharpening of these reflections may have been illusory because the spreading of the arcs would give this appearance.

2. When the filaments were treated slack, the absence of layer-line streaks[98] indicated an appreciable decrease in the β crystalline form. The disappearance of the β form was less marked when the filaments were treated under taut condition.

3. Appreciable changes in the spacing between planes in the direction of hydrogen bonding, of the order of 0.1-0.15 A have been observed for treated filaments.

It may be noted that the observed dis-orientation of 15° would produce about 3-4% contraction in length. However, this alone would not explain the large longitudinal shrinkage and high extensibility of filaments treated with magnesium perchlorate at 70°C.

The decrease in the hydrogen bond spacing and decrease in the β form in nylon as a result of treatment with polar reagents, may be termed ~~as~~ annealing[99] i.e. a considerable reduction of stress in the system. The reduction in stress may be attributed to increased rotational freedom of the chains in the polycrystalline[100] regions. These changes in polycrystalline regions may favour a closer alignment of chain molecules in the crystallites. Such an effect of changes in the polycrystalline regions, on chain molecules in the crystallites is easily understood, if one visualises the changes in terms of the fringed fibrillar structure of chain molecules, where primary chains may be considered as transmission lines between the crystallites and the polycrystalline regions. The annealing effect is clearly seen in the filaments which had been washed free from reagents. It is possible to visualise that this effect can account for an increase in the extensibility of filaments, which had been treated with the reagents at 70°C, and subsequently washed free from the reagents.

Fig. (13) and (14)[98] show the α crystal structure of nylon 66 and the arrangement of molecular sheets in α and β crystalline forms respectively. It is interesting to note that disappearance of the β form is related to the magnitude of strain in the system. An appreciable decrease in the β form, and insignificant changes in the α form suggest that the β component is more accessible to polar reagents. In view of its accessibility, it is suggested that the β form appears towards the edges of the crystallites.

SETTING OF NYLON 66 IN MAGNESIUM PERCHLORATE AND LITHIUM PERCHLORATE SOLUTION

Since the reagents appear to have an annealing effect on the nylon structure it was thought possible that they might be used to induce a degree of permanent set in ~~te~~ fibres.

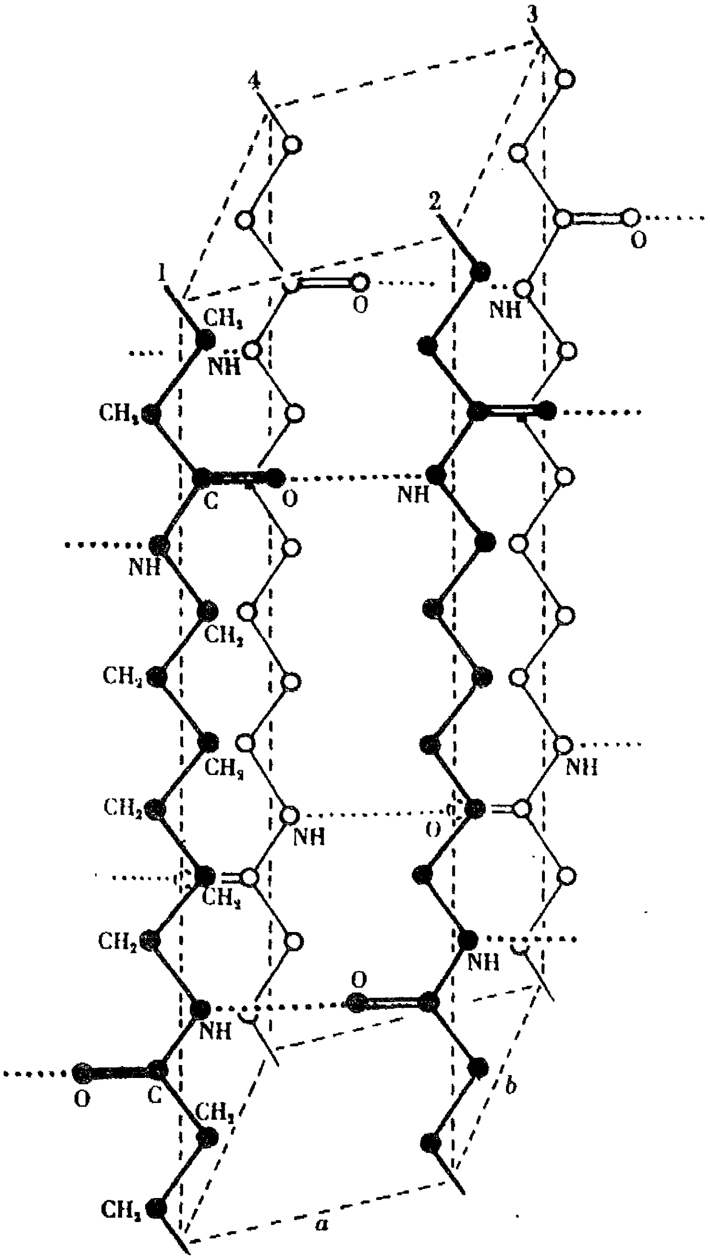


FIGURE 13. Structure of α crystal of 66 polyamide.

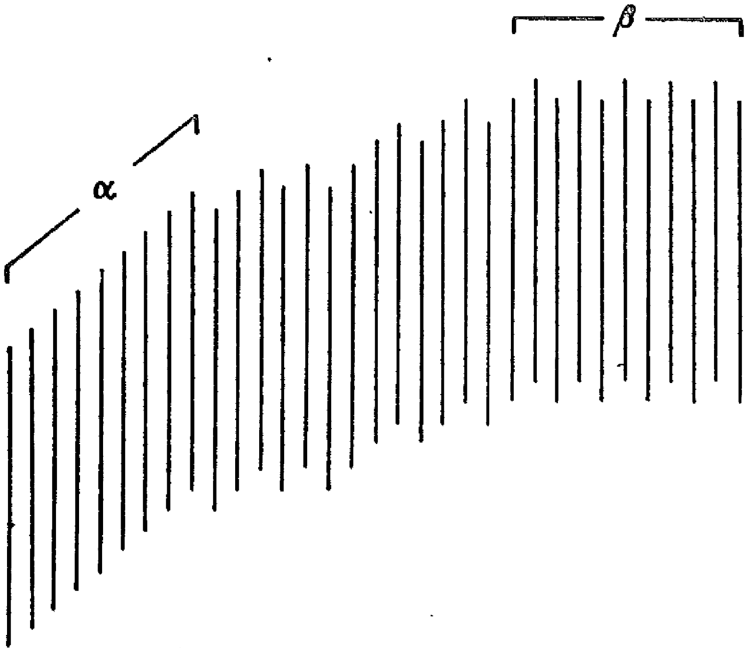


FIGURE 14. α, β and intermediate forms of nylon. Lines represent sheets of molecules seen edgewise.

To test this hypothesis the following experimental procedure was carried out and X-ray photograph was obtained at each stage.

1. The diffraction pattern of nylon filaments was obtained.
2. The dry filaments were stretched 5 per cent.
3. The filaments were immersed under taut condition in boiling water for one hour.
4. The filaments were relaxed in water at 60°C by releasing previously imposed strain, they were then dried in an oven at 60°C for 12 hours and the change in length was measured with a ruler.
5. The filaments thus conditioned were stretched 5 per cent and treated in magnesium perchlorate solution while taut at 70°C for one hour.
6. The treated sample was relaxed in distilled water at 60°C, washed free from reagent, dried in an oven at 60°C for 12 hours and finally examined for changes in length and diffraction pattern.

At the end of each experiment a small amount of supercontraction (about 1 per cent of the original length) was noticed. There were insignificant changes in the X-ray pattern. It was evident that these reagents did not have any setting effect on nylon 66.

SPECTROSCOPIC INVESTIGATION

Experimental methods

Infra-red absorption studies were made on a Grubb Parsons double beam infra-red spectrometer (type 54, serial number 419). The spectral absorption was studied in 2 - 15 μ region. A detachable polariser made from silver chloride sheets (supplied by the makers), was introduced in the path of transmitted beam at the entrance slit of monochromator. The polariser with a transmission of 18% could be rotated relative to the direction of stretching of the film, in order to examine the dichroism of partially oriented films.

Granullar samples were usually prepared by the Nujol-mull technique,[101] but for fine powders the potassium chloride disc method was preferred. For polymer films the use of a liquid medium was avoided: the films were mounted with Araldite on suitable lead or stainless steel washers and clamped in the standard brass holders, used for routine spectral analysis. For examination with polarised infra-red radiation, narrower strips (1/8 in.) of films were used to obtain an appreciable dichroic effect. Almost invariably films prior to examination were desiccated for 12 h. under vacuum to minimise obscurity in spectra due to broad OH bands.

High resolution N.M.R. study of liquid samples was were made on a Perkin Elmer N.M.R. instrument operating at a frequency of 14 MC/Sec.

RESULTS

The spectral data have been reproduced in figures (6-12) as a plot of intensity of transmitted radiation, increasing from top to the bottom of the spectral peaks, against the wavelength: wave numbers have been written against the important peaks. The term intensity was preferred, as no quantitative measurements of absolute parameters were involved in the interpretation of various results.

(a) Model compound

Pure N-ethyl acetamide (liquid) was used as a model compound for polyamides. Infra-red and N.M.R. spectra of the pure liquid and of a solution of lithium bromide in pure N-ethyl acetamide were examined.

The addition of a polar reagent to N-ethyl acetamide results in a viscous solution. Fig. 6 shows the changes in the spectral absorption in the infra-red region. A broadening of the bands in 6 μ region and a shift of NH band to a lower frequency by 14 ± 4 cm^{-1} were observed.

The N.M.R. spectrum of the pure liquid shows a broad band for the imido protons. The presence of polar reagent results in a sharpening of the broad band, in spite of the increased viscosity of solution.

(b) Nylon 66 Films

A systematic study of the effect of polar reagents on nylon 66 films, treated at different temperatures, (ranging

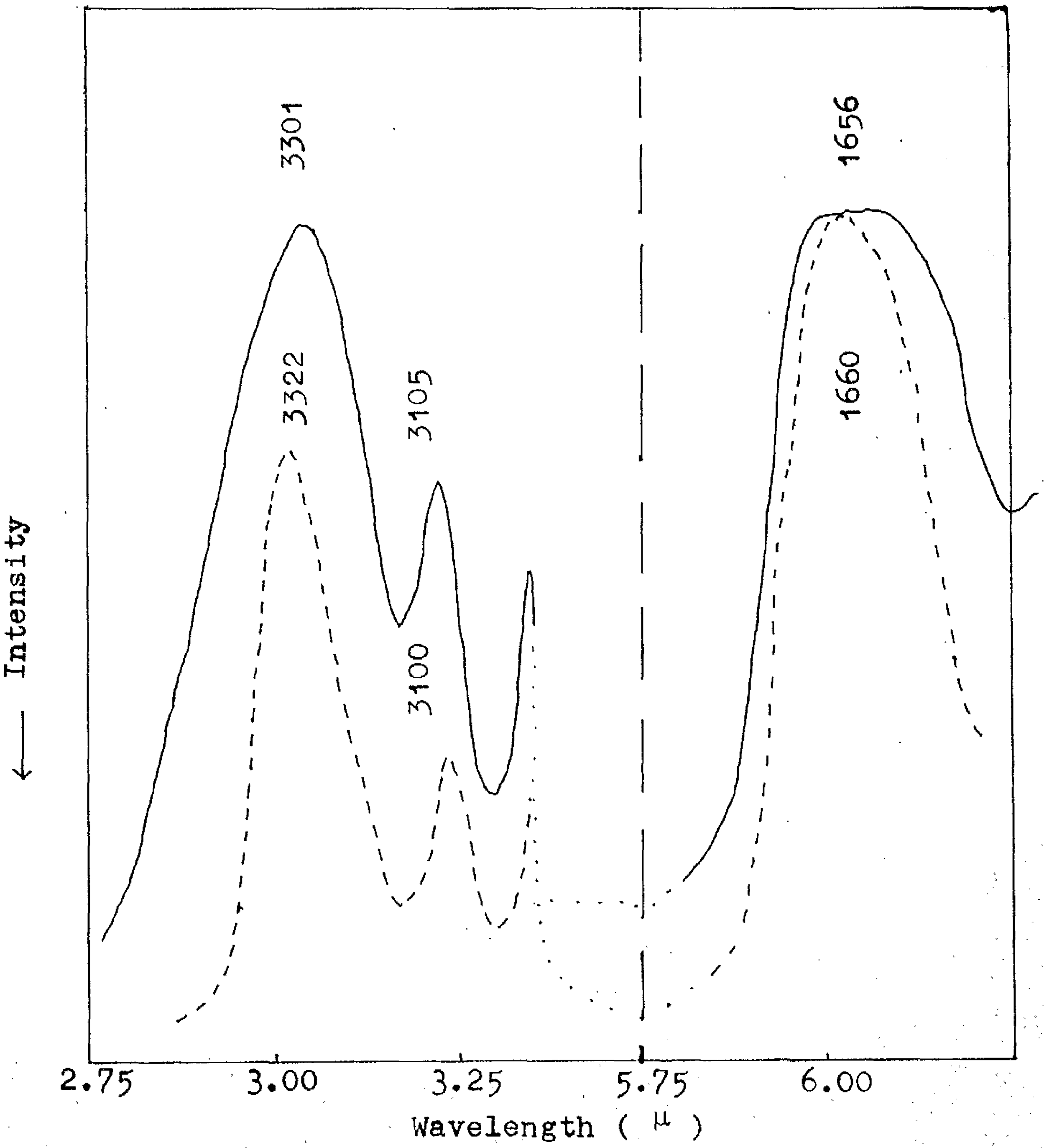


Fig.6. Infra-red spectra of model compound.

------ Pure N-ethyl acetamide

______ Pure N-ethyl acetamide and lithium bromide.

from 20 - 90°C) for 12 hours, was carried out by infra-red methods.

Apparently all the three polar reagents had a similar effect and to avoid confusion only the most prominent changes in spectral absorption, in case of films treated with magnesium perchlorate solution at 80°C, are reproduced in Fig. 7.

The most noticeable feature of the spectra is the appearance of the new band at 3390 cm^{-1}, and apart from broadening of the bands in $6\,\mu$ region, no other significant changes are noticed. The absence of absorption bands e.g. reminiscent of $CONH_2$ groups,[44] does not favour a possibility of degradation of molecular chains. It seems from the spectra that the new band at 3390 cm^{-1} has a slight parallel dichroism. It may be noted that the use of polarised radiation helped resolution of the new band at 3390 cm^{-1} from NH band at 3305 cm^{-1}. The efficiency of these reagents in bringing about any changes was in the following increasing order, lithium bromide < lithium perchlorate < magnesium perchlorate and an increase in the temperature of the treatment enhanced the effect of polar reagents.

(b.1.) Deuterated films

Fig. 8. shows the spectral absorption of untreated and of treated films which had previously been deuterated. The band, which appears on deuteration corresponding to the new peak at 3390 cm^{-1}, is at 2518 cm^{-1} and there is some

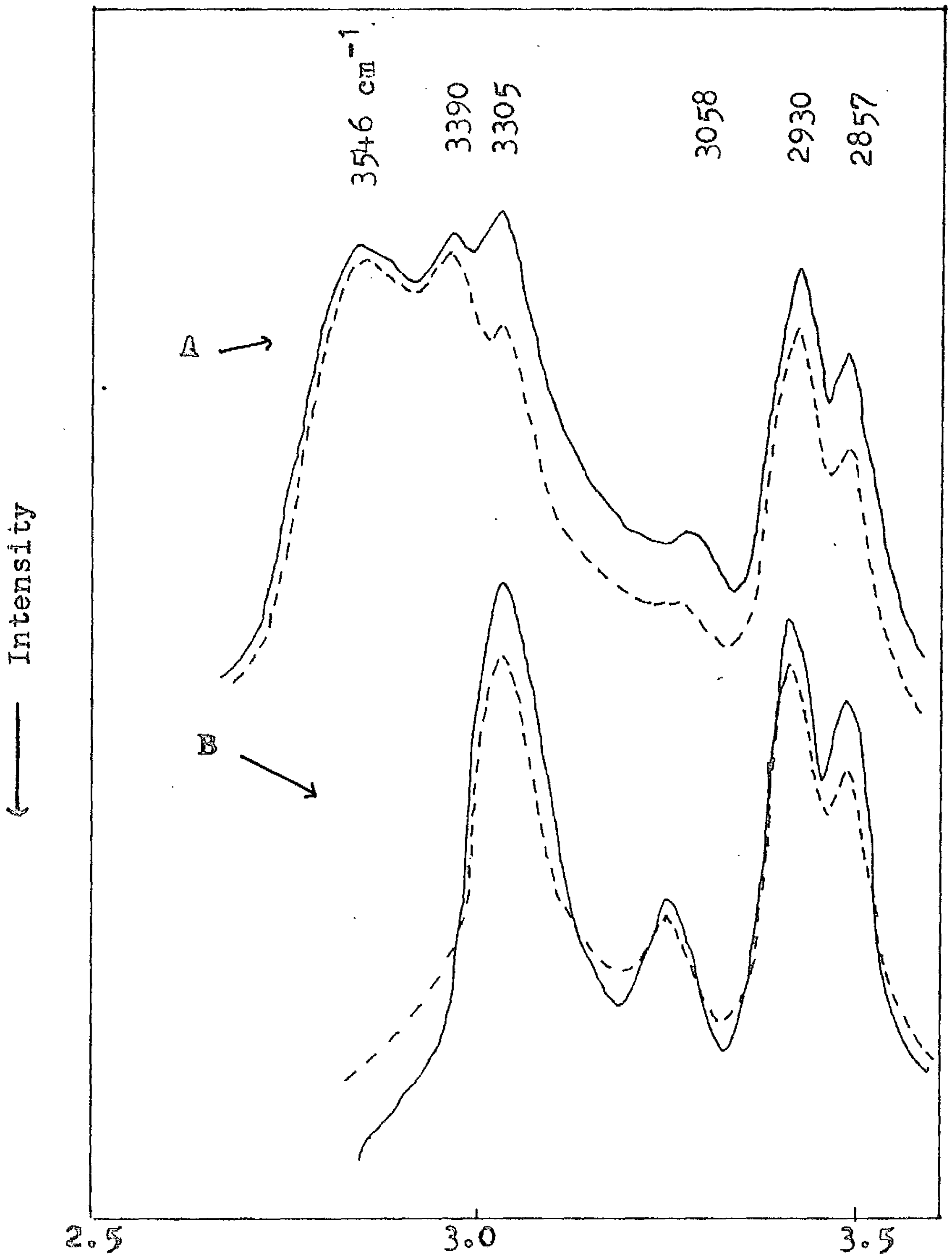


Fig.7. Infra-red spectra of nylon 66.
A= Treated in magnesium perchlorate, 80°C, 12 h.
B= Untreated film.
Polarised ---- Parallel, ——— Perpendicular to direction of stretching.

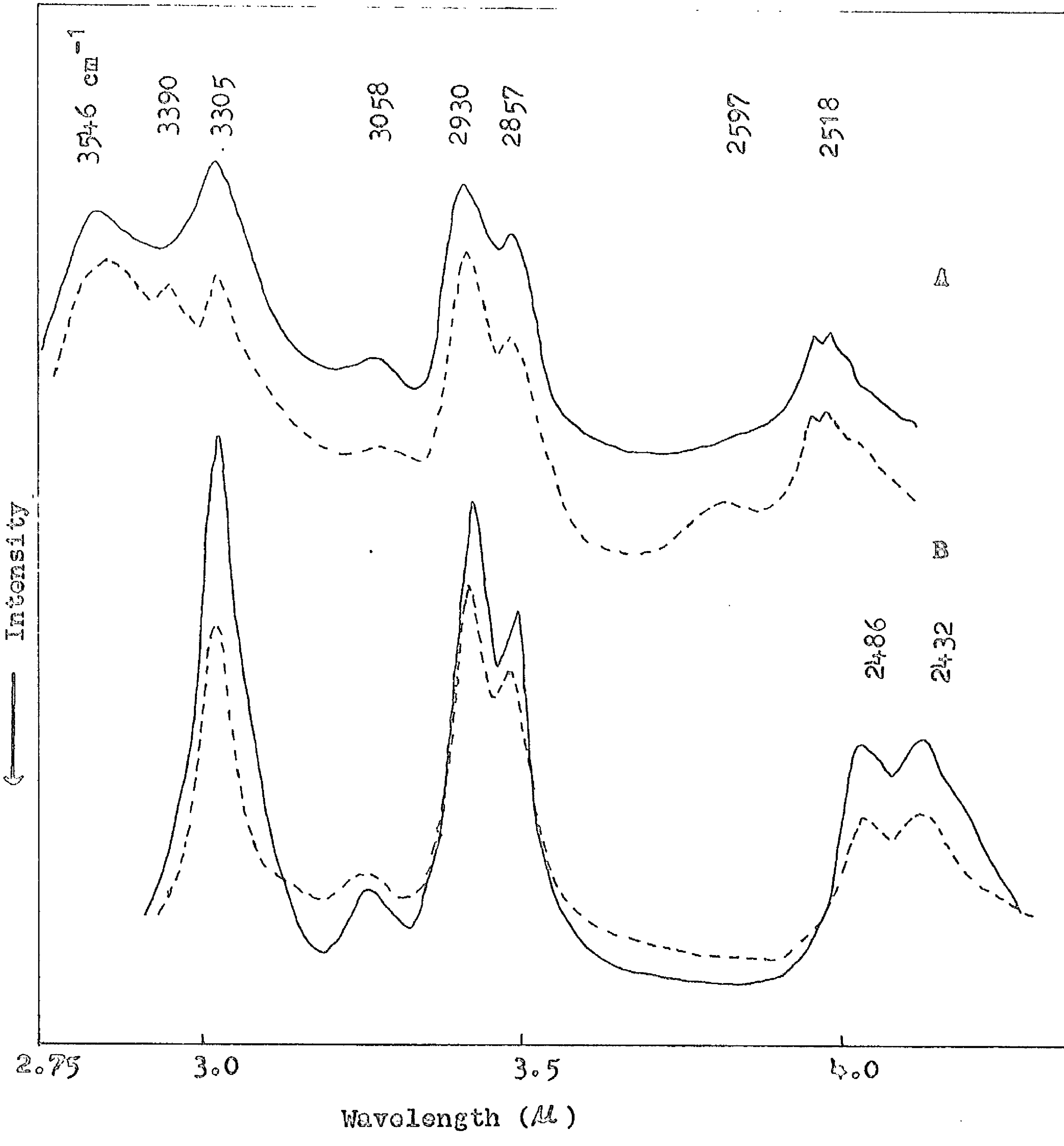


Fig.8. Infra-red spectra of nylon 66.

A= Treated in magnesium perchlorate, and deuterated.

B= Untreated film,deuterated.

Polarised ---- Parallel, ——— Perpendicular to direction of stretching.

indication of splitting and broadening of this band towards lower frequency.

Fig. 9 shows the variation in the profile of this band with period of deuteration, and resulting changes in the spectral absorption in 2 - 15 μ region. It is clear from these results that there is a weak band at 2469 cm^{-1} and a shoulder at 2428 cm^{-1} on the low frequency side of the 2518 cm^{-1} band. An appreciable decrease in the intensity of the band at 2597 cm^{-1} was observed even during the scanning period. Fig. 10 shows a very small change in the profile of 6 μ band.

The values of dichroic ratio for different bands at 3390 cm^{-1}, 3305 cm^{-1} and corresponding bands in the spectrum of deuterated material were calculated by the base-line technique;[102] these are given in Table (5).

(c) <u>Nylon 66 yarn</u>

When nylon 66 yarn was treated in aqueous solutions of polar reagents at boiling point (i.e. 120°C), a gelatinous residue was obtained. This was pressed between thin aluminium foils in a hot press at 100°C, to obtain thin films for spectral examination. To this end various other trials (rolling, squeezing with gloves on a rock salt plate) were also made. It was very difficult to get a reasonable film for obtaining a good spectrum as the presence of granular reagent caused discontinuity in the film and increased the

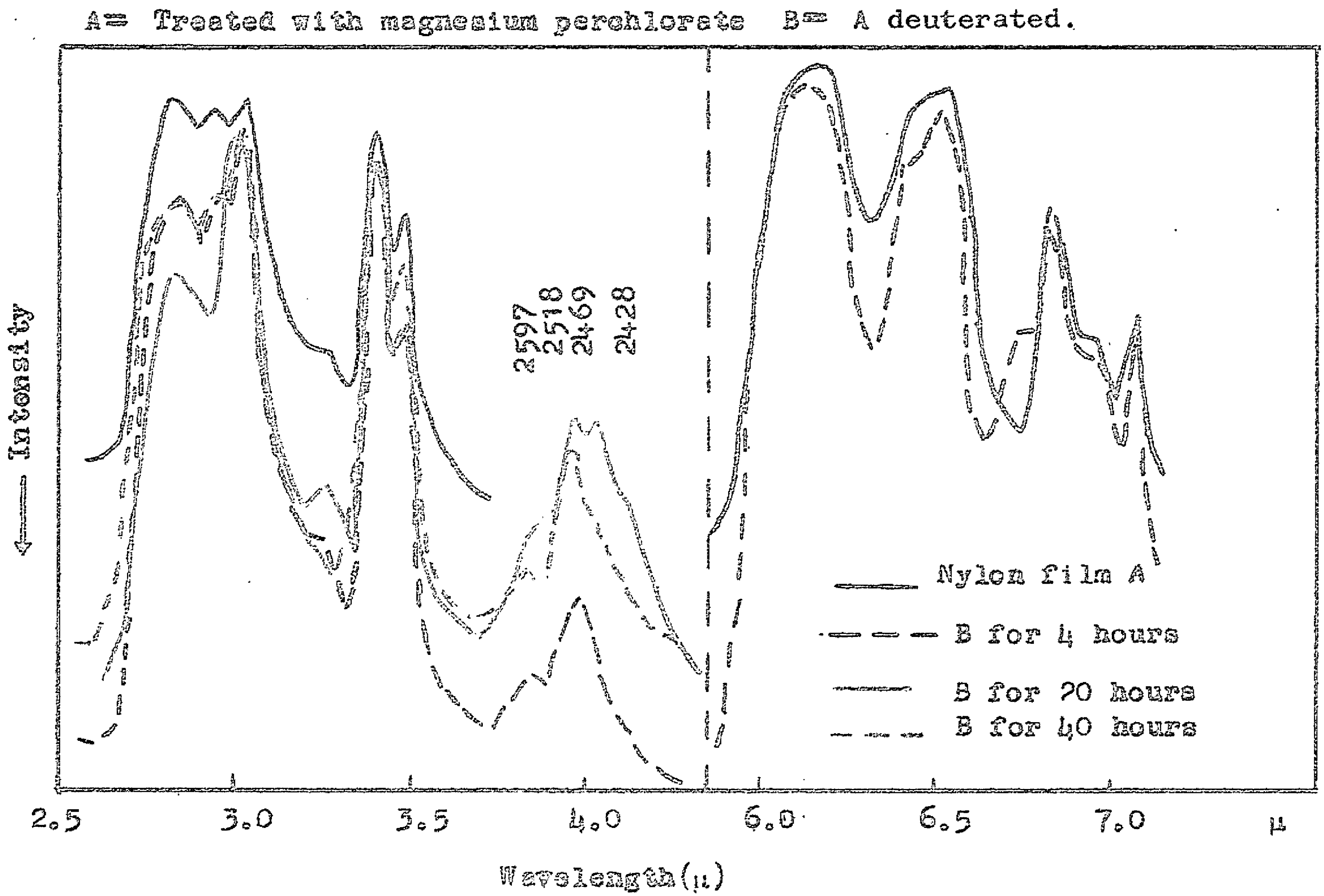


Fig.9. The changes in spectral absorption of treated nylonfilm when subjected to deuterium exchange for different periods.

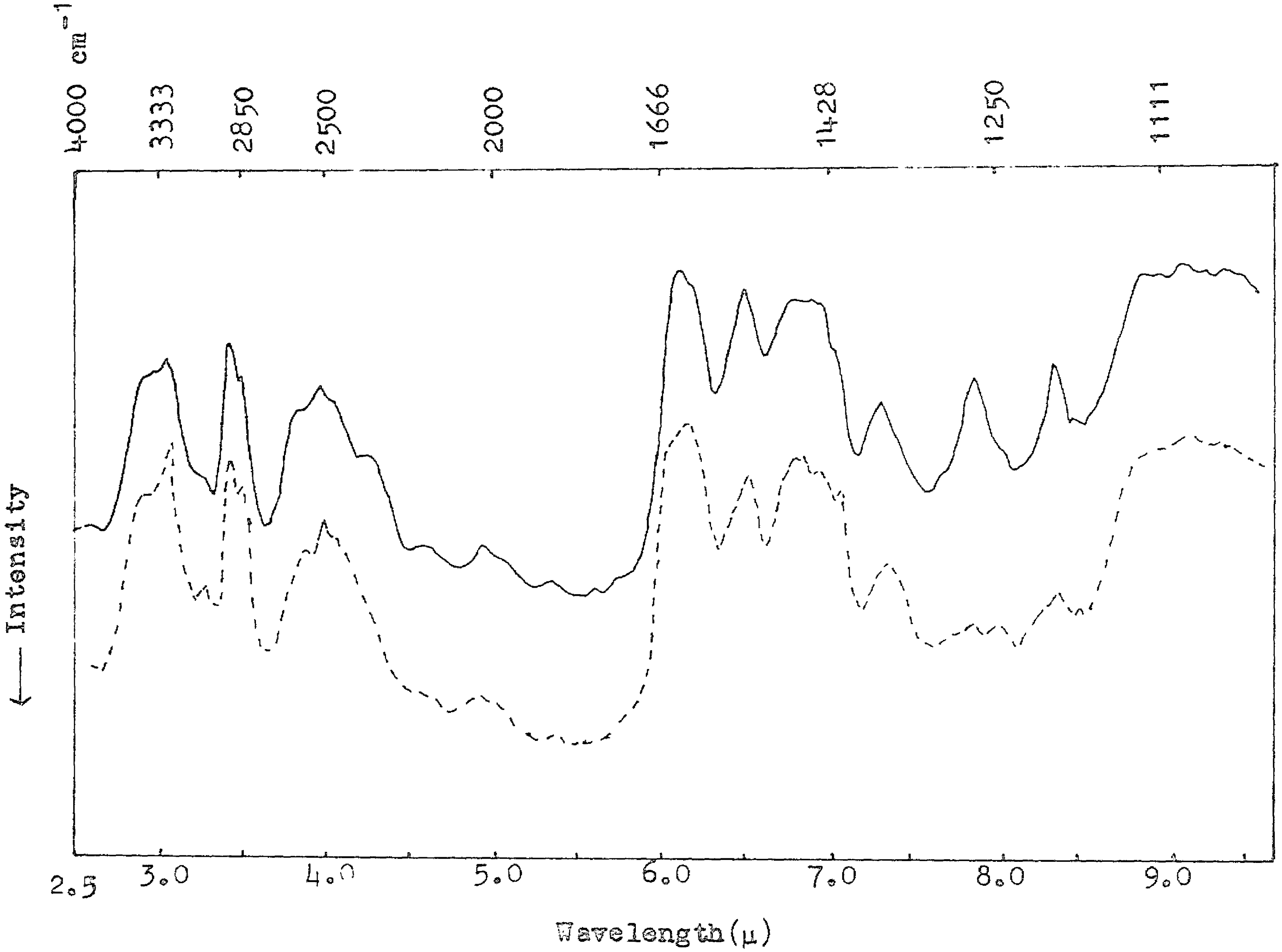


Fig. 10. Infra-red spectra of nylon 66, treated with magnesium perchlorate and deuterated. ---- Parallel, ______ Perpendicular to diretion of stretching.

TABLE 5. The effect of polar reagents on dichroism of NH band in nylon 66.

Treatment	Frequency cm^{-1}	Dichroic ratio
(A) <u>Nylon film treated with Lithium Perchlorate</u>		
(1) Unmodified nylon 66 film	3305	0.5
(2) Deuterated nylon 66 film	3305	0.3
	2480 2432	0.4
(3) Nylon film treated with	3305	0.2
lithium perchlorate, 55°C,	3390	1.3
24 h.		
(4) The film treated as in (3)	3305	0.3
was deuterated for 4 hours	2518	0.6
(5) The deuterated film as in		
(4) was further deuterated	3305	0.4
for 24 hours.		
(B) <u>Nylon film treated with Magnesium Perchlorate</u>		
(1) Unmodified nylon 66 film	3305	0.6
(2) Nylon film treated, 20°C	3305	0.3
12 h.	3390	1.6
(3) Nylon film treated 80°C	3305	0.4
12 h.	3390	1.3
(4) The nylon film treated as in	3305	0.4
(3) was deuterated for	2518	0.9
4 hours.		

scattering losses. However, from the spreading of the broad NH band to high frequency, and in some spectra an observed splitting of the broad band into two peaks (3390 and 3305 cm^{-1}) in the 3 μ region, it appeared that the polar ions had some effect on polar groups in nylon 66. It may be noted that reducing the intensity of adjoining broad bands due to OH groups, was a difficult task, mainly because of an inevitable presence of highly hygroscopic material in the samples being examined.

The gelatinous residue film was washed free from reagent, dried in an oven at 60°C, and examined for infra-red absorption. The new peak disappeared and the normal NH band at 3305 cm^{-1} was very strong. The gelatinous residue was also examined as follows.

1. The residue was dissolved in a minimum quantity of formic or dichloroacetic acid. The viscous solution thus obtained was allowed to evaporate free from acid on a rock salt plate, P.V.C. film or polyethylene film in an oven at 50°C, for 24 hours. The plate or film was then transferred to a vacuum desiccator which was evacuated for 12 hours. A thin film of the residue thus obtained was examined for infra-red absorption.

2. The residue was washed free from reagent and subsequently treated as in (1) and examined for spectral absorption.

The spectral absorption for residue films cast from formic acid is shown in Fig. 11. For films cast from dichloroacetic acid, similar effects but rather broader bands were observed. It was clear from the results that interaction resulting in the new band at 3390 cm^{-1} was retained in viscous solution. However, when a large amount of acid was used, it was found that the new band disappeared and only a normal NH band at 3305 cm^{-1} was observed for the washed residue.

(d) Acid treated nylon 66

Nylon 66 yarn was treated with 2N hydrochloric acid for one hour, and subsequently subjected to the same treatment on unmodified nylon. This also gave a ~~gelatinous~~ residue, which was comparatively less gelatinous and on cooling it became rather rigid. On washing it assumed a brittle form. This residue revealed similar spectral characteristics to those of the residue from unmodified nylon 66.

(e) Solution of nylon 66 in polar reagents

The solution in which nylon yarn was boiled, was dialysed in semipermeable dialysing bags till free from polar ions. A turbid suspension left in the dialysing bag was centrifuged, dried and examined for infra-red absorption.

The infra-red spectrum resembled that of a simple amide (e.g. iso-butyric amide).

(f) Polyacrylonitrile films

No significant change in the frequency of the cyanide (CN) peak was observed when Orlon films ~~were~~ treated with magnesium

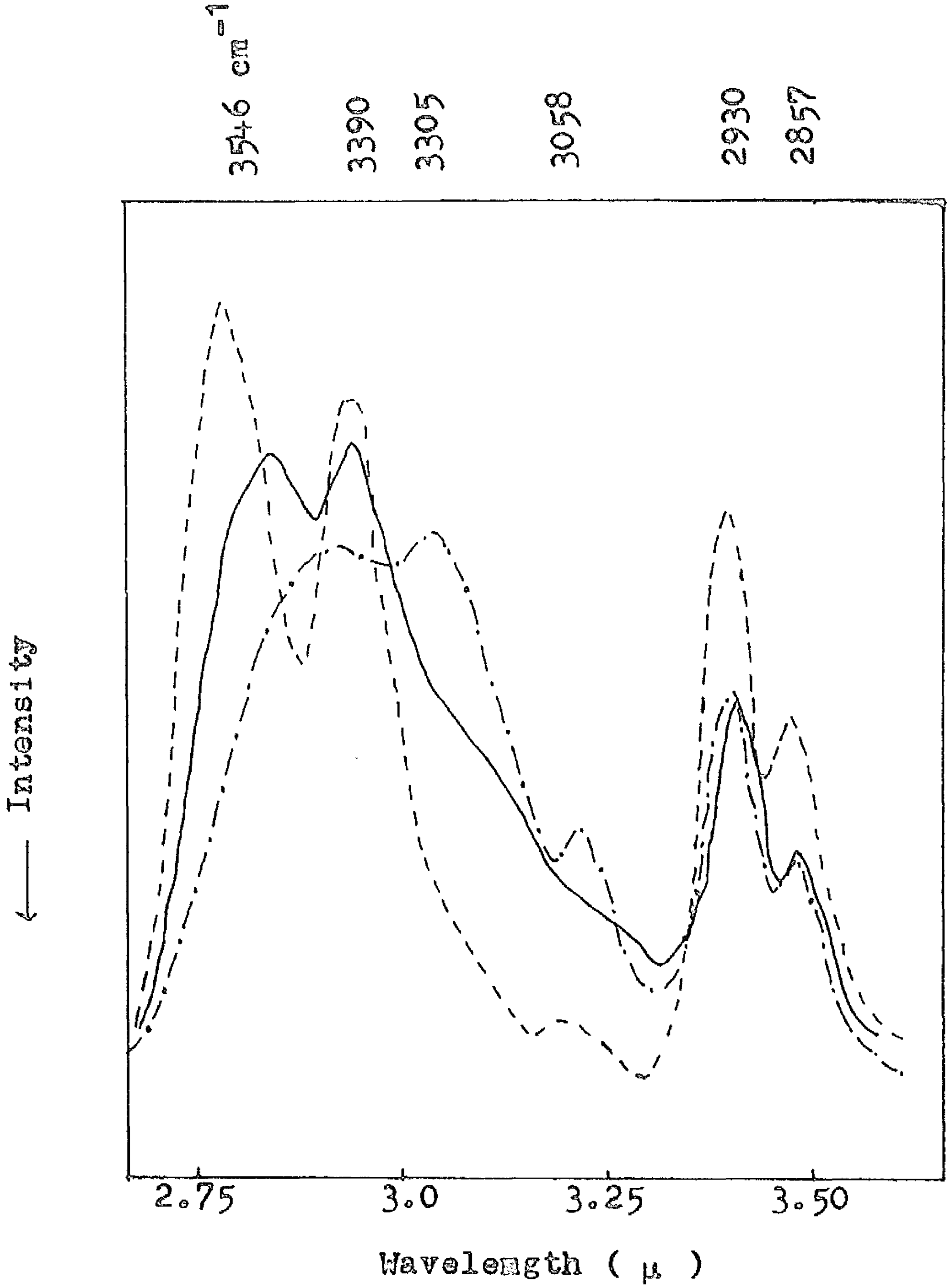


Fig.11. Infra-red spectra of nylon 66 residue recast from formic acid.

-·-·-·- Lithium bromide
------- Lithium perchlorate
——— Magnesium perchlorate

perchlorate at 30°C for 12 h. were examined for spectral absorption, and these films dissolved in the aqueous solution of polar reagent when the temperature was raised to 50°C.

(g) Auxiliary experiment

Nylon 66 yarn was dissolved in molten antimony trichloride. A small quantity of this solution was transferred to a rock salt plate in a glove-box maintained at zero humidity. A second rock-salt plate was placed on this and a thin film thus formed between the two plates was examined for infra-red absorption.

Fig. 12 shows a marked change in spectral absorption of nylon 66 treated with antimony trichloride. The new NH peak at 3400 cm^{-1} is in conformity with the published results.[52]

DISCUSSION

The addition of lithium bromide to N-ethyl acetamide increases the viscosity of the solution and this is in agreement with a similar effect reported by different authors.[103-107] The spectral evidence suggests that there is an increase in the strength of the hydrogen bond, which may be associated with the increased viscosity of solution. A broadening of the 6 μ band does not suggest any conclusive evidence as to the nature of interaction.

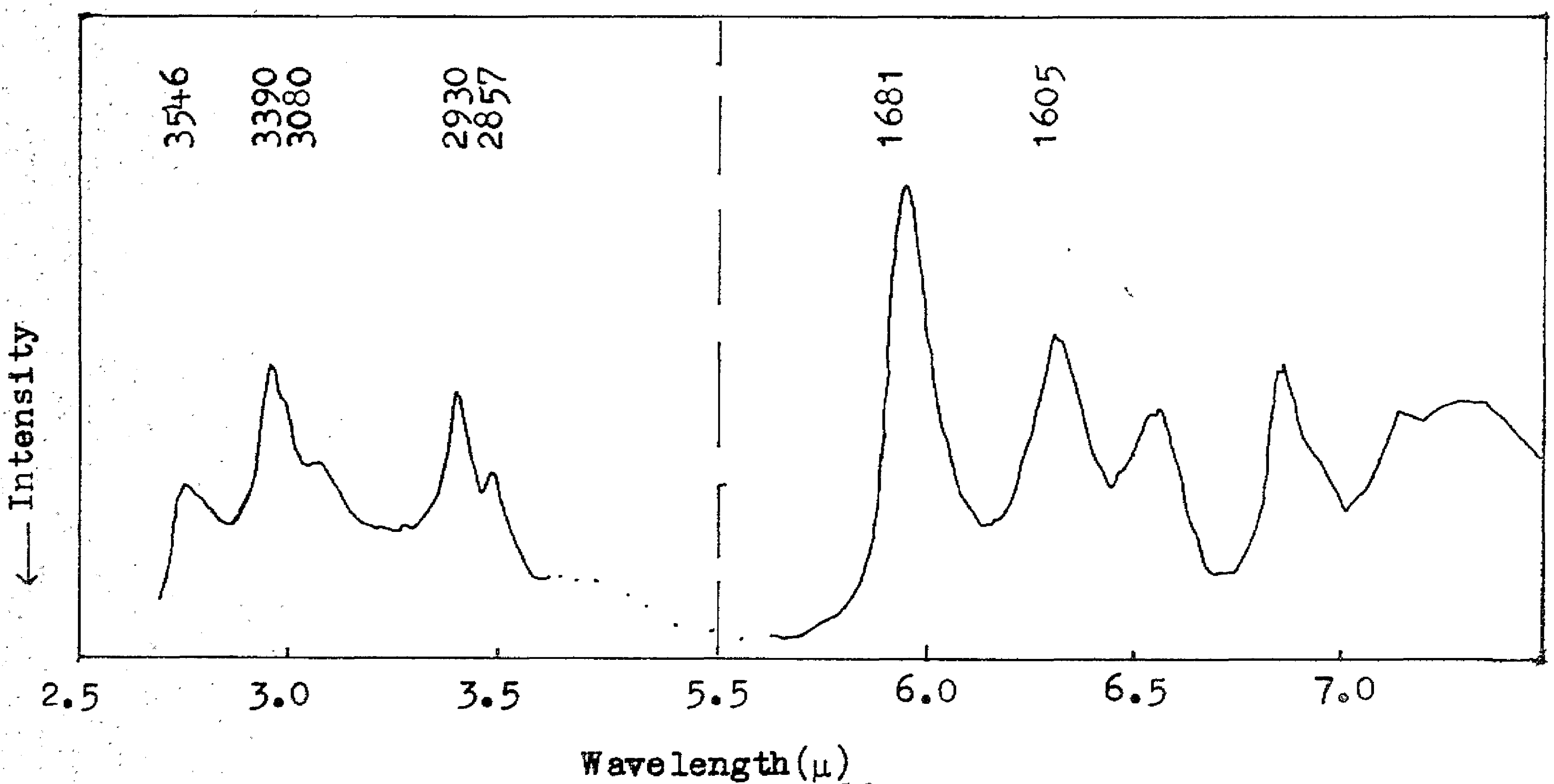


Fig.12. Infra-red spectrum of nylon 66, treated with molten antimony trichloride.

However, in spite of an increase in the viscosity of the solution, N.M.R. spectra reveal a sharpening of the broad band due to amido protons, and this may be attributed very tentatively, to a decrease in effective delocalization of the lone pair electrons at the nitrogen atom. This would indicate a weakening of intermolecular interaction at the polar groups, which is contrary to the observed spectral shift in the infra-red region as mentioned above. It is not clear at this stage as to what is the probable mechanism of interaction.

The spectra of nylon films treated with polar reagents reveal the presence of a new band at 3390 cm^{-1}. It may be suggested that the presence of polar reagents brings about some change in the vibration modes of the treated sample, and to this end various possibilities may be visualised as under.

1. The band at 3390 cm^{-1} is due to water molecules firmly bound as hydration shells of the polar ions.

2. It may be due to water molecules hydrogen bonded to NH groups. The role of polar ions in this case may be visualised as carriers for water molecules, which eventually interact with NH groups.

3. It may be due to free NH groups produced as a result of breakdown of hydrogen bonds.

4. It may be due to NH groups hydrogen bonded to CO groups on the same molecular chain (intramolecular bonding).

This may be visualised as a result of retraction of molecular chains which leads to a folded chain configuration.

Keeping in view the results obtained by various authors[51-54], it is suggested that the peak at 3390 cm^{-1} is a new NH band, and various supporting arguments are presented as follows.

(1) With the appearance of the new band, the intensity of the original NH band at 3305 cm^{-1} gradually diminishes. One finds a considerable splitting of the 3390 cm^{-1} peak from the adjoining 3546 cm^{-1} OH band, and the 3305 cm^{-1} NH band. These observations do not favour a possibility that 3390 cm^{-1} is due to OH groups of free water molecules.

(2) Table 5 reveals that the new peak has a slight parallel dichroism, and this does not favour its being due to sorbed water.

(3) A critical examination of changes on deuteration reveals the following possibilities.

(a The new peak at 3390 cm^{-1} is due to a component, which is the most accessible, since on deuteration it yields a band which readily changes to the OH band even during the time of scanning, when the nylon film is not in contact with deuterium oxide vapour. Presumably this is an O-D band, due to free water molecules on the surface of the film and attached to hygroscopic reagent.

(b) The new peak at 3390 cm^{-1} weakens on deuteration in preference to the normal NH band at 3305 cm^{-1}. Even on continued deuteration, the ND bands at 2486 cm^{-1} and 2432 cm^{-1} corresponding to the normal NH band at 3305 cm^{-1} do not appear to be very intense. However, a new band at 2518 cm^{-1} appears very strongly and it is suggested that this is the ND band corresponding to the 3390 cm^{-1} NH band. One would expect this if the interaction of the reagents with the polar groups occurs only in the accessible regions. In other words, the new peak at 3390 cm^{-1} is due to these groups which lie in the most accessible regions. The remainder of the groups contributing to the normal NH band at 3305 cm^{-1}, apparently lie in the less disordered or the crystalline regions. Therefore, the normal NH band is less susceptible to deuterium exchange.

(c) The spectrum of a deuterated unmodified nylon film shows the splitting of ND band at 2486 cm^{-1} and 2432 cm^{-1}, in accordance with the Fermi's resonance principle[108]. It is suggested that a similar mechanism might be responsible for the observed fine structure of the 2518 cm^{-1} band.

(d) On rehydrogenation, although the band at 2597 cm^{-1} disappears during the scanning period, little change occurs in the intensity of the 2518 cm^{-1} band: this indicates that the peak at 3390 cm^{-1} is probably not a simple OH band.

(4) X-ray evidence is that the interaction is confined to the less crystalline regions.

(5) The spectral changes in the 1400 - 1680 cm^{-1} are not very significant except for the broadening of the bands. Mandelkern et al[54] has recently attributed the broadening of the 1660 cm^{-1} band to the presence of water in the system. It is interesting to note that while using polarised light, the profile of 1660 cm^{-1} band changes with the direction of the electric vector, as shown in Fig. 10. It is suggested that the change in the profile of 1660 cm^{-1} band would occur only if it were a composite band, deriving its intensity from two bands with opposite dichroism. This is easily understood if one visualises that in the treated sample both the 3305 cm^{-1} NH band and the new peak at 3390 cm^{-1} may contribute to the intensity of the Amide I band (1660 cm^{-1}).

(6) The spectral examination of films cast from viscous solutions in formic acid of nylon treated with polar reagents, reveal the presence of the new peak at 3390 cm^{-1}. It is interesting to note that as expected, the use of large amount of acid restores the original NH band at 3305 cm^{-1}.

This is easily understood if one visualises that in dilute solution the polar ions will go into the solvent phase and the interaction with the polar groups in nylon will be considerably weakened. It is suggested that this is an interesting observation and may assume its importance in the study of chain configuration in solutions of polyamides.

(7) The spectral examination of the residue from acid-treated nylon provides additional evidence that the polar ions play a fairly consistent role. It may be recalled that Larose[109] had reported interesting spectral changes in nylon, as a result of hydrogen chloride sorption. Keeping in view a possible effect of hydrochloric acid on the non-specific Van der Waals' interactions, and the effect of polar reagents on specific interactions, it was thought reasonable to examine the combined effect of the two treatments on nylon 66. Contrary to the expected possibility of a severe effect, and a partial dissolution, the resultant product was found to be less gelatinous than that from unmodified nylon and it became rather brittle, when washed free from reagent. One is tempted to suggest that hydrochloric acid causes hydrolytic breakdown of the main chains and brings about a better alignment[109]. Larose[50] has reported an increase in the strength of hydrogen bonds for which he gives a number of alternative explanations, but he has not considered that it may be due

to a closer alignment of the chains.

(8) Dialysis of solutions of polar reagents in which nylon was treated at boiling point, revealed the presence of a very small amount (less than one percent of the weight of the treated sample) of a low molecular weight component, which had spectral absorption similar to that of a simple amide. As expected, the yield of this component was higher, when nylon films were used instead of nylon yarn (presumably because of a greater possibility of thermal degradation in the preparation of nylon films). It was reasonable to argue that polar reagents might bring about physical changes in nylon because they extract the low molecular weight component present in the original sample. However, when nylon films were treated in saturated solution of beryllium sulphate, at boiling point, it was found that although the films were not affected, the spectral examination of the dried contents of the solution, revealed the presence of CO and NH groups. This clearly indicated that low molecular weight material may be extracted by solutions of other reagents and that polar reagents had a more specific effect on nylon; the extraction of impurities being an inevitable side effect, having little significance in producing drastic physical changes in nylon 66.

Thus the spectral evidence indicates a strong interaction between polar reagents and the polar groups in nylon 66. There is little doubt that the new peak is due to NH groups, but it is not very clear as to what mechanism is involved in this spectral shift. It is therefore logical to deduce a probable interaction mechanism, and in doing so various data will be assessed as follows. To avoid repetition, discussion of the remaining aspects of the present results will be reviewed at a later stage.

MECHANISM OF INTERACTION

It is important to note that any proposed mechanism should take into account a consistent role played by the ions, and also various physical changes should be explicable in the light of the interaction mechanism. Keeping in view the characteristic properties of the polar ions, it would be interesting to recall briefly the part played by the ions in various systems.

(1) The polar ions (Li^+ in lithium perchlorate) have been used as catalysts in polymerization of monomers[110] and the proposed cationic mechanism indicates that the ions co-ordinate at the lone pair electron site in the monomer group.

(2) There is no significant effect on polyethylene films. It seems that these reagents do not affect the non-specific interaction forces, which are responsible for cohesive energy in polyethylene.

(3) Polyvinyl alcohol fibres dissolve in the polar reagents and it seems that a large number of specific interactions are affected.

(4) Orlon films dissolve in polar reagents, although the presence of hydrogen bonding in polyacrylonitrile is a remote possibility in view of recent spectral evidence[111] and the N.M.R. studies.[112] It has been reported that the lone pair electron of the nitrogen atom (cyanide group) plays a decisive role in various phenomena, e.g. cuprous ion technique[113] used in dyeing of Orlon. There is therefore little doubt that if there is any interaction in Orlon, it would be confined to the cyanide groups and that the nitrogen atom would play the most important part.

(5) Supercontraction of wool fibres in lithium bromide solutions suggests the breakdown of hydrogen bonds. Mandelkern et al[56] have proposed that the interaction of lithium bromide with wool may be visualised as an interference with the phenomena of resonance at the CONH groups.

(6) Silk fibres dissolve in polar reagents. Infra-red and X-ray studies reveal that interaction involves a retraction of molecular chains. Silk has numerous CONH groups along the molecular chains, with a relatively small amount of non-specific interaction responsible for the cohesive energy of the fibres. Probably, the polar reagents interact with

the peptide groups and weaken the specific interaction at these groups, resulting in an increased rotational freedom of the chains which would favour a new configuration. Since CONH groups are so closely spaced a possibility of a folded configuration with intra-chain hydrogen bonding is favoured, as a result of polar interaction.

(7) The action of polar reagents on nylon 66 is interesting because nylon combines to some extent the characteristics of both polyethylene and silk fibres. The long polyethylenic segments give rise to non-specific interactions, which do not allow the complete dissolution of nylon in the polar reagents.

Considering the two possible resonance structures of the peptide group, one may reason out the most probable configuration of electrophilic ions with respect to the ligand.[114]

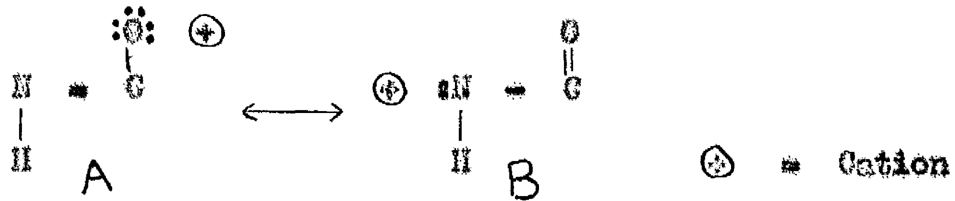


Fig. 1A

(1) The marked change in 3 μ region (NH stretching mode) and the absence of changes in the amide I band (essentially the C=O stretching vibration)[115] do not favour co-ordination as in (A). It may be objected that the

broadening of the amide bands in the presence of water would mask any effect in this region. As suggested earlier the broadening may be due to a combined contribution of 3305 and 3390 cm^{-1} bands to the amide I band. On the other hand, when nylon 66 is dissolved in antimony trichloride the presence of a NH peak at 3400 cm^{-1}, amide I band at 1680 cm^{-1}, and amide II band at 1605 cm^{-1} indicates that reagents which attack C=O groups [52] can bring about more radical changes in the spectrum than is found with polar reagents. The above changes in the amide bands indicate the presence of $CONH_2$ groups, and it is suggested that the action of antimony trichloride leads to the degradation of molecular chains and results in a large number of $CONH_2$ groups.

(2) Co-ordination through the nitrogen atom as shown in (B), generally results in a lowering of the NH stretching frequency,[116] unless the ligand is highly associated by hydrogen bonding, when the frequency may be raised.[117] Hence the increased frequency observed here may well result from an ionic interaction as shown in (B).

(3) N.M.R. studies on the model compound suggest that the lone pair electrons of the nitrogen atom, in N-ethyl acetamide plays an important part.

(4) Though NH groups have been considered as passive groups in amides, it may be noted that there is evidence which indicates reasonable activity of these groups in nylon,

e.g. hydroxy-ethylation involves co-ordination with the nitrogen atom.[118] Recently Vickerstaff et al[119] have proposed that the Procinyl dyes are also reactive to imido groups in nylon, apart from their reactivity with the end groups, and their study of a model compound confirms this proposition.

(5) It was shown earlier that the treatment with magnesium perchlorate at 20°C, results in a small decrease in the initial modulus and a reduction in extensibility prior to rupture, which was attributed to a possible elimination of gliding of the segments. On the other hand, if one visualises an ion-dipole interaction, which favours a single-bonded (B) structure, this would impart greater flexibility to the molecular chains, resulting in a decrease in the initial modulus and a closer alignment of the polyethylenic segments: the latter would oppose gliding of the segments with respect to one another. This explanation seems to be a more satisfactory one and supports the proposed interaction mechanism. In view of this mechanism, the earlier suggestion (page 36) may be discarded since this implied a strengthening of hydrogen bonds, contrary to the infra-red spectral evidence. It may be noted that relaxation of internal stresses as a result of treatment with polar reagents, agrees fairly well with the evidence from X-ray diffraction studies (see page 40).

It is concluded that there is a high probability of an ion-dipole interaction at the nitrogen atom[107] in polyamides, when they are treated with the polar reagents.

CHAPTER III

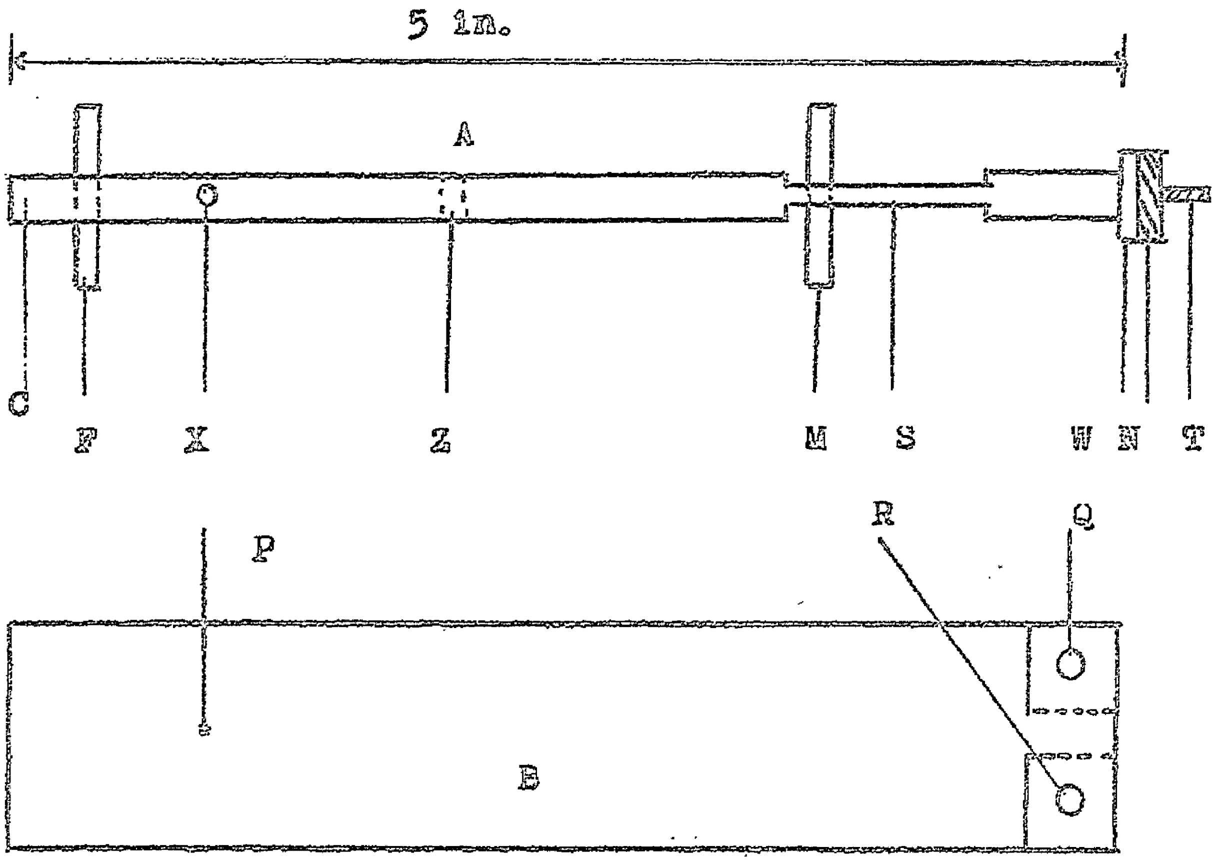
MATERIALS

The materials used in the present investigation were nylon 66 yarn 210 denier (34 filament) with 1/2 turn per in. Z twist, and Japanese Tram silk 170 denier with 4 turns per in. S twist. The raw silk was degummed by a two bath process using 0.1% soap solution, at 95° C. The pH of this degumming bath was maintained at 10 by addition of sodium carbonate. After two hours of degumming, the silk was thoroughly washed free from soap and alkali, and tested for the presence of sericin gum with Shirlastain D. The tensile strength and the breaking extension of these materials at 20°C and 65% r.h., as measured on a Cambridge extensometer, were 7.4 g./denier 16% extension, and 3.3 g./denier, 14% extension, respectively.

SPECIMEN HOLDER

The specimen holder was made of a 12.5 cm. long stainless steel tube 0.6 cm. diameter which carried a fixed pin (F) at one end, and a movable pin (M) sliding in a 2 cm. long slot at the other end of the tube (see Fig. 15, and plate 1). The pin M was fitted in one end of the screwed rod T and could be traversed in the slot S by turning the nut N which bore against the end of the tube. To minimise friction between the nut and the edge of the cylindrical

C.. Stainless steel tube
F..Fixed pin
M..Movable pin
S..Slot
T..Threaded rod
N..Nut
W..Washers
Z..Hole in the middle for winding
X..Hole near the fixed pin to facilitate stretching.
P.. Pin fitted on the platform
Q,R..Knobs to clamp the holder on the platform



PLAN VIEW

Fig.15. A... Specimen holder B... Brass platform used for stretching operation

tube, two washers (W), one made from a Teflon sheet and the other of stainless steel, were interposed between the edge of the tube and the nut. Two holes, one in the middle (Z), and the other (X) near the fixed pin were drilled to facilitate the mounting of yarn on the two pins, and subsequent stretching operation respectively.

MOUNTING OF THE YARN

The yarn used in all the experiments was previously desiccated under vacuum and subsequently conditioned at 65% r.h., and a pair of clean rubber gloves was used to handle the yarn and the specimen holder. To facilitate winding of the yarn, the holder was supported at the centre (Z) on a rod; the winding was carried out under a constant tension of 3.5 g. using the Shirley constant tension winding tester: about 0.1 g. of material was mounted between the pins in form of two hanks of 8.5 cm. length, one on each side of the frame, for each experiment.

STRETCHING TECHNIQUE

The holder was placed on a brass platform (B) in such a way that the pin (P)projecting on the surface of the platform, fitted in the hole (X), as shown in Fig. 15 and plate 1. At the other end of the holder, a brass clamp (C) with a groove in the centre, was placed and firmly clamped with suitable knobs (Q, R). This end of the holder had to be firmly clamped to avoid shearing of the slot due to the tilting of the cylindrical tube resulting from enormous torque involved in the turning of the nut. The nut was turned with a 2 B.A. box-spanner to produce a desired extension, and the changes in length were measured by a ruler reading to 0.5 mm.

GRAVIMETRIC ANALYSIS

All weighings were done on a very sensitive balance, which could weigh to $\pm 5 \times 10^{-6}$g. The weight of the empty holder was noted at the beginning of each experiment. After completing winding, the mounted yarn was desiccated for 4 hours under a vacuum to ensure that the equilibrium with the experimental humidity condition was attained by way of absorption. The initial weight of the empty holder was subtracted from the combined weight of the holder and yarn, to obtain original weight of the yarn used in the experiment. The holder was removed from the balance pan and stretching of the yarn was carried out as described above. The holder was weighed again to find changes in the combined weight of the holder and yarn with lapse of time: the instant stretching was completed being recorded as zero time. When a sensible equilibrium value for the combined weight was attained, the yarn was removed from the pins without slackening (turning of the nut), and the final weight of the empty holder was noted. To find out the weight of the stretched yarn, the final weight of the empty holder was subtracted from the combined weight of the holder and yarn after stretching.

TEMPERATURE AND HUMIDITY CONTROL

The experiments were carried out in a conditioned room at 20 ± 2°C, and to maintain different humidities, the balance was enclosed in a glove-box as shown in Fig. 16. It consisted of an aluminium case with a Perspex front, fitted with two rubber gloves. The Perspex front was fitted with suitable flanges, and it could easily be removed when it was so desired. The transfer of the holder was done through one of the holes in the Perspex front by temporary removal of the glove. Originally a rubber sheet was laid to serve as the bottom of the glove-box, however at zero humidity some leakage was noted, and the rubber sheeting was replaced by a sealed-on polyethylene sheet, which served the purpose satisfactorily. The desired humidity was maintained by the use of required saturated salt solution, and the air inside the glove-box was circulated by a blower to ensure a uniform vapour pressure. The humidity was recorded on a thermo-hygrograph and the values were checked by the use of a paper hygrometer and a Gregory hygrometer. No fluctuations in humidity during the course of experiments were noticed, and it may be noted that Gregory hygrometer served as a very sensitive device to detect such fluctuations. The difference

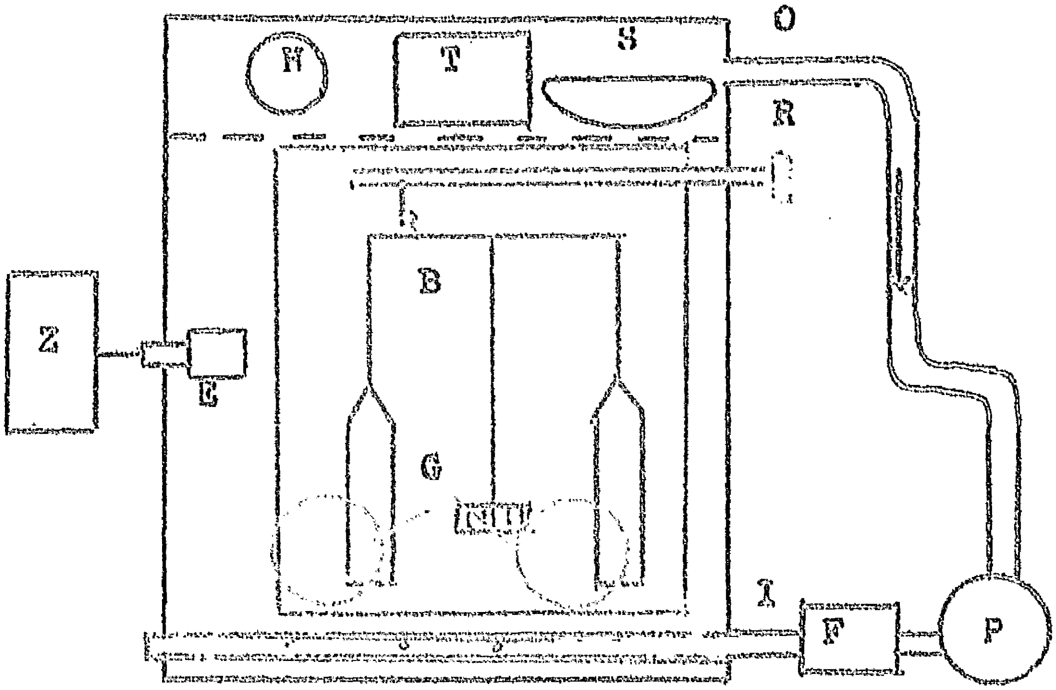


Fig.16. Schematic diagram of the glove-box.

B... Balance
G... Gloves (in front panel)
R... Extension rod for the movement of the rider.
S... Saturated salt solution
T... Thermo-hygrograph
W... Paper hygrometer
Z... Gregory hygrometer   E... Sensitive element
O... Outlet   I... Perforated inlet tube (at rear of box)
F... Glass fibres as a filter
P... Pump for the circulation of the air inside the glove-box

between values of humidity as obtained by different methods suggests that the noted values for humidity may be subject to correction by a factor of ± 2% at 66% r.h., and ± 3% for 13% and 93% humidity.

LONGITUDINAL SWELLING

A 13 cm. long filament of nylon 66 (6 denier), and a nichrome wire (to serve as a reference mark in measurement of changes in length) were suspended from a glass hook placed inside a vacuum tube. A load of 2.4 g./denier (corresponding to an extension of 6% being used as a median extension in the study of changes in regain with strain in the present work) was attached to the lower free end of the filament (see Fig. 17). The lower end of the vacuum tube was connected through a stopcock to a conical flask, which contained the required saturated salt solution. It was possible either to evacuate the tube or circulate the air inside the tube, through a bottle containing salt solution, with the help of a pump. The filament was conditioned for mechanical creep for one week at zero humidity, and then subjected to cyclic changes in humidity as follows:

$$0 \rightleftarrows 20 \rightleftarrows 55 \rightleftarrows 80 \rightleftarrows 100\%$$

The changes in length were measured with a travelling microscope, which could be read to 10 microns. The accuracy of the measurement was of the order of ± 0.05 per cent.

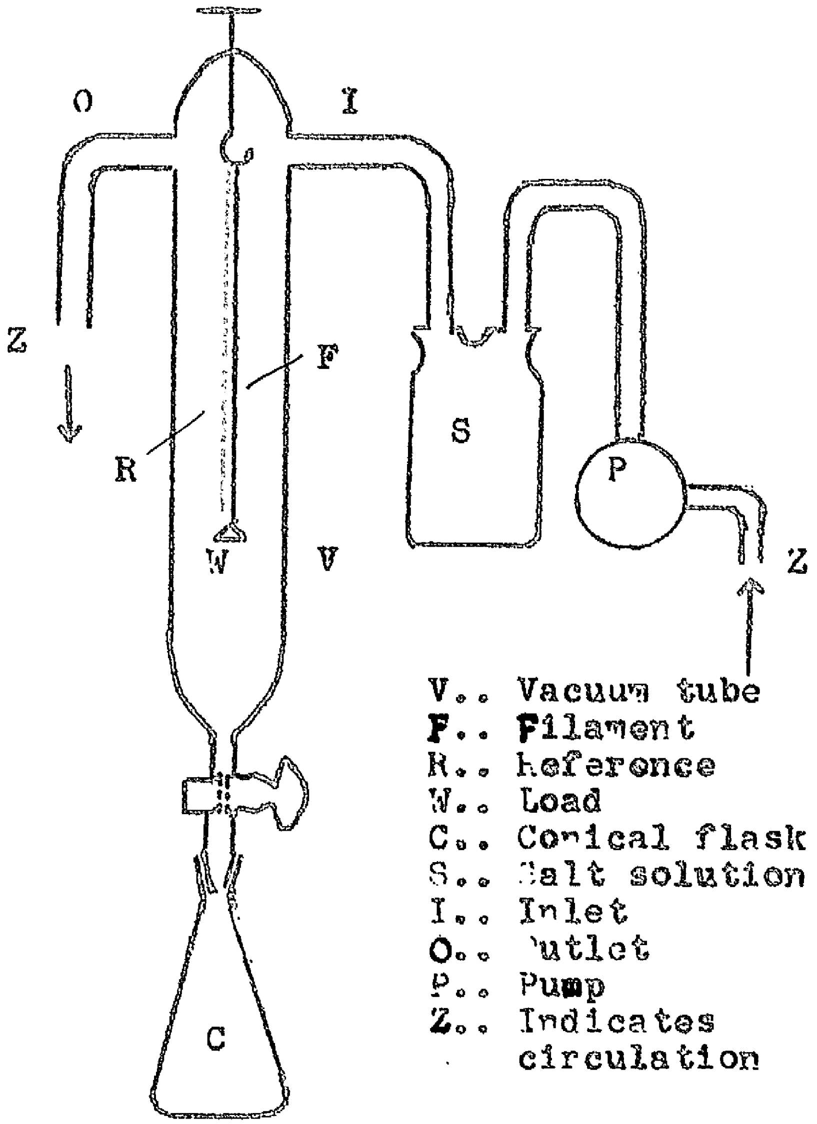


Fig.17. The apparatus for measurement of longitudinal swelling.

RESULTS

Auxiliary information

The change in the weight of the yarn has been expressed as a percentage of the dry weight i.e. as a change in % regain (dr%).

The experimental accuracy is estimated at ± 0.2% change in regain: this is based on the results of experiments carried out at zero humidity, and observed inconsistencies in the weight of the empty holder. It may be noted that the attainment of a sensible equilibrium weight (followed by little appreciable change) of the holder took about 20 minutes.

At the end of each experiment an inconsistent change up to ± 30 x 10^{-6} g. was found in the weight of empty holder. The increase in the weight was probably due to deposition of dust particles and adsorption of moisture film on the threaded rod of the specimen holder. As 80-100 lbs. force is involved to produce an extension of 10% for 0.1 g. of nylon 66, the decrease in the weight of empty holder may be attributed to a filing action resulting from friction between the nut and the threaded rod. A thin coating of lubricant could not be used since this would have provided a favourable surface for deposition of dust particles.

The instant at which stretching was completed was considered as zero time for finding changes in regain with time.

NYLON 66.

Changes in regain with strain

Fig. 18 shows a plot of typical curves for percentage increase in regain with time, at 66% r.h. Except for an initial decrease at low extension (2.3%), in general there was an initial rapid change followed by a gradual increase in regain, which reached a sensible equilibrium value in 30 minutes. At different humidities similar types of curves were obtained. Tables 6 - 10 show the experimental values for changes in regain with strain, at different humidities.

The equilibrium changes in regain with strain at different humidities are plotted in Fig. 19, as (dr%) against strain %. It is interesting to note that the experimental points except for those at 13% r.h. are distributed about a straight line (the mean slope of the line drawn through the various points was calculated by the method of least squares).

A plot of changes in regain against humidity in Fig. 20 shows that between 35% and 93% r.h., the humidity does not have a significant effect on the changes in regain. However, some deviation is clearly indicated at 13% r.h.

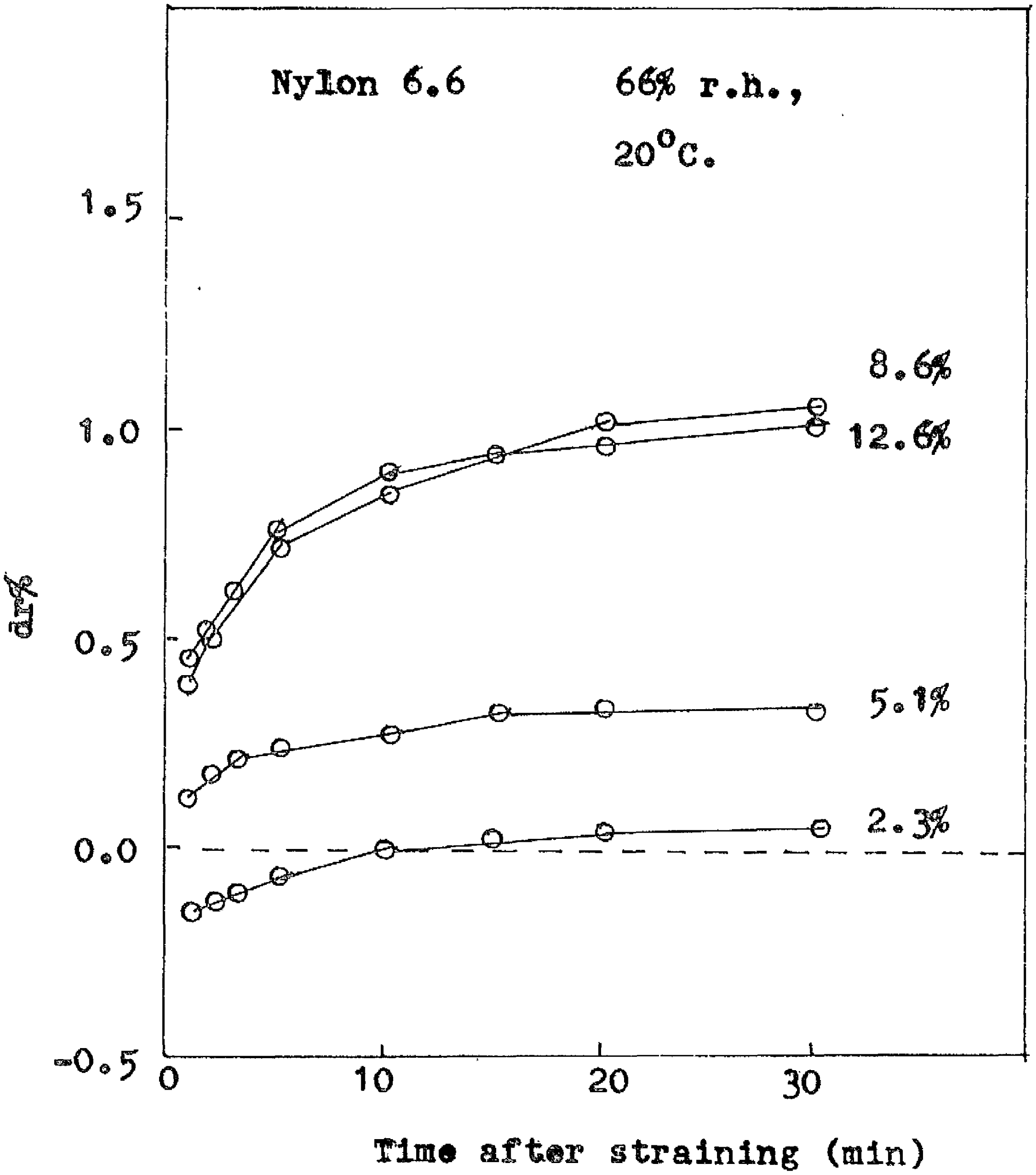


Fig. 18. Typical curves for percentage change in yarn mass(dr%) with time, at various strains.

TABLE 6. The changes in moisture regain at 13% r.h. and 20°C.

Time min.	1	2	3	5	10	15	20	30
Strain %			dr% at various extensions					
3.1	0.01	0.02	0.02	0.03	0.04	0.05	0.06	0.06
3.5	0.1	0.11	0.13	0.15	0.20	0.24	0.28	0.29
4.9	0.02	0.04	0.06	0.08	0.10	0.13	0.14	0.16
5.2	0.03	0.06	0.08	0.10	0.12	0.13	0.16	0.17
6.0	0.11	0.14	0.18	0.22	0.25	0.30	0.35	0.36
7.6	0.05	0.06	0.08	0.11	0.15	0.18	0.19	0.20
8.4	0.03	0.05	0.09	0.11	0.14	0.18	0.18	0.19
8.8	0.04	0.06	0.08	0.10	0.14	0.18	0.19	0.20
8.8	0.15	0.18	0.22	0.25	0.30	0.33	0.36	0.37
9.2	0.16	0.20	0.23	0.30	0.35	0.40	0.42	0.45
11.2	0.18	0.21	0.2 4	0.28	0.30	0.35	0.39	0.40

TABLE 7. The changes in moisture regain at 35% r.h. and 20°C.

Time min.	1	2	3	5	10	15	20	30
Strain %	dr% at various extensions							
2.9	0.02	0.05	0.07	0.10	0.15	0.18	0.21	0.23
3.5	0.10	0.11	0.13	0.15	0.18	0.20	0.21	0.23
5.2	0.17	0.21	0.23	0.26	0.34	0.40	0.43	0.47
6.9	0.26	0.29	0.32	0.38	0.45	0.50	0.54	0.58
8.1	0.45	0.48	0.52	0.58	0.65	0.70	0.73	0.76
11.5	0.44	0.51	0.57	0.66	0.80	0.91	0.98	1.05
12.0	0.65	0.74	0.80	0.86	1.05	1.16	1.19	1.27
12.5	0.58	0.67	0.73	0.82	0.97	1.08	1.15	1.17

TABLE 6. The changes in moisture regain at 55% r.h. and 20°C.

Time min.	1	2	3	5	10	15	20	30
Strain %	dr% at various extensions							
2.4	0.22	0.25	0.26	0.28	0.31	0.35	0.38	0.4
3.0	0.20	0.22	0.24	0.28	0.30	0.33	0.35	0.35
3.2	0.12	0.14	0.15	0.18	0.20	0.21	0.22	0.23
4.8	0.15	0.2	0.28	0.35	0.40	0.43	0.45	0.47
6.5	0.25	0.29	0.33	0.38	0.45	0.55	0.63	0.67
6.8	0.22	0.30	0.35	0.40	0.45	0.50	0.55	0.57
7.6	0.25	0.30	0.35	0.40	0.48	0.55	0.60	0.64
8.8	0.35	0.38	0.43	0.52	0.60	0.70	0.78	0.85
10.0	0.33	0.37	0.41	0.53	0.61	0.65	0.70	0.75
11.6	0.42	0.53	0.65	0.72	0.81	0.98	1.1	1.11
12.4	0.45	0.50	0.62	0.70	0.80	0.95	1.12	1.17
13.6	0.41	0.58	0.64	0.76	0.85	0.91	1.10	1.12

TABLE 9. The changes in moisture regain at 66% r.h. and 20°C.

Time min.	1	2	3	5	10	15	20	30
Strain %	dr% at various extensions							
2.3	-0.15	-0.13	-0.10	-0.06	0.01	0.03	0.05	0.05
4.4	0.08	0.14	0.16	0.23	0.28	0.32	0.34	0.34
5.1	0.13	0.18	0.22	0.25	0.28	0.35	0.35	0.35
5.7	0.25	0.32	0.37	0.44	0.52	0.57	0.60	0.62
8.6	0.45	0.55	0.64	0.75	0.90	0.95	1.03	1.07
10.4	0.47	0.58	0.65	0.76	0.93	1.02	1.09	1.13
12.6	0.40	0.53	0.64	0.74	0.86	0.95	0.99	1.03
13.1	0.24	0.38	0.48	0.67	0.85	0.97	1.01	1.05

TABLE 10. The changes in moisture regain at 93% r.h. and 20°C.

Time min.	1	2	3	5	10	15	20	30
Strain %		dr% at various extensions						
2.3	-0.06	-0.02	0.02	0.04	0.07	0.08	0.08	0.08
2.9	0.06	0.12	0.15	0.18	0.21	0.22	0.22	0.25
5.8	0.10	0.14	0.20	0.27	0.32	0.35	0.35	0.34
8.3	0.13	0.26	0.35	0.47	0.61	0.70	0.73	0.73
9.2	0.22	0.35	0.44	0.55	0.67	0.72	0.75	0.76
10.8	0.21	0.33	0.42	0.52	0.65	0.69	0.70	0.73
12.5	0.36	0.54	0.71	0.94	1.16	1.30	1.37	1.40
14.0	0.49	0.69	0.87	0.99	1.30	1.45	1.57	1.58
15.4	0.67	0.92	1.10	1.35	1.44	1.66	1.73	1.78

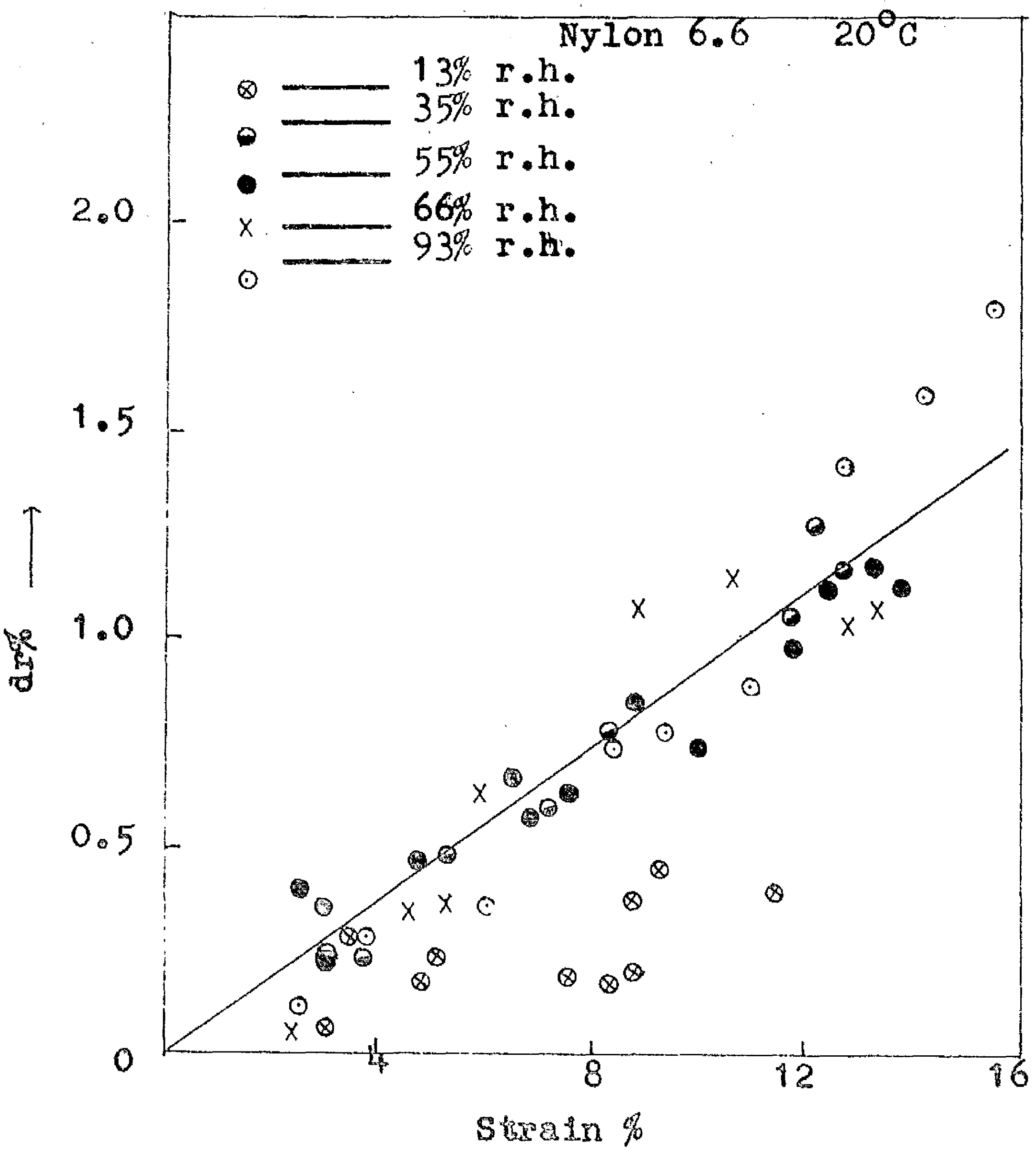
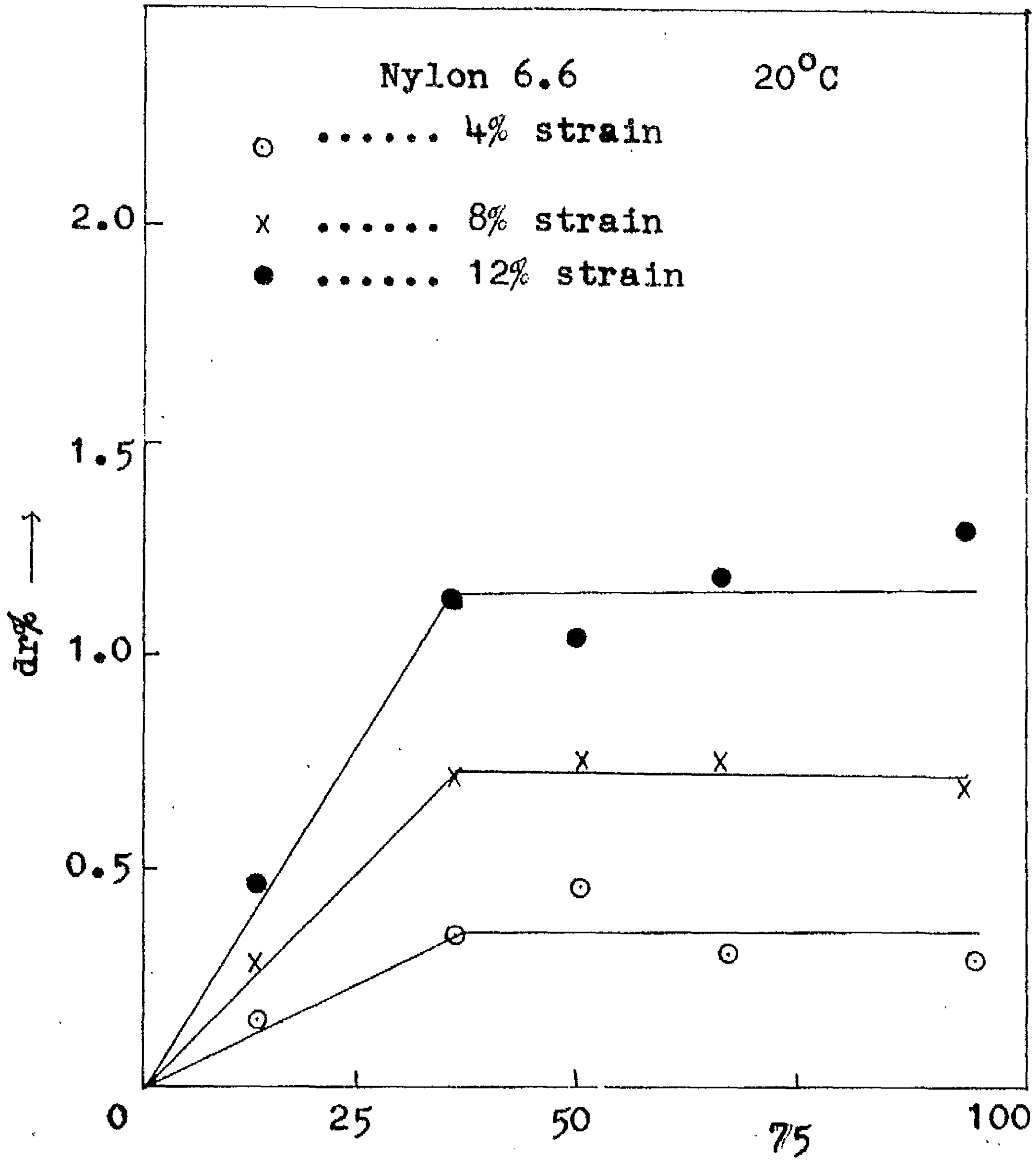


Fig.19. Percentage change in yarn mass(dr%) on applying tensile strain, for time of 30 minutes, after application of strain.



Relative humidity %

Fig. 20.Percentage change in yarn mass(dr%) on a applying tensile strain for time of 30 minutes after application of strain, at different humidities.

and it is presumed that at zero humidity there will be no change in regain.

The changes in length of nylon fibre with cyclic changes in humidity between 0 - 100% r.h. under a constant load of 2.4 g./denier are plotted in Fig. 21. Theoretically, the changes in regain with strain, and the changes in length with varying humidity, under a constant load, can be co-related by the use of the following thermodynamic equation:

$$l\,(\partial r/\partial l)_h = -\frac{1+r}{\rho_r\, V p_0}\,(\partial l/\partial h)_f\,(\partial f/\partial l)_h \;\ldots\ldots\; (6)$$

l = length (cm.)

r = fractional regain

h = relative humidity, expressed as a fraction

P_o = vapour pressure of water, at 20°C (in dynes/cm^2)

ρ_r = density of fibre at regain r (g/cm^3)

V = specific volume of aqueous vapour at relative humidity h. (cm^3/g)

f = stress (dynes/cm^2)

A ... Values from Speakman(1946)

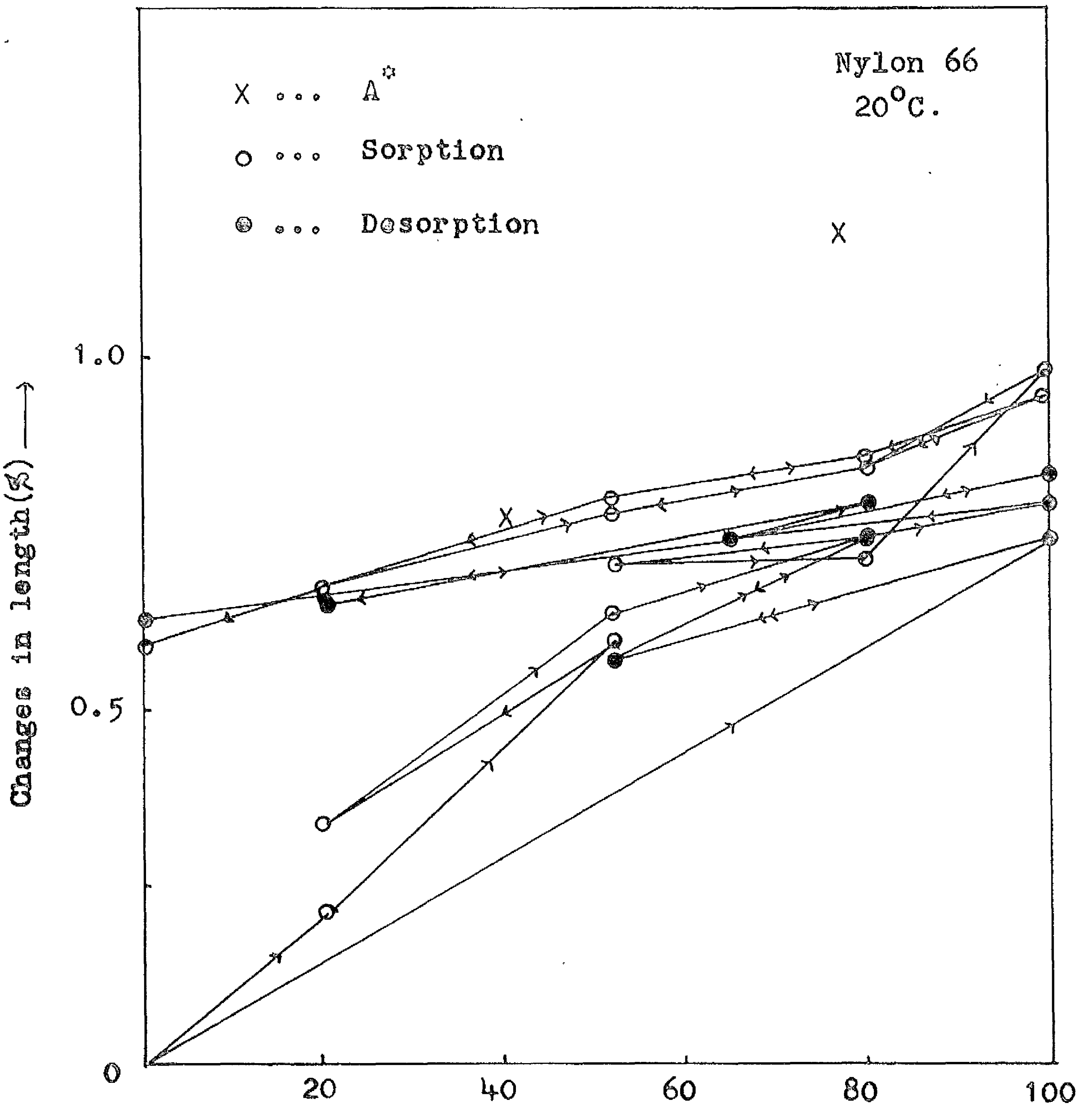


Fig. 21. Percentage change in length of nylon filament, with changes in humidity, under a constant load of 2.4 g/denier.

Suitable values of $(\partial r/\partial \ell)_h$, from Fig. 19 and $(\partial \ell/\partial h)_f$ from Fig. 21 were substituted in the above equation to determine the value of modulus. The values of various other quantities that appear in this equation are recorded in Table 11.

TABLE 11. The values of various quantities at 20°C used in the thermodynamic equation.

$(\partial r/\partial \ell)_h$ from Fig. 19.	r[76] at 65% r.h.	p_o[122] dynes/cm^2	ρ_r[76] g/cm^3	V[122] cm^3/g at 65% r.h.	$(\partial \ell/\partial h)_f$ from Fig. 21
0.093	0.042	2.33×10^4	1.14	8.9×10^4	0.0072

As laws of thermodynamics can be extended to true reversible systems, this would mean that the calculated value of modulus from this equation is a true reversible modulus. To verify the applicability of this equation, the calculated value was compared with the experimental value of reversible modulus,[120] obtained from the results of a cyclic loading test carried out at 65% r.h. and 20°C. The agreement between the calculated (3×10^{10}) and experimental values (5×10^{10}) dynes/cm^2 of reversible modulus is quite reasonable. However, in view of the fact that the calculated value is in a better agreement with the modulus of nylon (3.4 x 10^{10} dynes/cm^2) as read from Fig. 3 (stress-strain curve of nylon 66), one is tempted to suggest that this matter needs further consideration.

Table 12 shows a close agreement between the values for changes in regain as reported by Meredith and Hsu,[96] and the present values obtained from gravimetric methods.

SILK

Changes in regain with strain

The changes in regain with strain at three different humidities (35%, 66% and 90%) have been plotted in Fig. 22. The mean slope of the straight line drawn through the points for each humidity was calculated by the method of least squares. It is interesting to note that the changes in regain are insignificant at both low and high humidity.

TABLE 12. Changes in Regain with strain of nylon 66.

Strain %	A	B	C
5.0	0.85	0.50	0.47
10.0	1.15	1.00	0.93
15.0	1.40	1.50	1.40

A [96] = Results based on stress relaxation of nylon (Predicted values).

B [96] = Changes in regain calculated by use of the thermodynamic relation.

C = Results obtained from present gravimetric methods.

A* ... At 35% r.h. for time of 30 minutes after application of strain.

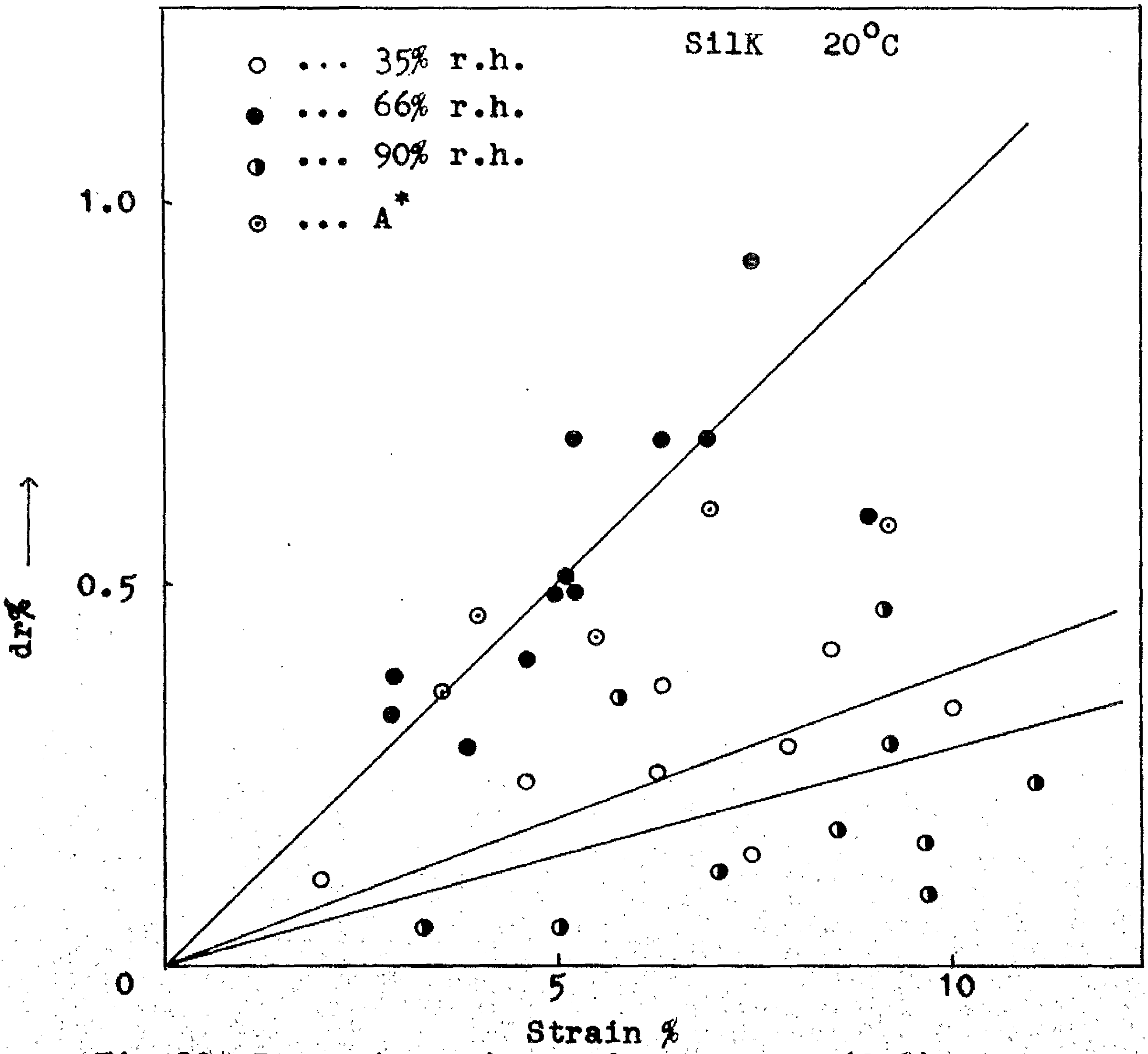


Fig.22. Percentage change in yarn mass(dr%) on applying tensile strain, for time of 24 hours after application of strain.

DISCUSSION

Nylon

One might expect that when a material is strained it might lose its sorbed contents like moisture by a 'squeezing' action. In fact the present results show that there is a definite increase in regain with strain. The changes in regain for nylon are even more significant when one compares them with those for viscose, which has a higher initial regain. To understand these results one may examine the Poisson's ratio of these materials. The increase in volume of bulk nylon 66, calculated from the known value of Poisson's ratio (0.4),[122] is found to be 1.6% for 8% extension: this agrees fairly well with the observed changes in regain.

Fig. 18 shows typical curves for changes in regain with time at various extensions. An initial decrease in regain at a low extension may be due to evaporation losses resulting from frictional heat effects.[93] However, considering the experimental accuracy, this is an insignificant decrease, and it does not show itself at higher extensions, where one finds appreciable changes in regain. It may be noted that there is a reasonable agreement between the period of completion of sorption relaxation [123] and that required for the attainment of a sensible equilibrium value for extra sorption (about 15 minutes).

In Fig. 19 all points are distributed around a mean linear slope and therefore, to some extent changes in regain with strain occur irrespective of surrounding humidity, which is contrary to what one would expect normally, i.e. a higher regain change at a higher humidity. The results imply that the same number of un-relaxed sites relax due to extra sorption at different humidities. At a given strain the population of un-relaxed sites will be greater at a low humidity (35%) than that at a higher humidity (93%). As availability of water vapour molecules partially governs the rate of diffusion, at 93% r.h. one would expect a sudden relaxation of stress due to extra sorption. At a lower humidity the probability of relaxation due to increase in non-specific interaction is relatively greater than that at a high humidity. Thus at 35% r.h. decrease in accessibility of the structure and the limited amount of available water vapour molecules restrict extra sorption on un-relaxed sites. The interplay of these factors strike at a balance in such a manner that the changes in regain are comparable at different humidities. In other words, the relative contribution to stress relaxation from non-specific interaction (thermal agitation) and extra sorption at un-relaxed sites, varies with relative humidity.

If a smooth curve were drawn through various points in Fig. 19 for a single r.h. (say 65%), it would consist of three distinct regions.

(1) Initial curvature convex to the strain axis.

(2) A fairly linear upward slope in the middle of the curve.

(3) A smooth bend (concave to the strain axis) towards the end of the curve.

It should be noted that this curve bears a close resemblance to the stress-strain curves for nylon 66,[124] and it is interesting to interpret it in the light of this resemblance.

The initial part of the curve signifies negligible change in moisture regain, and it may be said that 2-3% extension involves only an entropy change in overcoming the short range elastic forces responsible for restraining the entropy force of retraction.

The linear part shows a sudden rise in moisture regain and suggests changes in the internal energy of the system (which are related to interaction at peptide groups in nylon 66). Thus beyond 2-3% extension, deformation probably results in an increased single bond character of the N-C bond and this imparts greater rotational freedom to the chains resulting in partial or complete disappearance of mutual interaction at some peptide groups (resonating sites). The change in internal energy partly accounts for an increase in the free energy of the system or an increased affinity for moisture at the resonating sites. At the same time any increase in the flexibility of primary chains will favour a closer alignment of intervening polyethylenic segments and this may bring about the following changes, which would oppose an increase in sorption.

(1) An appreciable decrease in the accessibility of the structure to moisture.

(2) An increase in non-specific interaction along polyethylenic segments which might favour N-C double bond character or effectively increase the rate of relaxation of an un-relaxed site.

The final part of the above mentioned curve suggests two possibilities.

(1) There is no more increase in free or un-relaxed sites.

(2) There is an appreciable decrease in accessibility which overcomes any increase in affinity for moisture.

The second possibility seems to be more reasonable.

To summarise, the phenomenon of relaxation will depend on:

(1) Intensity of deformation.

(2) The increase in free energy of the polar groups.

(3) The accessibility of the structure.

(4) The availability of water vapour molecules in the surrounding atmosphere.

It is interesting to visualise the changes in regain, in terms of changes in free energy, at different humidities as follows.

It is reasonable to assume that a given amount of strain would result in an increase in the energy of the system, which will be distributed as a change in free energy and the entropy of the system. At a low humidity, one would expect a higher increase in free energy as compared with that at higher humidity, and the corresponding changes in entropy may be determined by the following thermodynamic equation.

$$dH = dF + TdS \quad \ldots\ldots\ldots \quad (8)$$

H = Enthalpy

F = Free energy.

S = Entropy

T = Absolute temperature.

Immediately after the start of relaxation, the free energy decreases gradually at a low humidity, due to limited availability of water molecules. Some of the free un-relaxed sites may relax due to thermal agitational forces. On the other hand, a large number of water molecules occupy the free un-relaxed sites at a higher humidity and result in a sudden reduction of free energy. It is possible that the entropy effects and the above-mentioned factors strike a balance and result in extra sorption independent of r.h. as observed in the present investigation.

Fig. 22 reveals that the changes in length with humidity are similar to those reported by Speakman,[76] and an insignificant effect of load on longitudinal swelling is in agreement with the findings of Treloar[92] on viscose filaments. The observed residual elongation at zero humidity, on the desorption cycle may be attributed to the combined effect of creep and inadequate desorption.

A close agreement with Hsu's results as shown in Table 12 is rather interesting and it offers an incentive for examining the co-ordination between phenomenon of relaxation and the mechanism of sorption. Changes in regain calculated thermodynamically from Changani's[96] work on the longitudinal swelling of nylon 66 with changes in humidity agree with the present results. This confirms the validity of thermodynamic equation and favours a possibility of application of the laws of thermodynamics to the systems comprising textile fibres.

Silk

For silk fibres, the changes in regain with strain depend on the surrounding humidity. At a low humidity (35%)

and a high humidity (90%), the change in regain is less than that at 65% r.h. It is suggested that at low humidity silk may have certain free sites, and the effect of strain may not depict itself in a proportional increase in regain. On the other hand at a high humidity, a possibility of free water hydrogen-bonded to sorbed water molecules may not be ruled out in the original state. On straining, a decrease in accessibility may decrease the amount of free water, and effectively little change in regain may occur as a result of strain. It is interesting to note that at 35% r.h. the initial increase in regain for 30 minutes after the completion of stretching, gradually diminishes over a longer period of 24 hours and reaches a new equilibrium value. This phenomenon is easily understood if one visualises that although there is an immediate effect of strain, which improves the affinity for sorption, the low availability of water vapour molecules in the surroundings does not favour the extra sorption, and the initially sorbed molecules are knocked out as a result of a time dependent phenomenon known as thermal agitation.

CHAPTER IV

GENERAL DISCUSSION

The present investigation has been a two-fold one, employing spectroscopic techniques and thermodynamic methods and the results of both are explicable in terms of an interaction mechanism, which is based on a fundamental postulate that the phenomenon of resonance plays an important part in determining the molecular interaction in polyamides like nylon 66. At this stage it is logical to extend these findings to various observed phenomena in nylon 66, with particular relevance to the present investigation.

To deal with various physical properties it is essential to understand the role of water in polyamides. Tsuboi[74] suggested that water goes on to CO groups, and Wood[51] has concluded from quantitative analysis that water, unlike more drastic polar reagents, e.g. phenol and formic acid does not change the intensity of the original NH band at 3300 cm^{-1} and no new band appears at a higher frequency. One may ask at this stage, if water sorption results in a definite increase in the total energy of the system, how this increase is assimilated in the system as a whole. The absence of any change in the infra-red vibration spectra due to sorption, and a possibility of bringing about such spectral changes with disaggregating reagents (used in the present investigation) suggests that the difference between the action of polar reagents and water may be purely due to magnitude of the energy change in the system. In other words water sorption is not a sufficiently energetic interaction to bring about changes in the vibration modes of the system. At this stage, one is left with only one possibility, i.e. sorption brings about changes in the rotational energy levels of the system.

SETTING OF NYLON

Earlier it was shown that polar reagents have no setting effect on nylon, although they produce an annealing effect, which is also noticed when nylon is set with steam at 140°C.[125] In view of the above postulate, it is suggested that the same macroscopic effect on crystallites results from two different mechanisms. In the case of the ion-dipole interaction, the vibration modes of the system are affected, in the polycrystalline regions, and there may be an accompanying increase in rotational freedom of the chains giving rise to the observed annealing of nylon. On the other hand the presence of water molecules in steam-setting mainly affects the rotational modes of the system, and very high thermal agitation facilitates a perfect alignment of the chains in new positions of minimum free energy. The effect of high temperature (140°C) may show itself in the vibration modes of the system to some extent, but temperature alone does not bring about the desirable setting of nylon. It is difficult to conclude whether rotations are mainly responsible for the setting effect at this stage but it seems probable that weakening of intermolecular interaction alone may not be sufficient to stabilise the structure in the desired state.

INFLUENCE OF MOISTURE ON VISCOELASTIC PROPERTIES OF NYLON 66

Earlier it was shown that changes in regain are in agreement with Hsu's predicted values,[96] which were based on Meredith's[126] theory concerning the effect of moisture on rigidity, and it would appear that the present results support this theory. However this matter requires further consideration for the following reasons.

1. The suggested presence of free NH groups in the non-crystalline regions of nylon[126] is not acceptable in view of the spectral evidence.

It is well known that the position of the NH stretching band and of the amide I band are influenced by hydrogen bonding and any appreciable proportion of free NH groups would make themselves obvious in the infra-red absorption spectrum. Trifan and Terenzi[127] estimated that no more than one per cent (1%) free NH groups is present in a series of nylons including even-odd members. Miyake[125] has investigated different types of nylons, and concluded from quantitative estimate of optical densities that the amide groups form hydrogen bonds almost completely, irrespective of the number of methylene groups.

2. The contribution to relaxation due to thermal agitation is same at different humidities,[129] but this is doubtful in view of the interpretation of the present results.

3. The assessment of the relative contributions of the two superimposed stress relaxation mechanisms[129] seems to have been oversimplified. Though both mechanisms may be unidirectional in isolated systems, when superimposed their interdependence and a possible opposition to each other cannot be ruled out. Thus an impulse due to thermal agitation may lead to a simultaneous relaxation of an un-relaxed site and breakdown of a weak interaction between sorbed water and polar site.

It may be recalled that Meredith suggested the presence of free NH groups in order to explain the sigmoid shape of the curves for changes in relative rigidity modulus with changes in regain, and it remains to be seen how such phenomena can be explained otherwise.

Woodward et al[129] have recently reported that the β loss modulus peak disappears when nylon is completely dried, and it is evident from the nature of these changes that small additions of water (0.9%) can bring about significant changes in the α' loss modulus peak and increase the modulus(e') at $-100^\circ C$ as indicated by a decrease in the height of γ loss modulus peak. The increase in modulus (e') at $-100^\circ C$ has been confirmed with the help of N.M.R. studies. It is suggested that if the presence of water may bring about a closer packing of methylene groups, and as a result of this interaction, the contribution of CH_2 groups to γ peak decreases and a new peak appears at high temperature. Thus the effect of initial regain may not be detected by the measurement of rigidity, but can be easily detected in terms of sensitive structural parameters like the loss modulus with the help of precision techniques. It may be further argued that closer packing of methylene groups may oppose the decrease in rigidity modulus resulting from increased rotational freedom of polar groups, in the initial stages of moisture sorption.

VISCOELASTIC DEFORMATION IN POLYMERS.

In view of the above postulates attention is drawn to some basic concepts about viscoelastic deformation in polymers.

1. It has been customary to say that on straining,

secondary bonds are broken and as a consequence certain phenomena are observed. Actually it would be appropriate to say that straining brings about certain changes in the primary chains and as a consequence secondary interactions are affected. In other words primary chains serve as essential transmission lines between the source of energy and the affected secondary interactions. Since specific secondary interactions depend largely upon the electron density at the polar groups, it is difficult to conceive changes in secondary interactions without any changes in the primary chains.

2. The intensity of interaction between two peptide groups depends on the character of N-C bond: this interaction will be more when N-C enjoys a double bond character. The double bond character of the N-C bond imparts an intrinsic inflexibility to the primary chains.

3. Mutual displacement of polar interaction sites,[71] along the axis of the strain occupies an a priori role in various hypotheses presented by different authors. However if a hypothetical system comprising two molecular chains with ends gripped in suitable jaws, which allow axial rotation for the chains, is visualised as being subjected to longitudinal deformation, one finds it difficult to explain the effect of strain on polar sites in terms of hydrogen bonding. The difficulty is

appreciated if one realises that this hypothetical system does not allow the misalignment of the CO and NH groups in neighbouring chains in spite of the fact that the vectorial distance between any two points along the two main chains may increase due to induced tensile deformation. Assuming that this system be strained, it is not easy to visualise how it would relax if left at zero humidity, unless the long polyethylenic segments intervening between the polar groups, play a part in various physical phenomena. It is interesting to note that a hypothetical approach to this system can be formulated as follows.

Assume that the system has a number of permissible rotational energy levels and that in the original state, on an average, it is confined to low energy levels. On straining, the original equilibrium between different energy states is upset, and on an average the system spends more time in high rotational energy levels, and since the polar groups and the methylene groups have some mutual inductive effects they would always be in equilibrium as regards electron density along the polyethylenic segments. The increase in rotational energy may or may not be sufficient to affect the intensity of polar interaction, and bring about changes in the vibrational modes of the polar group. The completion of straining is followed by a time-dependent phenomenon known as stress relaxation: the rate of relaxation at zero humidity depending largely on the initial increase in the energy of the system. The relaxation of the stress takes place because of a closer interaction of polyethylenic segments due to increased rotational freedom of the chains, which may decrease the inductive effect of methylene groups and in turn affect the electron density at the polar sites. This intrinsically opposes the induced stress by favouring interchain interaction at the polar group. To summarise, it has been suggested that individual chains can play an important part in relaxation mechanism, by virtue of their long polyethylenic segments, an essential part of the structure hitherto ignored.

A tentative acceptance of the above views leads to the following possible interpretation of viscoelastic properties of nylon 66.

1. A close examination of Kubie's results reveals that the effect of water sorption from (0-20% r.h.) on the loss modulus (α' peak) at 20°C is comparable to that of raising the temperature to 125°C, at zero humidity.[130] Though the magnitude is comparable, the mechanism involved might be different, since the effect of temperature on nylon is well depicted in the shift of NH vibration band to a higher frequency,[26] whilst moisture has no such effect. The two mechanisms differ in the degree of interaction with polar groups. Whereas interaction due to water molecules results in changes in the rotational energy of

polar groups and reduction of the Van der Waals attraction force between polyethylenic segments, temperature mainly affects the polar interactions. Though the polyethylenic segments may rotate more freely at high temperature, they are probably well within the effective Van der Waals radii; this view finds some support from the X-ray diffraction study of nylon,[13] which reveals that at 150°C, the 010 reflection merges with the 100 reflection.

Regain varies with strain irrespective of the surrounding humidity, which implies some mechanism responsible for such a balanced sorption. While dealing with hypothetical system at zero humidity it was clearly shown that polyethylenic segments may play an important part in relaxation mechanism and it is now suggested that accessibility of the structure, which controls sorption depends largely on the interaction of these segments. It is conceivable that a close co-operation between polar groups and polyethylenic segments may result in a balanced extra sorption with strain.

The role of extra sorption resulting from an induced deformation is easily understood as follows. It is assumed that there are three (low = L, medium = M and high = H) possible rotational levels in the fibre-water system under consideration and that the populations of these states are l, m, and h. In the original fibre-water system,

$$l > m > h,$$

at any instant and they are in an equilibrium state. On straining there is a sudden change in this equilibrium in such a way that the new population is in the following order,

$$h > m > l.$$

It was shown earlier that the effect of water is only to increase the rotational energy of the system. Therefore in the strained state, due to the high free energy of the polar sites, water is sorbed in the system, and, since it favours an increased population in the medium(M) energy level, its presence increases the possibility of relaxation of highly excited H levels, producing a new population equilibrium in which,

$$m > l \text{ or } h.$$

STRESS RELAXATION OF VARIOUS FIBRES IN AQUEOUS MEDIUM

It is interesting to review the stress relaxation behaviour of various fibres in distilled water as reported by Lemiszka and Whitwell.[132] Those authors have suggested that scission of the specific and non-specific interchain interactions is responsible for the observed relaxation of stress. Keeping in view the consistent role of water in the stress relaxation of various fibres and rubbers, one is tempted to suggest that some basic structural features of these high polymers are involved in the phenomenon of stress relaxation. However, the differences in the availability of interchain interactions in various fibres, and the observed disparity in the behaviour of vulcanised and non-crosslinked rubbers like polyisobutylene, reveal some ambiguity in the mechanism proposed by the above authors. It is suggested that the stress relaxation in aqueous medium is due to the interaction of water with the rotational energy levels of the polymer chain molecules.

APPENDIX I

The changes in length of silk fibres with cyclic changes in humidity (0-100% r.h.), under a constant load of 1g/denier were measured. The results are shown in Fig. 23. It is interesting to note that there is a striking similarity between a large increase in length of silk fibres, with a change in humidity from 50% to 80% r.h., and the results of Stress relaxation of silk in an atmosphere of fluctuating humidity.

However, a possibility of mechanical creep need not be ruled out and it is suggested that this matter deserves further investigation, preferably on mechanically conditioned fibres.

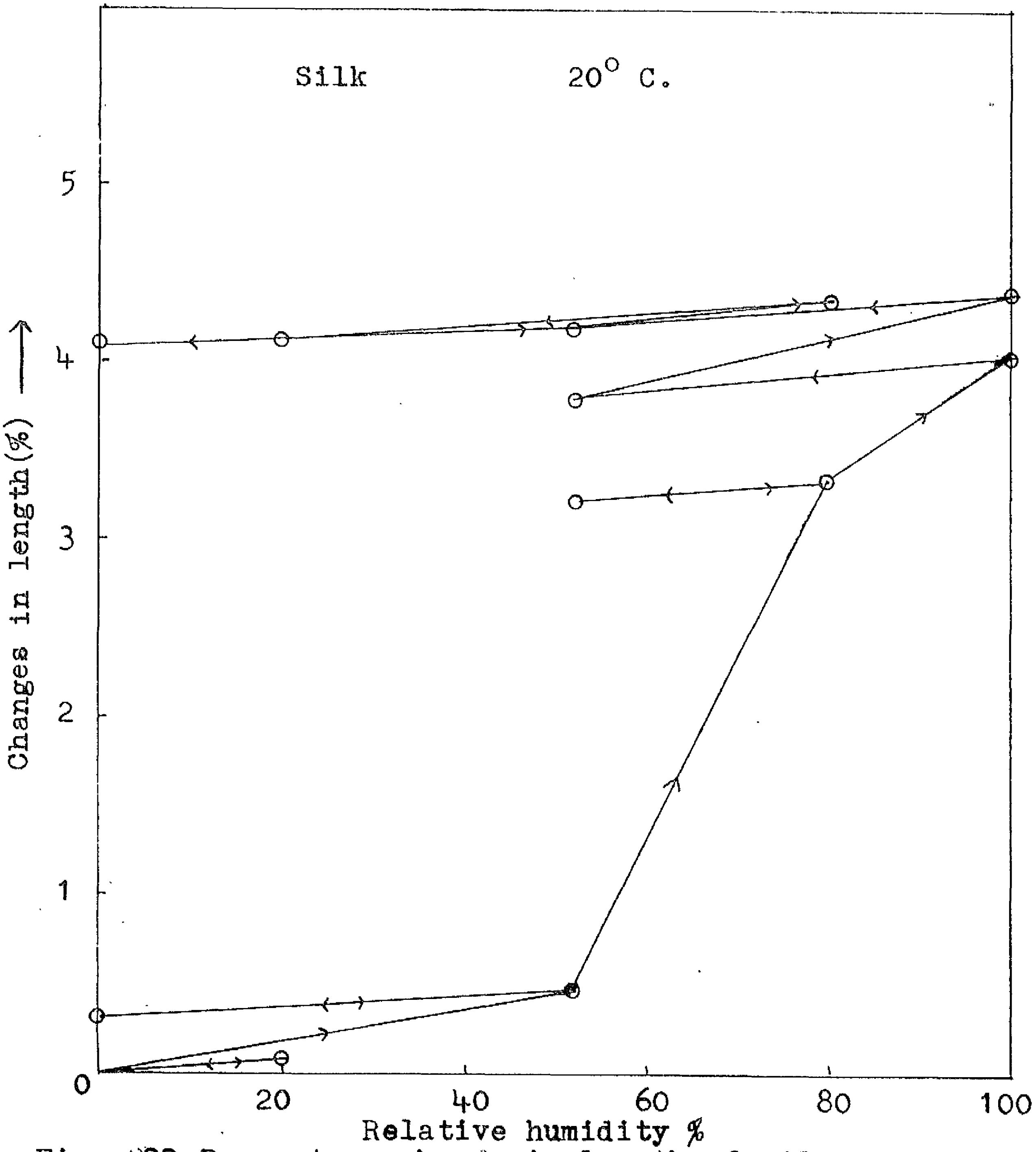


Fig. 23. Percentage change in length of silk yarn, with changes in humidity, under a constant load of 1.0 g/denier.

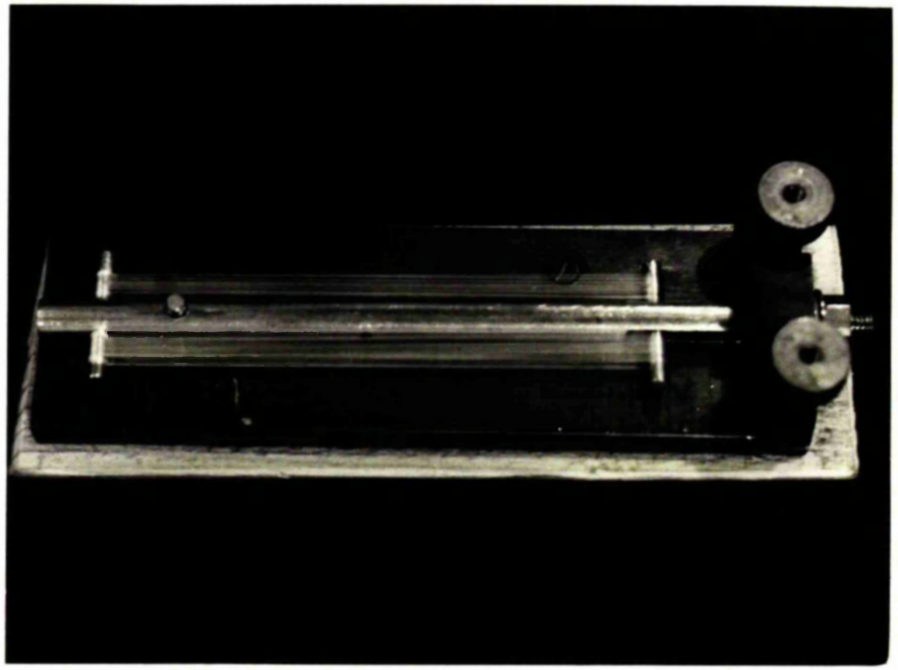


Plate.1. The specimen holder and the brass platform.

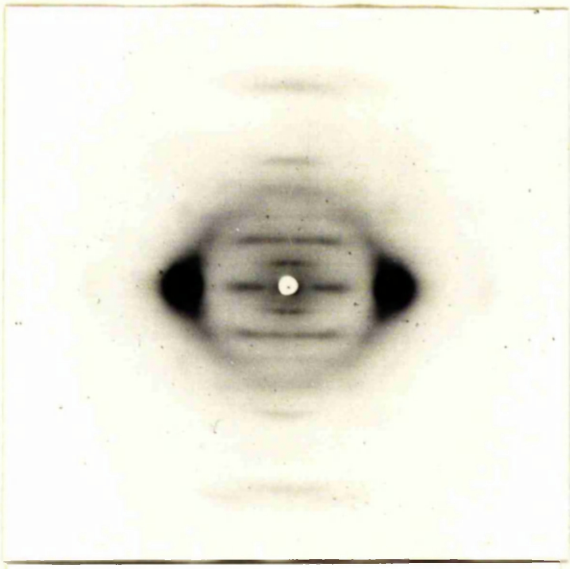


Plate.2. Nylon 66.

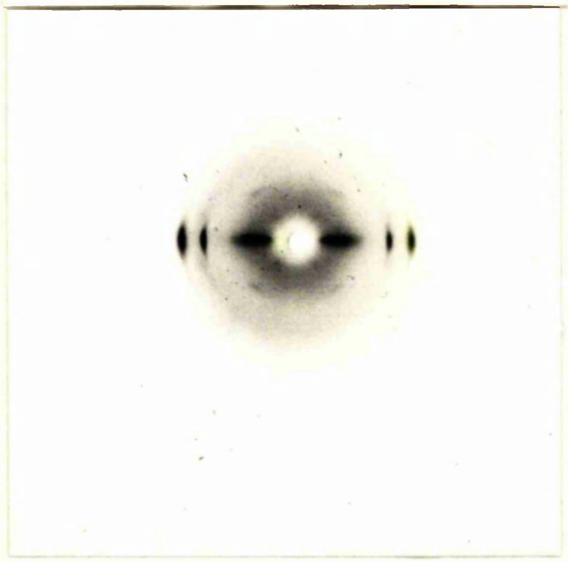


Plate.3. Nylon 66 treated with magnesium perchlorate at 100 °C, 20 h.

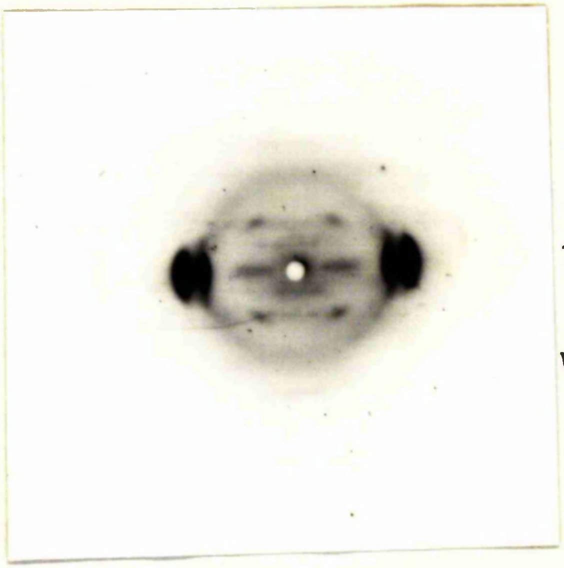


Plate.4. Nylon 66 treated with lithium bromide at 100 °C, 24 h. and subsequently washed with water.

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