A study of the configurational properties of high polymers in solution and in bulk

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A STUDY OF THE CONFIGURATIONAL

PROPERTIES OF HIGH POLYMERS IN SOLUTION

AND IN BULK.

by

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Submitted for the Degree of Doctor of Philosophy

of Loughborough University of Technology

March 1971

Department of Chemistry
All the work presented in this thesis has been carried out by the author, except where otherwise acknowledged, and has not previously been presented for a degree at this University or any other institution.
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ABSTRACT

The polymerisation of the cyclic ethers oxacyclobutane and tetrahydrofuran to poly(trimethylene oxide) and poly(tetramethylene oxide) has been achieved using p-chlorophenyldiazonium hexafluorophosphate catalyst. Their unperturbed dimensions and dipole moments have been investigated.

Single theta solvents, cyclohexane at 25.0°C for poly(trimethylene oxide) and 1-hexene at 44.8°C for poly(tetramethylene oxide) were found, and from viscometry and light scattering the unperturbed dimensions of the two polymers were determined. As an alternative, unperturbed dimensions for poly(trimethylene oxide), from intrinsic viscosities in non-ideal solvents, using the Stockmayer-Fixman and Kurata-Stockmayer extrapolation techniques, were obtained. Average values of the unperturbed characteristic ratio $r_0^2/n_1^2$ were 3.8 and 4.9 for poly(trimethylene oxide) and poly(tetramethylene oxide) respectively.

Dipole moments at theta conditions agree with bulk measurements and with theoretical predictions. Values of $\mu^2/\text{nm}^2$ for poly(trimethylene oxide) were $0.41 \pm 0.05$ at theta conditions, $0.42 - 0.50$ for bulk polymer and for poly(tetramethylene oxide) $0.66 \pm 0.05$ and $0.53 - 0.64$ respectively. Theoretical predictions are $0.47$ and $0.50 - 0.60$ respectively. Agreement between bulk and theta values suggest that the bulk sample reflects unperturbed chain statistics.

Poly(tetramethylene oxide) has a strong preference for one configuration as evidenced by its single stable crystalline form. Poly(trimethylene oxide) has three possible configurations of comparable low energy and varying conditions can cause a significant difference in the population of the configurations. The $\mu^2/\text{nm}^2$ value of $0.77 \pm 0.07$ for poly(trimethylene oxide) in a non-ideal solvent is explained on these grounds.
Unperturbed chain dimensions of poly(4-chlorostyrene) and poly(3-chlorostyrene) were obtained, the former from experiment at theta conditions and the latter from a graphical correlation of chain expansion, \( \theta \), to second virial coefficient, deduced from data obtained from poly(trimethylene oxide), poly(tetramethylene oxide) and poly(4-chlorostyrene). The unperturbed chain dimension sequence shown by polystyrene and the substituted polystyrenes is discussed in terms of their crystalline structure and in connection with their low temperature dielectric and mechanical relaxations.
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CHAPTER 1
INTRODUCTION

1.1 Outline and objectives of study

About forty years have passed since it was recognised that some important materials, either occurring in nature or synthesised in the laboratory, consist of very large molecules. During that time the field of macromolecular chemistry has grown at a spectacular rate.

The simplest of all macromolecules are the synthetic linear organic polymers, which consist of long unbranched chains of one, two or three different kinds of subunits or monomers. More complex polymers arise when non linear structures are formed, of which the simplest of the many possibilities are branched polymers. In such structures the longest linear sequence provides the back bone of the polymer. If the side chain is composed of different monomers from those making up the back bone chain then the result is termed a graft copolymer. Two other types of non linear polymer are the crossed-linked, and space network polymers, in which the polymer structures have a far more intricate pattern. The work that follows deals entirely with the first group described above, that is, synthetic linear polymers, with relatively simple structures.

In the practical utilisation of synthetic high polymers molecular chain length is the most critical factor. The mechanical strength of a rubber, plastic or fibrous polymer generally falls off below a molecular weight of about 25,000, and at the other end of the scale for very high molecular weights a limit is reached where for any further chain extension there is not the corresponding increase of mechanical properties. If the sample is polydisperse with respect to molecular weight it is most easily characterised by the viscosity average molecular weight. Other molecular weight averages can provide a useful indication of quality control since samples prepared by given procedure should have a fixed molecular
weight distribution function. However the molecular weight distribution will be of less importance to the mechanical characteristics of a bulk polymer since it does not affect the properties to the same extent, although that is not to say that the presence of very low molecular weight material (e.g. monomer) cannot sometimes be very deleterious.

Polydispersity, molecular size and shape are all properties of the polymer chain that can be obtained in solution. Indeed it is impossible to obtain direct information on molecular size in any other way as polymer molecules cannot be vaporised to a measurable extent. These studies are carried out at a high dilution so that the property observed is that of the isolated molecule. Solution properties cannot be expected to relate directly to phenomena of the high polymer in bulk, although correlations between the two will exist in some form.

The 'spatial' configurations of linear macromolecules, natural or synthetic, are reflected in their average dimensions, either in dilute solution or in the amorphous state. Other properties of a chain molecule which reflect its configuration include its mean square dipole moment, its optical anisotropy and its spectral properties. Using statistical mechanics, properties of chain molecules can be evaluated on a theoretical basis, by averaging over all possible configurations. These will arise from continuously varying all angles of rotation about the bonds of the structure, and also by varying bond angles and bond lengths to the extents permitted by the structure. For a long chain this is a formidable task, but can be considerably abbreviated by using the rotational isomeric state model, whereby only discrete values of each rotation angle are considered. This provides a method of determining which of the immense number of possible configurations a long polymer chain may adopt, are statistically probable.

In an endeavour to predict the polymer chain conformation of macromolecules in the bulk amorphous polymer, the author has studied chain dimensions and dipole moments via dilute solution techniques and
then determined dipole moments of the same polymers in bulk amorphous state.

All physical properties of matter are a reflection of molecular structure. The particular properties discussed so far were chosen because their relation to molecular structure is a direct one. Other properties which are also easily measured, such as density, are less directly linked to molecular structure and are therefore less easily adapted for structural information. Secondary physical properties of this kind, especially such properties as tensile strength and flexibility are naturally of immense importance when adapting a macromolecule to commercial use.

1.2 Polymer chains in bulk

All high molecular weight polymers are solids at room temperature. They can be divided into two classes a) wholly amorphous and b) partly crystalline. The experimental work here is only concerned with the amorphous state.

Intramolecular forces experienced by a molecule impose a definite pattern or arrangement of the chemical bonds. The existence of these constraints, as previously mentioned, limits the configuration of a molecule by restricting bond lengths and bond angles to certain values.

Chain conformational information can be obtained from a variety of sources. The rubber-like elasticity of an amorphous polymer for instance can be used for this purpose. The major part of rubber elasticity effects due to the entropy of elasticity are insensitive to chain structure. The minor part, however, concerned with the internal energy changes on stretching, are structure sensitive. The heat expelled in the stretching of a rubber consists of the difference between the work done in deforming the sample and the increase in its internal energy. Therefore, via differences in the energy levels of rotational isomeric states of the chain molecule, configurational information can be obtained. It is usual to carry out measurements of stress as a function of temperature at fixed sample length.
Some fifty years ago it became generally realised that the determination of the electric dipole moments of molecules should prove a valuable means of studying molecular structural problems. Within the last twenty years the application of wave mechanics has led to a greatly improved understanding of the factors giving rise to molecular asymmetry in molecules and as a result the use of dipole moment determination has become even more important.

Electrical properties of the molecule comprise a combination of the electronic, atomic, ionic and orientational polarizations. In the absence of impurities the ionic term is normally trivial. The application of an electric field will cause the dipole to partially orientate, the degree of orientation being a function of the frequency of the applied field. It is also limited by the rate with which the dipoles can undergo rotation. This rate can be expressed in terms of a relaxation time which, in its turn, is dependent on the thermal motions of the molecules tending to oppose the orientation of the dipole. Consequently dipole orientation will be both frequency and temperature dependent. However, even in the absence of relaxation processes, as in the ideal gas, the Debye relation $\frac{\varepsilon^2}{3kT}$ still shows a temperature dependence. The dielectric properties of the polymer, provided it is polar, are therefore closely related to the fundamental motions of the polymer structure as well as to the chain configuration.

1.3 Polymer chains in solution

Interaction between amorphous polymers and liquids is usually slow, taking place in two stages. Firstly the polymer absorbs the solvent to give a gel and this slowly disperses to give a solution.

In a good solvent the free energy of interaction between polymer segments and solvent will be more favourable than that between polymer segments themselves. This is a thermodynamically more favourable situation and the polymer chain will tend to an expanded or perturbed state. In a poor solvent the reverse is true and the interaction
between polymer segments opposes the entropy of mixing effect. As a result the polymer chain contracts, becomes highly coiled and may adopt its unperturbed state.

There is no necessary correlation between the 'goodness' of a solvent and the ease of dissolution of the polymer. This is probably because factors other than the thermodynamics of the polymer solution are present such as diffusion. For instance, poly (methyl methacrylate) dissolves quite slowly in benzene, but much more rapidly in chloroform, despite the fact that they are both good solvents.

Polymer solutions are also typically viscous which is another factor likely to cause the process of solution to be slow. It will also restrict the concentration levels at which measurements (say viscosity) can be performed by normal techniques. At high concentrations, the polymer chains will become entangled and the segmental motion of one chain will not be independent of another. It is therefore usual for polymer properties to be studied in dilute solution (1 - 2% by weight of polymer), where the polymer molecules are well separated from one another.

Whereas for low molecular weight substances the classical techniques of freezing point depression and elevation of boiling point are used, as molecular weight increases to the macromolecular range these experimental methods become insensitive and other effects become more prominent. This led to such newer techniques as viscometry, ultracentrifugal sedimentation, and light scattering being used for molecular weight determinations. Light scattering theory is applicable to both large and small molecules but since molecular weights of small molecules are more easily measured from their colligative properties the light scattering method was not developed until the characterisation of high polymers warranted it. Similarly ultracentrifugal sedimentation principles hold for molecules of all sizes but for small molecules it is
both less convenient and less precise than classical methods.

The determination of molecular weights of polymeric materials presents, in general, two problems not normally encountered with low molecular weight substances. The first problem arises because polymer samples contain molecules with a range of molecular weights. Secondly, a feature which arises whenever the physical properties of polymer solutions are studied, the concentration dependence of these properties is much more pronounced and non-ideal than is the case with low molecular weight substances.

Osmotic pressure determinations can give a rapid measure of molecular weight over a large range but this method becomes impracticable if the molecular weight becomes too large, (>1,000,000), since graphical procedures become inaccurate and intercepts too small. When the relative difference in size of polymer and solvent molecules is small additional problems are imposed on the semi permeable membrane.

A second phenomena suitable for macromolecular characterisation is the frictional resistance of the medium to the flow of the macromolecule. A large chain molecule may change its shape quite considerably by rotation about the bonds connecting neighbouring atoms. The energy differences for the transition from one conformation to another are not large so that even small effects due to solvent-solute interaction could alter the conformation of the polymer chain. The expansion or contraction of the chain may be studied by following changes in the frictional properties of the solution. In addition, the characteristic dimensions of a polymer may be estimated from the angular distribution of scattered light which therefore gives us two independent methods of estimating the same quantities. Viscometry is used quite readily as a direct approach for calculating unperturbed dimensions, the same information from light scattering however is not easily obtained and consequently the literature does not readily reveal light scattering.
data at theta conditions. Unperturbed dimensions can also be found from viscosity data in good solvents via the treatments of Flory - Fox - Schaefgen (1), Kurata - Stockmayer (2), and Stockmayer - Fixman (3).

This investigation uses both the direct and indirect approaches for calculating unperturbed polymer dimensions, viscometry and light scattering techniques at theta conditions and also theoretical treatments as listed above.

In addition the proximity of polymer molecules in solution can lead to inter and intramolecular dipole interactions, as must occur in the bulk state. If, however the chains are separated from one another by nonpolar molecules intermolecular interaction should not arise. Consequently solution dipole moments were measured at high dilution and a study was made of the effects in both good and bad solvents. The question arises, as will be discussed later, as to whether the dipole moment of molecules with chain dipoles is affected by chain configuration.

1.4 Requirements of model polymer systems

The investigation required a linear high polymer which was dielectrically active. A linear polymer was chosen because of the additional problem arising with polar side groups as to exactly defining the dipole orientation. A polymer with a main dipole is therefore required. Poly (ethers) with their carbon oxygen and oxygen carbon bonds are ideal for this purpose. The oxygen and carbon valence angles are 110°, which allow the ether molecule to form a zigzag chain if other constraints permit. However it is not all poly (ethers) that exhibit large dipole moments. Poly (2,6 - dimethyl p-phenylene oxide) for instance has a dipole parallel to the main chain (4) which will be partially compensated for by the electron donating effect of the alkyl substituents. The overall dipole moment of the polymer is therefore small and molecular weight dependent. Poly (alkane oxides) however with the general formula \[ [(\text{CH}_2)_n \text{O}]_x \] show a dipole moment per monomer unit,
perpendicular to the axis of the chain, which is largely independent of molecular weight. This group of polymers were therefore chosen for the investigation and throughout the text the following abbreviations have been used for the various members of the series.

- poly (methylene oxide) P,M,O
- poly (ethylene oxide) P,E,O.
- poly (trimethylene oxide) P,Tri,M,O.
- poly (tetramethylene oxide) P,Tetra,M,O.
- poly (pentamethylene oxide) P,Penta,M,O.
- poly (hexamethylene oxide) P,Hexa,M,O.

A further study of chain dimensions was made on two substituted poly (styrenes) namely poly (3-chlorostyrene) and poly (4-chlorostyrene) in order to assess possible correlations of conformations with low temperature loss peaks in these systems.

1.5 Configurational studies of polymer chains

There are several methods available for chain configurational studies such as viscometry, light scattering, optical anisotropy, spectral determinations and dipole moment determinations. The present investigation has utilized some of these techniques and has particularly been concerned with the methods of viscometry, light scattering and dipole moments.

The poly (ethers) lend themselves very readily to this form of analysis. Dipole moments of the first two members of this series P,M,O and P,E,O have been studied fairly extensively and the results have been reviewed by McCrum et al (5). The work described here has involved bulk dipole moment measurements on the next two members of the series P,Tri,M,O and P,Tetra,M,O. Wetton and Williams (6) have studied P,Tetra,M,O and the work here extends some original data to
some well characterised samples. It is only within the last year that there has been any data at all available for P.Tri.M.O., and this work, conducted in these laboratories by Wetton and Fulcher (7), has involved a molecular relaxation study of the polymer via dielectric studies.

Flory and Mark (8,9) have calculated for P.E.O. the theoretical mean square chain dimensions and mean square dipole moments from appropriate statistical weights and geometrical parameters assigned by them to the chain structure. These compare very favourably with the experimental dipole moments obtained by Marchal and Benoit (10,11), Uchida et al (12) and Kotera et al (13). Beech and Booth (14) have calculated unperturbed dimensions of P.E.O. from intrinsic viscosities in good solvents and also from viscosities at theta conditions. Prior to this unperturbed dimensions of P.E.O. (15 - 18) had come entirely from data in good solvents. Similarly the mean dimensions and dipole moments have been calculated for P.Tetra.M.O. and P.Tri.M.O. by Mark (19,20). Comparatively few studies have been made on the dimensions of P.Tetra.M.O. in dilute solution (21,22,23) and of these only Evans and Huglin (22) have determined the unperturbed dimensions in a single theta solvent. There has been no reported data on the solution dipole moment of P.Tetra.M.O. at theta conditions. The only reported solution work on P.Tri.M.O. to date is by Yamamoto and Fujita (24) where they calculate the unperturbed dimensions by extrapolation of data in a good solvent. The polymer they have produced is only of low molecular weight (10,000).

P.Tri.M.O. and P.Tetra.M.O. were used for a detailed examination and subsequent comparison of dimensions and dipole moments in both good and theta solvents. The work required the finding of a theta solvent for each polymer, that was not only a single solvent but non-polar, as necessitated by dipole moment measurements.

Many authors have reported on the solution properties of
poly (styrene) and its derivatives. Poly (4-chlorostyrene) is no exception to this and work has been presented on the dimensions of this polymer by several workers (25-29). Poly (3-chlorostyrene) has received far less attention than its para isomer and as a result the information available on its dimensions is less abundant (30). The dimensions of these two polymers provides an interesting comparison due to the effect of the position of the chlorine substituent. As will be seen in the discussion, the crystal structure also reflects their differences. Results have been looked at in this light and used to discuss differences in their dynamic mechanical behaviour in the liquid helium range.
2.1 Spatial Configurations of Flexible Chain Molecules

2.1.1 Average dimensions, Analytical expressions

Polymeric substances can be divided into two groups according to whether their molecules are predominantly rigid or flexible. There are polymers which do not fit into either category as there are those which pass from the first classification to the second as the temperature is raised. We are only concerned with synthetic linear polymers whose molecules possess a great deal of flexibility.

Alternative dimensions used to describe the spatial extension of a flexible polymer molecule are the end to end distance, \( r \), and the radius of gyration, \( s \).

The end to end distance is normally measured as the root-mean-square average of the separation between the two ends of the polymer chain. If \( r \) is the distance between the ends

\[
\bar{r} = \left( \frac{1}{n} \sum_{i=1}^{n} r_i^2 \right)^{\frac{1}{2}}
\]

with the averaging being taken over all possible configurations. Theoretically, the distance is most easily calculated in terms of vectors. If \( \mathbf{r} \) is the vector drawn from one end of the polymer chain to the other then

\[
\left( \bar{r} \right)^{\frac{1}{2}} = \left( \mathbf{r} \cdot \mathbf{r} \right)^{\frac{1}{2}}
\]

To define the radius of gyration, consider the polymer chain to be made up of elements of mass \( m_i \) at a distance \( s_i \) from the centre of mass. The radius of gyration, \( s \), for a given configuration is the square root of the weight average of \( s_i^2 \) for all the mass elements.
For flexible chains, $s$ depends on the configuration and the root-mean-square average over all configurations is

$$s^2 = \frac{\sum m_i s_i^2}{\sum m_i}$$

Radius of gyration, for the Gaussian chains under consideration, is related to end to end distance by an equation derived by Zimm and Stockmayer (31) and Debye (32).

$$\bar{s}^2 = \frac{\bar{r}^2}{6} \quad ... (2.1)$$

The following discussion is phrased in terms of $r$, the end to end distance but similar arguments apply to $s_a$, provided equation (2.1) holds.

Initially we shall consider the hypothetical unrestricted polymer chain and then the effect of restricted rotation.

Consider a polymer chain of $n$ bonds of identical length $l$. Initially we are assuming, hypothetically, that the rotation angle $\phi$ is unrestricted and the bond angle $\theta$ is freely jointed, hence $\phi$ and $\theta$ can take any value.

The end to end vector $\bar{r}$ may be expressed as the sum of the $n$ bond vectors

$$\bar{r} = \sum_{i=1}^{n} \frac{\bar{1}}{i}$$
Then

\[ r^2 = \mathbf{r} \cdot \mathbf{r} = \sum_{i=1}^{n} l_i \cdot \sum_{j=1}^{n} l_j \]

and the average square of \( r \) may be written

\[ \overline{r^2} = \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{l_i \cdot l_j}{n^2} \]

For the freely jointed chain, the average projection of any bond vector on any other would then always be zero

\[ \frac{l_i \cdot l_j}{n} = l_i \cdot l_j \cos \theta = 0 \]

hence all terms of the summation with \( i \neq j \) become zero. The only terms remaining are those for which \( i = j \), which are merely the square of the length of the \( i \)th bond, \( l_i^2 \). Hence

\[ \overline{r^2} = \sum_{i=1}^{n} l_i^2 = nl^2 \quad \cdots (2.2) \]

If the bond lengths in the chain are not all identical then \( l \) takes on the value of the average root mean square bond length.

Supplement

With the bond angle \( \theta \) fixed, as is the case, the end to end distance is obtained from the following expression, first derived by Eyring (33).

\[ \overline{r^2} = nl^2 \left( \frac{1 + \cos \theta}{1 - \cos \theta} \right) \quad \cdots (2.3) \]
Molecular dimensions calculated under the assumption of free rotation are grossly in error. Even the freely rotating chain with a fixed valence angle $\Theta$ is quantitatively incorrect. The reason for this is that rotation about single bonds is restricted in so far as certain values of the angle $\Phi$ are more probable than others. Taylor (34), Benoit (35) and others (36,37) have shown that this requires the introduction of an additional multiplying factor and

$$\overline{r^2} = n l^2 \left( \frac{1 + \cos \Theta}{1 - \cos \Theta} \right) \left( \frac{1 + \cos \Phi}{1 - \cos \Phi} \right) \ldots \ldots (2.4)$$

which is a reasonable approximation when $n$ is large and $\cos \Phi$ is not too near unity. If the rotation is unrestrained $\cos \Phi = 0$ and equation (2.4) reverts to (2.3).

Each of the equations for $\overline{r^2}$ consist of two factors, one independent of the nature of the polymer, depending only on chain length, and the other dependent on the nature of the polymer, such as bond length, bond angle, or degree of restriction of rotation. In general, for all long flexible chains

$$\overline{r^2} = n \beta^2 \ldots \ldots (2.5)$$

where $\beta^2$ is a constant characteristic of the polymer. Equation (2.5) allows us to treat flexible chains, restricted by rotation, mathematically as if they were completely unrestricted chains with bond length $\beta$ which is larger than the actual average length $l$. $\beta/l$ can be taken as a measure of the stiffness of a polymer chain.

Kuhn (38) has shown that equation (2.5) is applicable to all flexible polymers, regardless of restriction of rotation. Flexible here being defined as a chain in which any two vectors drawn say
from carbon atom 1 to carbon atom \( n \) and from carbon atom \( n \) to carbon atom \( z \), bear no correlation in direction. A chain molecule which is sufficiently long can then be flexible, despite restriction between a structural unit and its more immediate neighbours. \( m \) structural units taken together are a statistical segment. The number of vectors required to represent a given configuration is \( n' = \frac{n}{m} \) where the number of structural units is \( n + 1 \). The length of each vector \( l_i \) will be different and the angles between them arbitrary. As long as \( n' = \frac{n}{m} \) is large enough for statistical analysis i.e. the chain is long and \( m \) is reasonably small, the polymer chain described in terms of the vectors \( l_i \) becomes a completely unrestricted chain and from equation (2.2) we have

\[
\overline{r^2} = n' \overline{l_i^2} = n' l_e^2 = \frac{n l_e^2}{m} \quad \text{(2.6)}
\]

where \( l_e \) is the root mean square length of a statistical segment.

Equation (2.6) is the same as (2.5) with \( \beta^2 = l_e^2/m \)

The equations derived in this section are similar to the equation of state for an ideal gas in that they neglect intermolecular long range and intramolecular interactions of the polymer molecules. In a real polymer chain these interactions do exist. The effect of this on chain dimensions is discussed in section 2.3.

2.1.2 Rotational isomeric state theories

In the rotational isomeric state approximation, originally put forward by Volkenstein (39) each molecule, or bond, is treated as occurring in one or another of several discrete rotational states. These states in general coincide with potential minima. There will
be fluctuations about these minima but they are ignored here, assuming that they will be of random sign and consequently mutually compensatory on the average properties of the chain molecule.

Most molecules show a threefold character of rotational potentials. The function, $E(\phi)$ over the range of $\phi$, 0 to $\pm \pi$, shows three minima. One for the trans ($0^\circ$) and two for gauche conformations ($\sim \pm 120^\circ$). Calculations and experiments indicate a displacement of the gauche minima of about $5-10^\circ$ from their symmetrical locations at $\pm 120^\circ$, due to large repulsions occurring in the cis conformation. The potential wells are separated by barriers greater than RT, hence the bonds are confined at ordinary temperatures to states near one or another of the minima in $E(\phi)$.

Following Flory (40), the rotational partition function, $z$, for a bond whose conformations are represented by $\mathcal{V}$ rotational states is given by

$$ z = u_1 + u_2 + \ldots + u_{\mathcal{V}} \ldots \ldots (2.7) $$

Here $u_1$, $u_2$, etc are the statistical weights applicable to the respective isomeric states. If unity is assigned to one of these states then other statistical weights may be expressed relative to this. If $u_1 = 1$ then

$$ u_\eta = \exp[-(E_\eta - E_1)/RT] \ldots \ldots (2.8) $$

where $E_\eta$ is the energy for state $\eta$.

A configuration ($\phi$) of an n-bond chain molecule can be defined in rotational isomeric state terms by $n-2$ numerals from a $\mathcal{V}$ digital system, as before $\mathcal{V}$ representing the number of rotational isomeric states chosen to characterise the rotational potential of a bond.
Hence if \( \mathcal{V} = 2 \), a configuration may be written by the series of digits

\[
2112122 \text{ etc.}
\]

Neglecting interactions of long range, the rotational potential affecting any given bond \( i \) depends only on \( \phi_{i-1}, \phi_i, \) and \( \phi_{i+1} \).

The total configurational energy may then be given as the sum of energies for first neighbour pairs. Hence, in the case of the binary state configuration

\[
E(\phi) = E_2 + E_{21} + E_{11} + E_{12} + \text{ etc.}
\]

The first term has a single index since it has no predecessor in the sequence. Each succeeding term has as its first index the latter index of its predecessor in the polynomial. In general

\[
E(\phi) = \sum_{i=2}^{n-1} E_1(\phi_{i-1}, \phi_i) = \sum_{i=2}^{n-1} \xi \eta^i
\]

\[\ldots\ldots(2.9)\]

where \( \xi \) denotes the state of bond \( i-1 \) and \( \eta \) that of bond \( i \). The energy \( \xi \eta^i = E_1(\phi_{i-1}, \phi_i) \) is the contribution to \( E(\phi) \) associated with the assignment of bond \( i \) to state \( \eta \), bond \( i-1 \) being in state \( \xi \).

The dependence of the rotational potential for bond \( i \) on \( \phi_{i+1} \) is accounted for in the next sum. The total energy is therefore a systematic sum of terms each dependant upon a pair of consecutive rotation angles.

Statistical weights \( u_{\xi \eta} \) corresponding to the energies \( E_{\xi \eta} \)
may be defined by

\[ u_{i}^{\xi \eta} = \exp(-E_{i}^{\xi \eta}/RT) \] ......(2.10)

and can be expressed in the form of a statistical weight matrix

\[ U_{i} = [u_{i}^{\xi \eta}]_{i} \] ......(2.11)

with states \((\xi)\) for bond \(i-1\) indexing the rows and states \((\eta)\) for bond \(i\) the columns. The statistical weight of a configuration of the chain as a whole is given by

\[ \mathcal{N}(\phi) = \prod_{i=2}^{n-1} u_{i}^{\xi \eta} \] ......(2.12)

which follows from equations (2.9) and (2.10).

In the case of n-alkane homologs, the simplest case possible, the statistical weight matrix takes the form

\[
\begin{pmatrix}
(t) & (g^+) & (g^-) \\
(t) & 1 & \sigma & \sigma \\
(g^+) & 1 & \sigma & 0 \\
(g^-) & 1 & 0 & \sigma
\end{pmatrix}
\] ......(2.13)

where \(\sigma\) is defined by

\[ \sigma = \exp(-E_{g}/RT) \] ......(2.14)

\(E_{g}\) being the energy of a gauche state relative to a trans. The
value \( \exp(-E_g + g - /RT) \) is approximated by zero. States of the preceding bond are shown to the left of each row and those for the bond under consideration are above the columns. Elements in the first column equate to unity by the convention above for reckoning energies relative to the trans state for bond 1.

Members of the poly (ether) series P,M,O,, P,E,O,, P,Tri,M,O,, P,Tetra,M,O,, etc., are all symmetric chains i.e. they are chain molecules whose structural units do not possess centres of asymmetry, and consequently their treatment is similar to that above for poly (alkanes). Fig. 1. shows in diagrammatic form the chains of the four polymers mentioned above.

The P,M,O,, chain has two bonds in its repeat unit, identical apart from the opposite direction. The bond angles \( \pi - \Theta_a \) and \( \pi - \Theta_b \) at the methylene group and oxygen, are nearly identical and approximately tetrahedral, i.e. \( \sim 70^0 \) (41). P.O.E,, P.Tri,M,O,, and P,Tetra,M,O, have three, four and five bonds respectively within the repeat unit. There are two kinds of bonds, C - O and C - C , their lengths are 1.43 and 1.53 \( \AA \) respectively (41). The two bond angles CCC and COC are nearly the same and can also be approximated to \( \Theta = 70^0 \). First order parameters, \( \sigma \) , are indicated above the plane of the diagram, and second order parameters, \( \Lambda \) , below. Second order parameters apply to the bond pair alongside the skeletal atom or group marked. They are therefore four bond interactions, for instance i-1, i-2 and i, i+1 alongside the O in P,Tri,M,O,

Since we are only directly concerned with P,Tri,M,O, and P,Tetra,M,O,, we shall limit the discussion to these two polymers. The parameters required to theoretically calculate mean square end to end distances and mean square dipole moments have been determined by Mark (42,43,44). He calculated conformational energies and
FIG. 1.

POLY[METHYLENE OXIDE] CHAIN

POLY[ETHYLENE OXIDE] CHAIN

POLY[TRIMETHYLENE OXIDE] CHAIN

POLY[TETRAMETHYLENE OXIDE] CHAIN
associated statistical weights from interatomic distances and by allowing for polar interactions of partial charges and by comparison with corresponding parameters for P.M.O. and P.E.O. They are given in Table 2.1.

Table 2.1 Conformational energies and statistical weights assigned to the P.Tri.M.O. and P.Tetra.M.O. chains.

<table>
<thead>
<tr>
<th>Energies (cal mole⁻¹)</th>
<th>Statistical Weights (20-25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_\sigma = 900$ (as in P.E.O)</td>
<td>$\sigma = 0.21$</td>
</tr>
<tr>
<td>$E_\sigma' = -200$ (+ 200)</td>
<td>$\sigma' = 1.4$ (+ 0.5)</td>
</tr>
<tr>
<td>$E_\omega'' = 500$</td>
<td>$\omega'' = 0.43$</td>
</tr>
<tr>
<td>$E_\omega' = 250$ (+ 250)</td>
<td>$\omega' = 0.65$ (+ 0.3)</td>
</tr>
<tr>
<td>$E_\omega'' = 340$ (+ 250)</td>
<td>$\omega'' = 0.55$ (+ 0.3)</td>
</tr>
</tbody>
</table>

The calculated results due to Mark, are shown in Table 2.2. The values for P.E.O. are also included.

Table 2.2 Calculated dimensions and dipole moments of poly(ethers)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temperature</th>
<th>$\frac{r^2}{n^1}$</th>
<th>$\frac{\mu^2}{nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.E.O</td>
<td>40°C</td>
<td>4.0</td>
<td>0.58 (25°C)</td>
</tr>
<tr>
<td>P.Tri.M.O.</td>
<td>25°C</td>
<td>3.4 - 4.3</td>
<td>0.47</td>
</tr>
<tr>
<td>P.Tetra.M.O.</td>
<td>20°C</td>
<td>4.6 - 5.3</td>
<td>0.5 - 0.8</td>
</tr>
</tbody>
</table>
Ranges of the calculated values correspond to ranges of the parameters in Table 2.1. Dimensions are given as the characteristic ratio \( \sqrt{\frac{r^2}{n^2}} \) where \( r \) is the end to end distance of a polymer of \( n \) bonds of mean square length 1. The mean square dipole moments were calculated using bond moments of \( M_c - 0 = 0.99D \) and \( M_c - c = 0.0D \) (43, 45). The quantity \( n^2 \) occurring in the denominator of the dipole moment ratio represents the sum of the squares of the individual dipole moments in the molecule.

The two sets of data, one for chain dimensions and one for dipole moments are well correlated by the rotational isomeric state treatment. The statistical weight parameters required for these calculations are consistent with other evidence. For P.E.O. they are in qualitative agreement with the conformation of crystalline P.E.O. Tadokoro (46) says this conformation is a \( 7_2 \) helix described by \( (ttg)_x \). That is the \( C - O \) and \( O - C \) bonds approximate to the trans \( (\phi = -8^o) \) state and the \( C - C \) bonds approximate to the gauche \( (\phi = 115^o) \) states. The same worker (47) has also shown that for P.Tri.M.O, the preference of a \( C - C \) bond plus pendant oxygen, for the gauche conformation and the preference of \( C - O \) and \( O - C \) bonds for the trans conformation (see fig.1), is confirmed by the occurrence of bonds \( i - 1 \) to \( i + 2 \) of the P.Tri.M.O, chain in the helical conformation \( ttg^{+} \) in its stable orthorhombic crystalline form. Lastly Tadokoro again (47) has shown that for P.Tetra.M.O, the symmetrical form \( tttt \) exists in the stable crystalline polymer. The conformations of P.Tetra.M.O, predicted to be lowest in energy are \( ttg^{+} - tg^{+} \) and \( ttg^{+} - tg^{+} \), which should differ only slightly from the \( tttt \) state.

2.1.3 Statistical distribution of Configurations

Having considered flexibility and average dimensions we are now concerned with the distribution of dimensions a chain molecule will adopt. We must determine the probability, \( W(r)dr \), that the
end to end distance of a polymer molecule lies between \( r \) and \( dr \).
The statistics involved is closely related to the problem of random
flight. The early work was done by Rayleigh (48) but more recently
Kuhn (49) and Guth and Mark (50) have applied it to polymer chains.

It is convenient to consider first the projection of the
configuration on one co-ordinate axis, say the \( x \)-axis. For the
solution of the problem in one dimension we require the probability
\( W(x)dx \) that \( x \) assumes a value between \( x \) and \( x+dx \). Provided that
the chain can be regarded as flexible, according to equation (2.2),
and ignoring excluded volume effects, this probability is expressed
by the Gaussian distribution

\[
W_x(dx) = \left( \frac{b}{\pi \frac{\alpha}{2}} \right) \exp \left( -\frac{b^2 x^2}{\frac{\alpha}{2}} \right) dx \quad \ldots \ldots (2.15)
\]

where

\[
b^2 = \frac{3}{2n^1^2}
\]

Similar expressions are obtained for the probability distributions
\( W(y) \) and \( W(z) \) for the components \( y \) and \( z \). The probability of
simultaneously finding a value of \( r \) between \( x \) and \( x+dx \) and \( y \) and
\( y+dy \) and \( z \) and \( z+dz \) may be taken as the product of the separate
probabilities

\[
W(x)W(y)W(z)dx dy dz = \left( \frac{b}{\pi \frac{\alpha}{2}} \right)^3 \exp(-b^2 r^2)dx dy dz \quad \ldots \ldots (2.16)
\]

Where

\[
r^2 = x^2 + y^2 + z^2
\]
If one end of the freely jointed polymer chain is fixed at the origin of a coordinate system and the chain is permitted to take any configuration at random, the probability that the other end occurs in the volume element $dx dy dz$ located at $x, y, z$ is given by equation (2.16). If the chain displacement vectors of a number of identical polymer molecules are plotted from the same origin then $W(x)W(y)W(z)$ also represents the density of distribution of the end points of these vectors.

The Gaussian function, equation (2.16) indicates that the most probable location of one end of the chain relative to the other is at $r = 0$. The density, or probability, decreases monotonically as $r$ increases in magnitude.

The probability that $r$ assumes a certain magnitude, irrespective of the direction of the vector $\mathbf{r}$, is given by multiplying $W(x)W(y)W(z)$ by the total volume $4\pi r^2 dr$ of all volume elements at a distance $r$ from the origin. Now, the probability that the chain length has a value $r$ to $r + dr$, irrespective of direction, is

$$W(r)dr = \left(\frac{b}{\pi} \right)^3 \exp(-b^2 r^2) \frac{4\pi r^2 dr}{4\pi r^2 dr}$$

The radial distribution function $W(r)$ shows a maximum at a value of $r$ greater than zero. This maximum occurs at $r = 1/b$, which therefore represents the most probable value of $r$. The most likely value of $r$ is different from the density function $W(xyz)$ since $W(r)$ is obtained from $W(xyz)$ by multiplying throughout by the volume element in which $r$ is constant. However, the size of the volume element $4\pi r^2 dr$ increases with $r^2$, hence the difference between the two functions. A detailed outline of this problem has been given by Debye and Bueche (51).
2.2 Thermodynamics of polymer solutions.

It is possible to explain the difference between real and ideal solution behaviour of small molecules through their heats of solution. Systems containing high molecular weight components show extremely large deviations from ideal solution behaviour. Thermodynamically these deviations are associated with a finite heat of solution, even when the heat of dilution is zero or positive, hence, polymer solutions are characterised by large positive excess entropies of dilution, $\Delta S_M$.

Most polymer molecules can be represented as flexible chains. At extreme dilutions any one of these can take a large number of configurations independently of its neighbour. The amorphous polymer will show a similar chain flexibility but now the molecular shapes are no longer independent of each other. The shape of each chain is governed by the available space left by its neighbour. This condition is eliminated when a molecular chain is transferred from the pure polymer to a dilute solution and this accounts for the positive entropies of dilution of polymer solutions.

There are, however, two distinct ranges of concentration in systems containing chain molecules. In dilute solution the loose molecular coils will only occasionally become intertwined and this will depend on the size of the individual coil. Consequently, $\Delta S_M$ will be sensitive to polymer chain length. At higher concentrations the available volume becomes less and the polymer molecules more entangled. In this concentration range interference between chains will depend on the fraction of the volume occupied by these chains.

To account for this effect Flory (52) and Huggins (53) formulated a theory based on the quasi-lattice model of the liquid. They determined the number of ways in which $N_1$ solvent molecules, of
molar volume $V_1$, and $N_2$ polymer chains, of molar volume $V_2$, could be distributed over the $N = N_1 + N_2$ sites of a lattice so that each lattice site is occupied either by a solvent molecule or one of the $V_2/V_1$ segments of a polymer chain. A basic assumption here is that in any given region of the polymer solution there is an equal density of chain segments. This will be valid for the concentration range under discussion i.e. where the polymer chains are freely entangled. In dilute solutions, however, it would not be so as the polymer molecules, representing high local concentrations of chain segments, are separated by regions of pure solvent.

If $W_1$ is the number of ways $N_2$ polymer chains can be arranged on a lattice of $N_2V_2/V_1$ sites (the pure disordered polymer) and $W_2$ the number of ways they can be arranged on the $N_1 + N_2 (V_2/V_1)$ lattice sites corresponding to the solution, the configurational entropy of mixing is given by

$$(\Delta S_M)_{\text{conf}} = k \ln \left( \frac{W_2}{W_1} \right)$$

This expression relates statistical mechanics to the thermodynamics of the system and both Flory and Huggins went on to show

$$(\Delta S_M)_{\text{conf}} = -k [N_1 \ln v_1 + N_2 \ln v_2]$$

where $v_1$ and $v_2$ are the volume fractions of solvent and polymer respectively. And,

$$\Delta S_M = -R [\ln v_1 + v_2 (1 - \frac{1}{M})] \ldots \ldots (2.17)$$
where $\Delta S_M$ is the experimentally accessible entropy of mixing, $m$ is $V_2/V_1$ and the gas constant $R$ replaces Boltzmann's constant $k$.

The free energy of mixing is made up from configurational probability and a free energy characterising nearest neighbour interactions. The latter is a short range effect and should be proportional to the number of contact points between solute and solvent i.e. proportional to the volume fractions of the components

$$\Delta H_M = \chi RT v_1 v_2$$

or

$$\Delta H_M = \chi RT v_2^2$$

since

$$\Delta G_M = \Delta H_M - T \Delta S_M$$

substituting from equation (2.17)

$$\Delta G_M = RT \left[ \ln(1 - v_2) + v_2 \left( 1 - \frac{1}{m} \right) + \chi v_2^2 \right]$$

\[ \ldots (2.18) \]

$\chi$ is the Flory - Huggins interaction parameter and equation (2.18) is known as the Flory - Huggins equation.

The changes of chemical potential on mixing for the two components are then

$$\Delta u_1 = RT \left[ \ln v_1 + (1 - \frac{1}{m}) v_2 + \chi v_2^2 \right]$$

and

$$\Delta u_2 = RT \left[ \ln v_2 - (m - 1) v_1 + \chi v_1^2 \right]$$
On expansion of the \( \ln v_1 = \ln(1 - v_2) \) term,

\[
\Delta u_1 = -RT \left[ \frac{v_2}{m} + \left( \frac{v_2}{m} \right)^2 + \frac{1}{3} \left( \frac{v_2}{m} \right)^3 \ldots \right]
\]

which compares with that obtained if the entropy of dilution had the ideal value as follows

\[
\Delta u_1 = -RT \left[ \frac{v_2}{m} + \frac{1}{2} \left( \frac{v_2}{m} \right)^2 + \frac{1}{3} \left( \frac{v_2}{m} \right)^3 \ldots \right] - \chi v_2
\]

In this case a large value of \( m \) would make mixing impossible if \( \chi \) had an appreciable positive value. Hence endothermic mixing of high molecular weight polymers with solvents is only possible because of the configurational entropy gained by flexible chain molecules in the process of dilution.

As we have already stated the theories dealt with so far, assume that the concentration of polymer segments is uniform throughout the solution. In the case of dilute solutions this does not hold and it is necessary to develop a new theory to describe the ideal and real dilute solution, for this concentration range.

For an ideal solution the chemical potential is given by

\[
U_1 = U_1^0 + RT \ln x_1 \quad \ldots \ldots \ldots (2.20)
\]

where subscript 1 denotes component 1, or solvent, and \( U_1^0 \) is its standard chemical potential and \( x_1 \) its mole fraction. For dilute solutions \( x_1 \) is very close to unity, hence for a two component system with \( x_1 \gg x_2 \)

\[
\ln x_1 = \ln (1 - x_2) = -x_2 - \frac{x_2^2}{2} \ldots \ldots -27-
\]
Substituting in equation (2.20)

\[ U_1 - U_1^0 = -RT \left( x_2 + x_2^2/2 + \ldots \right) \]

......(2.21)

If the concentration of solute is expressed as \( c_2 \) grams per millilitre then equation (2.21) becomes

\[ U_1 - U_1^0 = -RTV_1 c_2 \left( \frac{1}{M_2} + \frac{V_1}{2M_2^2} c_2 + \ldots \right) \]

......(2.22)

where \( x_2 = \frac{c_2 V_1}{M_2} \)

For non-ideal solutions the theory is analogous to that for non-ideal gases. The chemical potential is expressed as a power series in concentration, the coefficients \( A_2, A_3 \) etc., are known as the second, third etc., virial coefficients.

\[ U_1 - U_1^0 = -RTV_1 c_2 \left( \frac{1}{M_2} + A_2 c_2 + A_3 c_2^2 + \ldots \right) \]

......(2.23)

The first term is the same as in equation (2.22) so that ideal behaviour is attained as \( c_2 \) becomes very small.

Equation (2.23) shows \( A_2 \) to decrease with increasing molecular weight. In practice polymer solutions show large concentration dependance of \( U_1 \). A polymer solution can also separate into immiscible phases. Such features of non-ideal behaviour may be explained in terms of excluded volume, the volume that one polymer chain excludes to another.

In a very dilute solution with solute molecules separated from each other the chemical potential of the solvent is dependant only
on the change in entropy due to mixing, enthalpy and volume changes being zero

\[ u_1 - u_1^0 = -T(\overline{s}_1 - s_1^0) \]  \quad \ldots \quad (2.24)

where \( \overline{s}_1 \) is the partial molal entropy of the solvent and \( s_1^0 \) the molar entropy of pure solvent.

Consider the total number of ways \( N_2 \) identical polymer molecules, of excluded volume \( u \) can be distributed over a volume \( V \) of solution. The number of sites available for the first polymer molecule introduced into the solution will be proportional to \( V \). The first molecule excludes a volume \( u \), hence the number of sites available to the second molecule will be proportional to \( V - u \). The volume available to the third molecule \( V - 2u \) etc. As long as the final solution is sufficiently dilute to justify the assumption that the solute molecules are far apart and independent of each other, the total excluded volume will remain additive in the number of polymer molecules, and the total number of ways of arranging \( N_2 \) polymer molecules can be written

\[ W = K \prod_{i=1}^{N_2} [V-(i-1)u] \equiv K \prod_{i=0}^{N_2-1} V(1 - \frac{iu}{V}) \]  \quad \ldots \quad (2.25)

where \( K \) is the proportionality constant.

Since \( iu/V \) is always much less than unity in the dilute solution the logarithmic expansion of equation (2.25) may be done with neglect of higher terms. Further substitution of \( N_2 = n_2 \sqrt{N} \) where \( n_2 \) is the number of moles of solute and \( \sqrt{N} \) Avogadro's number and
\[ V = n_1 V_1^0 + n_2 V_2^0 \] where \( V_1^0 \) and \( V_2^0 \) are the partial molal volume of solvent and solute at infinite dilution. Thus

\[ \ln W = \text{Const} + \mathcal{N} n_2 \ln(n_1 V_1^0 + n_2 V_2^0) - \frac{(\mathcal{N} n_2)^2 u}{2(n_1 V_1^0 + n_2 V_2^0)} \]

\[ \ldots \ldots (2.26) \]

The entropy of mixing in terms of the Boltzmann equation is

\[ \Delta S_{\text{mix}} = k \ln W (\text{final soln.}) - k \ln W (\text{pure solute}) - k \ln W (\text{pure solvent}) \]

where \( R, \) the gas constant is equal to \( \mathcal{N} k. \)

Equation (2.26) is the value of \( \ln W \) for the final solution. That for pure solute and pure solvent is found by putting \( n_1 = 0 \) and \( n_2 = 0 \) respectively in equation (2.26). From this new expression for \( \Delta S_{\text{mix}}, \) \( S_1 - S_1^0 \) may be found by differentiating with respect to \( n_1, \) then substituting \( \frac{n_2}{(n_1 V_1^0 + n_2 V_2^0)} = \frac{c_2}{M_2} \)

the solute concentration in grams per c.c. and \( M_2 \) is the solute molecular weight.

\[ \bar{S}_1 - S_1^0 = R V_1^0 c_2 \left( \frac{1}{M_2} + \frac{\mathcal{N} u}{2M_2^2} c_2 \right) \]

and converting to chemical potential by equation (2.24) we get

\[ u_1 - u_1^0 = -R V_1^0 c_2 \left( \frac{1}{M_2} + \frac{\mathcal{N} u}{2M_2^2} c_2 \right) \]

\[ \ldots \ldots (2.27) \]

Equation (2.27) is identical with (2.23) where
The way a flexible polymer behaves by excluding other polymer molecules is similar to that of a solid sphere. The excluded volume, \( u \), is also closely related to the chain expansion parameter, \( \alpha \), which allows for the effect that a given segment of polymer chain can exclude other segments on the same chain. \( \alpha \) will be discussed more fully in section 2.3. However it is sufficient to note that \( u \) is not the sole factor in the interaction between segments. In a good solvent a polymer molecule will be surrounded by solvent molecules. This will effectively increase the excluded volume due to each segment. \( u \) will increase as too will \( \alpha \). In a poor solvent there will be a preference for segment - segment contacts, this effect decreases \( \alpha \) and produces a similar decrease in \( u \). In a sufficiently poor solvent \( \alpha = 1 \) and the molecule behaves as if its segments occupy no volume at all. Now the excluded volume becomes zero and hence so too does \( A_2 \), see equation (2.28). Under these conditions the polymer solution behaves ideally.

An increase in temperature decreases intermolecular and intramolecular attractive forces in so far as they are volume dependant. Hence temperature should have a marked effect on the chemical potential of a polymer solution, particularly in a poor solvent where the attractive forces become more important. Poor solvents should become better solvents as the temperature is increased since both \( \alpha \) and \( A_2 \) will increase.

The effect is shown quantitatively by an equation of Flory's (54)

\[
U_1 - U_1^o = RT (\kappa_1 - \psi_1) \frac{v^2}{2}
\]

\[ \tag{2.28} \]
where $\chi_1$ and $\psi_1$ are heat and entropy parameters. The ideal
temperature $\theta$ is defined by

$$\theta = \frac{\chi_1 T}{\psi_1} \quad \ldots \ldots \text{(2.29)}$$

so that

$$\psi_1 - \chi_1 = \psi_1 \left(1 - \frac{\theta}{T}\right)$$

Hence the excess chemical potential becomes

$$u_1 - u_1^0 = -RT \psi_1 \left(1 - \frac{\theta}{T}\right) v_2^2 \quad \ldots \ldots \text{(2.30)}$$

In a good solvent $\theta$ is negative, since $\chi_1$ is also negative,
u is always positive and $\alpha$ greater than unity. In a poor solvent
$\theta$ will be positive. When $T = \theta$, the chemical potential from
segment - solvent interactions is zero see equation (2.30), as
too is the free energy of interaction of the segments within a
given volume. The $\theta$ temperature is therefore that temperature at
which deviations from ideality vanish. The solvent under these
conditions is an ideal solvent. The substitution of equation (2.21)
is now more apparent. The $\theta$ temperature is characteristic of any
poor solvent - polymer system when $\lambda_2 = 0$ and $\alpha = 1$.

In general, a poor solvent for a given polymer becomes poorer
as the temperature is lowered. At some critical temperature $T_c$,
phase separation occurs. This critical point is also called the
consulate point and the conditions for phase separation at this
point require
Application of the critical conditions to the Flory Huggins equation (2.18) gives for the critical composition (52)

\[
\left( \frac{\partial^2 G_M}{\partial v_1^2} \right)_{T,P} = 0 \quad \text{and} \quad \left( \frac{\partial^3 G_M}{\partial v_1^3} \right)_{T,P} = 0
\]

which for large values of \( m \) reduces to

\[
(v_2)_{\text{crit}} = \frac{1}{(1 + m^3)}
\]

remembering that \( m = \frac{V_2}{V_1} \) and for the interaction parameter

\[
\chi_{\text{crit}} = \frac{(1 - \frac{\chi}{m})^2}{2m}
\]

\[
\approx \frac{1}{2} + \frac{1}{m^3}
\]

The critical value of the interaction parameter \( \chi \) reaches a limiting value of \( \frac{1}{2} \) at infinite molecular weight.

We can now directly equate the second virial coefficient term \( A_2 \) to the interaction parameter by equations (2.23) and (2.19). If we first substitute for \( v_2 = \frac{c_2 v_2}{M_2} \) into (2.19) we have

\[
\Delta v_1 = -RTc_2 v_1 \left[ \frac{1}{M_2} + (\frac{1}{2} - \chi) \frac{c_2 v_2}{M_2 v_1} \right] ...
\]

\[\ldots...(2.31)\]
and
\[ \Delta v_1 = -RTc_2 V_1 \left[ \frac{1}{M_2} + A_2 c_2 + A_3 c_2^2 + \ldots \right] \]

\[ \ldots \ldots (2.23) \]

hence
\[ A_2 = (\frac{1}{2} - \chi) \frac{v_2^2}{V_1 M_2^2} \]

\[ \ldots \ldots (2.32) \]

Therefore when \( \chi = \frac{1}{2} \), \( A_2 = 0 \). Consequently the consolute point and the parameter \( \Theta \) are one and the same point for infinite molecular weight, being the temperature at which the polymer solution becomes ideal.
2.3 **Excluded volume effect.**

Dimensions of a polymer chain in solution are influenced not only by polymer - solvent effects but also by the interactions between chain elements. These can be divided into short and long range interactions. The short range interactions, as explained previously, are those between atoms or groups separated by only a small number of valence bonds. They result in constancy of bond angle and hindered internal rotation.

The long range interactions are those between groups separated in the chain by many valence bonds, or even between segments of different polymer molecules. They are identical in nature and magnitude to Van der Waals interactions between two different molecules. These long range secondary interactions have so far been ignored from the discussion and in this respect the equations derived in sections 2.1 and 2.2 are analogous to the equation of state for ideal gases.

The repulsive force arises from the inability of molecules to occupy the same volume, and has the effect of making certain configurations of the polymer chain impossible. This will obviously occur to a greater degree in a molecule with a small end to end distance or one that is highly coiled. The result is to increase \( \overline{r}^2 \).

The ideal end to end distance achieved when the energy of interaction compensates exactly for volume exclusion will from now on be represented by \( \overline{r}_0^2 \). \( \overline{r}^2 \) will therefore be larger than \( \overline{r}_0^2 \). Flory and Fox (55) represented the difference between the perturbed and unperturbed dimensions by the expansion factor \( \alpha \). Thus we may write

\[
\overline{r}^2 = \alpha^2 \overline{r}_0^2
\]

\[
\overline{s}^2 = \alpha^2 \overline{s}_0^2
\]
The probability of a segment occupying space already filled by another segment increases with the number of segments in the chain. The expansion factor $\alpha$ is therefore molecular weight dependent.

A polymer chain will have a preference for a given configuration depending on solvent. In a good solvent the energy of interaction between polymer element and solvent molecule exceeds that between the polymer - polymer and solvent - solvent pairs, the molecule tends to expand and $\alpha$ becomes larger. In poor solvents where the energy of interaction is less, smaller configurations are preferred partly cancelling the effect of excluded volume, and $\alpha$ takes on a smaller value. If the energy of interaction compensates exactly for the effect of the physical excluded volume then $r^2 = r_o^2$ and $\alpha = 1$.

When this condition is achieved the polymer chain will assume its unperturbed configuration in which the overall dimension is determined by bond lengths and angles only. This will only occur in a poor solvent for a given polymer at its theta temperature. This precise temperature may be found by adjusting the temperature to the consulate point of chains of infinite molecular weight, usually by extrapolation of osmotic or light scattering data, to a solvent composition or temperature corresponding to zero second virial coefficient. Recently Peterlin (56) and Kurata and Stockmayer (2) have gathered data for a large number of polymers and tabulated theta solvents and unperturbed dimensions.

The effect of expansion of the flexible polymer chain in a good solvent has been studied both theoretically and experimentally. In sufficiently dilute solution the long range interactions between chain elements are represented by the binary cluster integral

$$ g = \int_0^\infty \left[ 1 - \exp(-W(r)/kT) \right] 4\pi r^2 dr $$
provided the pair potential of average force \( W(r) \) as a function of distance \( r \) is assumed to be of short range nature as required by \( \beta \ll (r^2)^{\frac{3}{2}} \). Some workers chose the negative sign for \( \beta \), the present choice makes the numerical value of \( \beta \) positive in most experimentally studied polymer solutions. The expansion factor \( \alpha \) is then a function of a single variable \( z \), defined by

\[
z = \left( \frac{3}{2\pi} \right) \frac{3}{2} \beta a^{-3/2} N^\frac{1}{2} \quad \ldots \ldots (2.33)
\]

for a chain of \( N \) links of length \( a \). In the absence of this type of interaction i.e., at \( T = 0 \) where \( \beta = 0 \), the mean square dimensions of the chain reduce to

\[
\overline{r^2}^0 = 6 \overline{s^2}^0 = N a^2
\]

which is identical to equation (2.2).

When \( z \) is small an exact expression for the expansion factor can be obtained from perturbation treatments of the interactions; as follows

\[
\alpha^2 = \frac{\overline{r^2}}{\overline{r^2}^0} = 1 + \frac{4}{3} z - 2.08 z^2 + \ldots
\]

\[
\ldots \ldots (2.34)
\]

or in terms of radius of gyration

\[
\frac{\alpha^2 s^2}{N} = \frac{\overline{s^2}}{\overline{s^2}^0} = 1 + \frac{134}{105} z - \ldots
\]

\[
\ldots \ldots (2.35)
\]

These have been derived by a number of workers (57 - 61).
The difference between $\alpha$ and $\alpha_5$ is due to the non Gaussian character of the chain, however it is usually small and may be neglected in most cases. Both these equations (2.34, 2.35) can be applied to systems in poor solvents near the Flory theta temperature but not in good solvents because of slow convergence of the series equation (2.19). As yet an exact equation for large values of $\alpha$ has not been derived. Attempts have been made to obtain a closed expression and several approximations have been obtained.

Flory (62) used a model in which the unperturbed chain was represented by a cloud of unconnected segments whose concentration was spherically symmetrical and was a Gaussian function of distance from the centre of gravity. It was assumed the excluded volume effect would expand all chain dimensions by the same factor so that segment distribution would maintain a Gaussian character. This led to

$$\alpha^5 - \alpha^3 = 2C_M(1/2 - \chi)M^\frac{1}{2} \quad \ldots \ldots (2.36)$$

The Flory interaction parameter $\chi$ is related to $B$ by

$$B = 2V_1(1/2 - \chi) \quad \ldots \ldots (2.37)$$

then equation (2.36) can be written

$$\alpha^5 - \alpha^3 = C'M \quad \ldots \ldots (2.38)$$

Where $V_1$ is the molar volume of solvent and $C_M$ and $C'$ are constants.

The assumption by Flory of equal expansion of the chain dimensions has been criticised by Krigbaum (63) and Ptitsyn (64). They pointed out that the most pronounced changes would be in the
central region of the molecular coil where segment density is 
highest. This would mean a sharper distribution function of chain 
end displacements than in the unperturbed state. This led 
Krigbaum (63) to conclude that the ratio \((\kappa^5 - \kappa^3)/M^2\) should 
not be molecular weight independent as implied by equation (2.36) 
but should pass through a minimum as the chain length is increased. 

A second criticism is the assumption of spherical symmetry of 
chain segment distribution. Kurata et al (65) suggested a model in 
which the chain segments are distributed uniformly within an ellipsoid 
of revolution chosen to give the same values for the principal radii 
of gyration as correspond to a Gaussian chain. The equation thus 
derived was

\[
\kappa^3 - \kappa = C g(\kappa) \kappa 
\]

\[
\text{where} \\
g(\kappa) = \frac{8 \kappa^3}{(3 \kappa^2 + 1)^2} 
\]

and the constant \(C\) is equal to 134/105 or 4/3 depending on the 
definition of \(\kappa\).

A similar equation was derived by Ptitsyn (64)

\[
\kappa^2 = 0.786 + [(1 + 9.36z)^{2/3}/4.68] 
\]

\[
\text{(2.41)} 
\]

and Fixman (59)

\[
\kappa^3 = 1 + 1.55z 
\]

\[
\text{(2.42)} 
\]
Thus there seems to be general agreement that some modification in the Flory expression for the long range interaction effects on chain dimensions is needed.
2.4 Theoretical treatments of viscosity

The approximate equations of the preceding section in which \( \alpha \) is related to \( z \), are used to estimate unperturbed dimensions of polymers. The first method, which may be called the Flory - Fox - Schaefergen (1) method is based on the combination of viscosity, \( [\eta] \) representing intrinsic viscosity defined in section 2.6.

\[
[\eta] = [\eta]_\theta \propto z^3
\]

(2.43)

where

\[
[\eta]_\theta = KM^\frac{1}{2}
\]

(2.44)

with Flory's excluded volume equation (2.36). The substitution of (2.43) and (2.44) into (2.36) yields

\[
[\eta]^{\frac{2}{3}} / M^{\frac{1}{3}} = K^{\frac{2}{3}} + 2C_\mu (\frac{1}{2} - \chi)K^{\frac{5}{3}} M/[\eta]
\]

(2.45)

Thus if viscosity data are available over a wide range of \( M \), \( K \) and \( \chi \) can be found from the intercept and slope of the line obtained by plotting \( [\eta]^{\frac{2}{3}} / M^{\frac{1}{3}} \) versus \( M/[\eta] \). The unperturbed mean square end to end distance can readily be calculated from \( K \) since

\[
K^{\frac{2}{3}} = \bar{\phi}_0^{\frac{2}{3}} (\bar{x}_e^2 / M)
\]

(2.46)

Both \( \bar{\phi}_0 \) and \( K \) are constants independent of \( M \). \( \bar{\phi}_0 \) is supposed to be the same for all flexible linear polymers, \( K \) is peculiar to a given polymer. We are therefore able to calculate the unperturbed dimension independently of theta conditions.

The Kurata - Stockmayer (2) treatment is similar. In this case substitution of equations (2.43) and (2.44) into (2.39) gives
\[ [\eta]^{2/3} / M = K + 0.363 \frac{\alpha}{\rho_o} B [g(\alpha \eta)^M / [\eta]^{1/3}] \]

......(2.47)

B is a polymer - solvent interaction parameter, \( \alpha \eta \) expansion from viscosity data.

The awkward form of equation (2.47), however, necessitates a lengthier graphical procedure than the one of Flory, Fox and Schaeffgen. The same may be said of methods based on the Ptitsyn relation.

A third method due to Stockmayer and Fixman (3) becomes apparent when we substitute equations (2.43) and (2.44) into (2.42) and put

\[ z = \left( \frac{3}{2\pi} \right)^{3/2} \frac{3}{M} \frac{z}{1^3} \]

......(2.48)

where \( 1^2 = \left( \frac{\rho_o^2}{\rho} \right) / M \)

then,

\[ [\eta] = K M^{1/3} + 0.31 \frac{\alpha}{\rho_o} B M \]

......(2.49)

B in equations (2.47) and (2.49) is related to the Flory interaction parameter \( \chi_1 \) by

\[ B = \left[ \frac{2\bar{v}}{\gamma} \right]^{1/2} \left( 1 - \chi_1 \right) V_1 \sqrt{A} \]

......(2.50)

where \( \bar{v} \) is the specific volume of polymer, \( V_1 \) the molar volume of solvent and \( \sqrt{A} \) Avogadro's number.

Equations (2.33) and (2.48), and (2.37) and (2.50) are obviously the same, with

\[ B = \frac{\alpha}{2.2} \frac{\rho_o}{c M} \]
where \( m = \frac{M}{n} \), the average molecular weight of a skeletal bond. \( c \) is an arbitrary constant required to express the number and length of effective segments, \( N \) and \( a \), in terms of those of the real chain elements, \( n \) and \( l \).

Stockmayer - Fixman's equation (2.49) is simple and precise, with the effects of short and long range interactions separated into two independent terms. The graphical treatment is simply to plot \( [\eta] / M^\frac{1}{2} \) against \( M^\frac{1}{2} \). The ordinate intercept equals \( K \) and the slope is directly proportional to the polymer - solvent interaction parameter \( B \).

The procedure required for the Kurata - Stockmayer relationship, equation (2.47) is more involved. \( [\eta]_0^\frac{2}{3} / M^\frac{1}{3} \) is first plotted against \( \frac{2}{3} M^\frac{1}{3} / [\eta]^\frac{1}{3} \), ignoring \( g(\alpha_\eta) \) and an approximate value of \( K \) found. This allows us to calculate \( [\eta]_0, \alpha_\eta \) and \( g(\alpha_\eta) \) from equations (2.44) (2.43) and (2.40). Then, using this result replot \( [\eta]_0^\frac{2}{3} / M^\frac{1}{3} \) against \( g(\alpha_\eta) M^\frac{1}{3} / [\eta]^\frac{1}{3} \) and find an improved value of \( K \). The convergence of this procedure is rapid enough so that the final value of \( K \) is found in the second trial.
2.5 **Light Scattering**

Much of the early work in the interpretation of light scattering was done by Lord Rayleigh who concerned himself with the scattering by gases. The intensity of scattered light depends on the polarizability of the molecules compared with that of the medium in which they are suspended, it depends also on their size and on their concentration. The equation derived by Rayleigh showed the ratio of scattered light to incident light to be given as follows

\[
\frac{I_s}{I_0} = \frac{16 \pi^2 \alpha^2 \sin^2 \theta}{\lambda^4 r^2} \quad \text{.....(2.51)}
\]

where \( \lambda \) is the wavelength of the light in vacuo, \( r \) is the distance from the observer to the scattering centre and \( \alpha \) is the polarizability of the particle. Equation (2.51) is true for cases when the scattering centres are small compared with the wavelength of light. It is assumed that the particles are isotropic and are arranged at random at large distances from each other and as a result make independent contributions to the scattering.

The angular dependence of scattering is given by the term \( \sin^2 \theta \). If vertically polarized light is used, and observations are made in the horizontal plane, the scattered intensity will be independent of angle. Incident light used for scattering experiments, however, is more often unpolarized rather than polarized. An unpolarized light beam is equivalent to the superposition of two plane-polarized beams, independent in phase and of equal intensity, with their planes of polarization perpendicular to one another. The intensity of scattering, \( I_0 \), is therefore the sum of two terms, each representing the scattering from half the incident intensity. The
intensity of scattered light to incident light may now be written as

\[ \frac{I_\theta}{I_0} = \frac{2\pi^2(1 - \cos^2 \theta)(dn/d\theta)^2 M}{\sqrt{\lambda^4 r_s^2}} \] .......(2.52)

(dn/d\theta) represents the variation of refraction index of the gas with concentration, M is its molecular weight, \( \sqrt{\lambda} \) Avogadro's number, and \( r_s \) the distance to the point of observation. The Rayleigh ratio is defined as

\[ R_\theta = \frac{r_s^2 \theta}{I_0(1 + \cos^2 \theta)} \] .......(2.53)

which reduces equation (2.52) to

\[ \frac{Kc}{R_\theta} = \frac{1}{M} \] .......(2.54)

where the constant K is given by

\[ K = \frac{2\pi^2(dn/d\theta)^2}{\sqrt{\lambda^4}} \] .......(2.55)

Applying Rayleigh's theory to solutions of small molecules gives an equation similar to (2.54). Much of this work has been done by Debye (66) and his result is

\[ \frac{Kc}{R_\theta} = \frac{1}{M} + 2A_2 c^2 + 3A_3 c^3 + ... \] .......(2.56)
A_2, A_3 etc., are the virial coefficients and the constant K is now modified by a term in the refractive index of solvent, n_o.

\[
K = \frac{2 \pi^2 \frac{dn}{dc} n_o^2}{\mathcal{N} \lambda_o^4} \quad \cdots \cdots (2.57)
\]

When the dimensions of the scattering particles exceed about one twentieth of the wavelength of the light used, the intensity of the scattered light is reduced due to destructive interference. The particles can no longer be regarded as single isolated scattering centres. The irregularly coiled polymer particles in dilute polymer solutions fulfill the condition of isotropy but, especially if their molecular weights are large, their mean dimensions approach the wavelength of the light. Destructive interference occurs due to scattering from centres within the same molecule and the overall intensity drops. As the scattering angle drops so does the interference until it vanishes as \( \theta \) approaches zero. To carry out a quantitative evaluation of this effect for a particle which may be represented as an assembly of N scatterers, the destructive interference must be averaged over all possible orientations, relative to the incident beam. Such a calculation gives

\[
P(\theta) = \frac{1}{N^2} \sum_{i} \sum_{j} \sin \frac{kr_{ij}}{krij} \quad \cdots \cdots (2.58)
\]

where \( P(\theta) \) is the factor by which scatter is decreased, due to interference, \( r_{ij} \) is the distance between the scattering points, and

\[
k = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right)
\]
where $\lambda$ is the wavelength of the light in the scattering medium, as deduced by Debye (67).

From equation (2.58) we see that $P(\theta)$ becomes independent of particle shape as $\theta$ approaches zero and hence becomes directly a measure of the dimension of the polymer molecule. This is unique since it is the only measurement of dimensions which does not make initial presumptions regarding shape.

If the solution is sufficiently dilute then the average distances between solute molecules will be large compared to the wavelength of light, then $P(\theta)$ will represent only destructive interference. Expanding equation (2.58) gives

$$P(\theta) = \frac{1}{N^2} \left[ N^2 - \frac{1}{3!} \sum \sum k^2 r_{ij}^2 + \frac{1}{5!} \sum \sum k^4 r_{ij}^4 - \ldots \right]$$

$$\lim_{\theta \to 0} P(\theta) = \frac{1}{N^2} \left[ N^2 - \frac{1}{3!} \sum \sum k^2 r_{ij}^2 \right]$$

The radius of gyration of any assembly of identical particles is related to the $r_{ij}$ values by

$$\overline{s^2} = \frac{1}{2N^2} \sum \sum r_{ij}^2$$

therefore

$$\lim_{\theta \to 0} P(\theta) = 1 - \frac{1}{3} k^2 \frac{\overline{s^2}}{\lambda^2}$$

$$= 1 - \frac{16 \pi^2}{3(\lambda^2)} \frac{\overline{s^2}}{\lambda^2} \sin^2 \left( \frac{\theta}{2} \right)$$

$$\ldots \ldots (2.60)$$

-47-
or, since \(1/(1 - x) = 1 + x\) when \(x\) is small.

\[
\lim_{\theta \to 0} \frac{1}{P(\theta)} = 1 + \frac{16 \pi^2 - \frac{s^2}{3} \sin^2(\theta/2)}{\lambda^2}
\]

\[\ldots (2.61)\]

It is important to know exactly what quantity is being measured when dealing with molecular weights and polymer dimensions. The Rayleigh ratio of a monodispersed species at zero angle is given by equation (2.56) as

\[
R_0 = \frac{KcM}{1 - 2A_2cM}
\]

However polymer solutions are very rarely, if ever, monodispersed. For a polydisperse sample, providing the concentration is low, the Rayleigh ratios of the components are additive. Thus

\[
R_0 = \sum_i (R_0)_i = \frac{K \sum_i c_i M_i}{\sum_i (1 + 2(A_2)_i c_i M_i)}
\]

Therefore

\[
\frac{Kc}{R_0} = \frac{\sum_i c_i}{\sum_i c_i M_i} + \frac{2 \sum_i (A_2)_i c_i M_i}{\sum_i c_i M_i} \sum_i c_i
\]

\[= \frac{1}{M_w} + 2(A_2)_2 c \quad \ldots (2.62)\]

where \(c_i\) is the concentration in grams per cubic centimetre of each dissolved species, and \(M_i\) the corresponding molecular weight.
\[ \sum_{i} c_i = c \] represents the total concentration. Hence, the light scattering method yields the weight average molecular weight, irrespective of the nature of the molecular weight distribution, and the \( z \) average second virial coefficient.

Similarly for large particles, the Rayleigh ratios are the sum of the separate species

\[ R_{\theta} = K \sum_{i} M_i P_i(\theta) c_i \]

therefore

\[ \frac{Kc}{R_{\theta}} = \frac{\sum c_i M_i - \frac{16 \pi^2}{3(\lambda^2)} \sin^2(\theta/2) \sum M_i c_i (s^2)_{1}}{\sum c_i M_i} \]

\[
\sum_{i} (s^2)_{1} = \frac{\sum_{1} M_i c_i (s^2)_{1}}{\sum_{1} M_i c_i} = \frac{\sum_{1} N_i M_i^2 (s^2)_{1}}{\sum_{1} N_i M_i^2} 
\]

\[
\text{For small values of } \sin^2 \theta/2, \text{ following the same procedure as from equation (2.60) to (2.61)}
\]

\[
\frac{Kc}{R_{\theta}} = \frac{1}{M_w} \left[ 1 - \frac{16 \pi^2}{3(\lambda^2)} \sin^2 \theta \frac{(s^2)_{z}}{2} \right] 
\]

\[
\text{where}
\]

\[
\frac{(s^2)_{z}}{2} = \frac{\sum_{1} M_i c_i (s^2)_{1}}{\sum_{1} M_i c_i} = \frac{\sum_{1} N_i M_i^2 (s^2)_{1}}{\sum_{1} N_i M_i^2} 
\]
Therefore the mean square radius of gyration we have determined is the \( z \) average value.

In the derivation of all the equations given above it has been assumed that the scattering particle is optically isotropic. When the scattering particles are anisotropic scattering at \( 90^\circ \) is no longer completely plane polarized. Polarizability will vary with direction and the two vectors will not coincide. As a result, the light scattered normal to the incident beam is no longer completely polarized in the vertical plane but reinforced by an additional horizontal component. The scattering is therefore greater than theoretically expected and the ratio of horizontally to vertically polarized light is not zero. This ratio is known as the depolarization ratio, \( P_u \), where the subscript \( u \) denotes unpolarized light.

Cabannes (69) has shown that the excess scattering due to anisotropy may be related to the depolarization ratio

\[
C = \frac{6 \pm 6 P_u}{6 - 7 P_u}
\] .......(2.65)

Geiduschek (70) has suggested that in most cases where non zero values of \( P_u \) have been reported it is not at all certain whether the measured values of \( P_u \) really reflect anisotropy. However as Peaker (71) explains depolarization may also arise due to the finite size of the scattering particles, this being an effect independent of anisotropy. It may be large for small molecules (for instance benzene at \( 25^\circ \)C is 0.4) however polymer molecules usually show very little depolarization in excess of that arising from the solvent. The largest observed has been 0.04 for polystyrene in methyl ethyl ketone (72). If depolarization is appreciable then it will influence the angular distribution of scattering and will
have to be corrected for as described above.

The sensitivity of the light scattering method depends on the magnitude of the constant $K$, equation (2.57), which in turn depends on the square of the difference between the refractive indices of the solute and of the solvent. Before scattering intensities can be converted to molecular weights, the scattering at zero concentration and zero angle must be found since equations (2.56) and (2.61) are only valid when extrapolated to zero. Both extrapolations may be performed graphically on the same plot by the method of Zimm (73,74). This is explained fully in section 3.2. From such a plot the weight average molecular weight is obtained, the $z$ average end to end distance and the $z$ average second virial coefficient.

Both polydispersity and branching effect the angular distribution of light scattered by a Gaussian coil. As a result the zero concentration line is no longer asymptotic and the deviation from ideal behaviour is marked by curvature. The initial slope of this line will give the radius of gyration or end to end distance of a chain having $z$ average molecular weight. Benoit (75) has show that the ratio of the initial slope $S_0$, to the slope of the asymptote, $S_\infty$, characterises the breadth of the molecular weight distribution since

$$\frac{S_0}{S_\infty} = \frac{2}{3} \frac{N_z}{N_w}$$

where $N$ represents the degree of polymerisation. Consequently the determination of $N_z$, the $z$ average molecular weight readily follows.
2.6 Viscosity.

High polymer molecules have the property of greatly increasing the viscosity of the liquid in which they are dissolved, even when present at low concentrations (although there are a few remarkable exceptions). The higher the molecular weight within a given series of linear polymer homologs, the greater the increase in viscosity as concentration is increased. Hence, viscosity measurements afford a measure of molecular weight. This is not an absolute value for the molecular weight since the dependence of intrinsic viscosity on molecular weight must be established in each individual case by comparison with molecular weights determined by an absolute method.

The viscosity of a polymer solution depends also on the size of the polymer molecules in solution. However, to derive a meaningful relationship the concentration of the solution must be such that there is no entanglement between the different polymer molecules. On the other hand size also depends on the thermodynamic interactions between solvent and polymer as described in section 2.3. The relationship between size, as expressed by the expansion factor $\alpha$ and the solvent-polymer interaction constant is given by equation (2.38). It would be expected therefore for a polymer solution in a good solvent to have a higher viscosity than in a bad solvent, provided solvent within the polymer coils moves largely with the polymer.

Since the increase of viscosity is very small at low concentrations, the best procedure is to measure it at several concentrations and then extrapolate some function of it to zero concentration.

The ratio of the viscosity $\eta$ of a solution to the viscosity $\eta_0$ of the pure solvent is called the relative viscosity and is given by $\eta_R$.
\[ \eta_R = \frac{\eta}{\eta_o} \]  

The relative increase of the viscosity with respect to solvent is called the specific viscosity and is denoted by 

\[ \eta_{sp} = \frac{\eta - \eta_o}{\eta_o} = \eta_R - 1 \]  

and the intrinsic viscosity is defined by 

\[ [\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} = [(\eta_R - 1)/c]_{c \to 0} \]  

The latter term is the most significant of the various quantities as regards size and shape of the polymer molecules on the viscosity. The ratio \( \eta_{sp}/c \) is a measure of the specific capacity of the polymer to increase the relative viscosity, and the limiting value of this ratio at infinite dilution is called the intrinsic viscosity.

A number of empirical relationships showing concentration dependence of viscosity have been proposed. Huggins (76) showed that

\[ \eta_{sp} = [\eta]c + k'[\eta]^2c^2 \]  

where \( k' \) is approximately constant for a series of polymer homologs in a given solvent.

The intrinsic viscosity may also be defined (76) as follows

\[ [\eta] = [\ln \eta_R/c]_{c \to 0} \]
and when the natural logarithm series is expanded equation (2.69) becomes equivalent to equation (2.71). It follows from equation (2.70) that

\[
\frac{\ln \eta_R}{c} = [\eta] + k'' [\eta]^2 c^2 \quad \ldots \ldots \ldots (2.72)
\]

where \(k'' = k' - \frac{1}{2}\). Generally \(k''\) is negative and smaller in magnitude than \(k'\), consequently \(\ln \eta_R/c\) changes less rapidly with concentration than \(\eta_{sp}/c\).

The dependence of intrinsic viscosity on molecular weight was expressed by an empirical relationship by Mark and Houwink (77)

\[
[\eta] = K M^a \quad \ldots \ldots \ldots (2.73)
\]

\(K\) and \(a\) are constants for a given polymer solvent and temperature. Equation (2.73) has been found to apply to a large number of polymer solvent systems (with fractionated polymers) over wide ranges of molecular weight. Once \(K\) and \(a\) have been established, the measurement of \([\eta]\) provides a convenient method of determining the molecular weight of the sample.

The equations so far apply to homogeneous polymers or at least narrow fractions. In dilute solution the second term of equation (2.70) is negligible and the specific viscosity is proportional to the concentration. For a polydisperse sample the contribution to the specific viscosity of individual molecules can be considered to be additive, thus

\[
\eta_{sp} = \sum \eta_{sp}^i \quad \ldots \ldots \ldots
\]
where $i$ is the number of species. According to equation (2.73) we may write

$$\eta_{sp} = K \sum_{i} M_i^a c_i$$

and since this solution is extremely dilute

$$[\eta] = \frac{\eta_{sp}}{c} = K \sum_{i} \frac{M_i^a c_i}{c}$$

where $c = \sum_{i} c_i$ is the total concentration of the polymer species. If we now define the viscosity average molecular weight $M_v$ as follows

$$M_v = \left[ \sum w_i M_i^a \right]^{\frac{1}{a}} = \left[ \frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right]^{\frac{1}{a}}$$

where $w_i = c_i/c$ is the weight fraction of species $i$ in the polymer and $N_i$ is the number of molecules of that species, then

$$[\eta] = K M_v^a$$

The intrinsic viscosity is most frequently used in characterization of molecular weights of flexible chain polymers. It is also frequently employed for the estimation of the dimensions of the molecular coil. The hydrodynamic properties of polymer molecules in solution are determined by their dimensions. This dependence is, however, often complex and two treatments are commonly used. One, due to Debye (32) where the polymer chain is treated as a free draining coil. Secondly due to Flory (54,62) where the polymer chain is
considered to be an impermeable coil and is thus equivalent
to a solid sphere.

The most convenient model of a polymer molecule for this
treatment is the 'pearl necklace' model in which the chain consists
of a number of beads joined by rigid links.

Let us first consider the free-draining coil. The pearl necklace
consists of \( x \) number of spherical beads of radius \( a \). From Stokes' law the force \( F' \) acting on one of these beads in a liquid of
viscosity \( \eta_o \) and relative velocity \( v \) is

\[
F' = 6\pi a v \eta_o
\] 

\[
\ldots \ldots (2.75)
\]

and the frictional coefficient \( F \) is given by

\[
F = \frac{F'}{v} = 6\pi a \eta_o
\] 

\[
\ldots \ldots (2.76)
\]

The frictional effects acting on the beads give rise to a torque
tending to rotate the coil. When the molecule rotates, however,
new frictional forces are brought into play as segments in the
upper and lower portion of the coil move across the field. For
dynamic stability the sum of the torques acting on the molecule
must be zero and as a result the molecule reaches a compromise
by rotating with an angular velocity, \( w \), equal to half the shear
gradient, \( q \), of the liquid i.e., \( w = \frac{q}{2} \). A complete derivation
of this has been given by Debye (32) in his original treatment.

The velocity at any point in the rotating molecule relative
to the flowing solvent is \( sq/2 \) where \( s \) is the distance of the
point from the centre of the molecule. For the free-draining
model \( sq/2 \) is also the relative velocity of the medium in the
vicinity of a bead since we assume that frictional effects of the
beads are small and the motion of the surrounding medium is only
very slightly disturbed by the movement of the polymer molecule, 
relative to the medium. The frictional force acting on a bead 
is $F_{sq}/2$ and the rate of energy, $E$, dissipated by the action of 
the bead is the product of the force and the velocity, or $F (sq/2)^2$.
The total energy dissipated per unit time by the molecule is therefore 
the sum of each term for the beads, hence

$$\frac{dE}{dt} = \frac{3}{2} \pi a \eta_o d^2 \sum s^2$$  \hspace{1cm} (2.77)

If the polymer concentration is $c_c/cc$, $cN/M$ is the number of 
polymer molecules per cc. The total viscosity is therefore

$$\eta = \eta_o + \frac{3}{2} \pi a \eta_o \frac{N}{M_0} \overline{s^2}$$  \hspace{1cm} (2.78)

where $M_0 = M/x$, the molecular weight of a bead. The intrinsic 
viscosity, which is defined as the limiting value of $(\eta - \eta_o)/\eta_o c$ 
at infinite dilution, see equations (2.68) and (2.69), for a free 
draining molecule is given by

$$[\eta] = \frac{3}{2} \pi a \frac{N}{M_0} \overline{s^2}$$  \hspace{1cm} (2.79)

Hence the intrinsic viscosity is proportional to $\overline{s^2}$, the mean square 
radius of gyration, which, according to equation (2.1) is proportional 
to $r^2 = \propto 2 \frac{M_0}{x}$ and thus to the molecular weight. Disregarding 
the effects of intramolecular interactions on chain configuration 
we may write

$$[\eta] \propto M$$  \hspace{1cm} (2.80)
Since $\alpha^2$ normally increases with $M$, the intrinsic viscosity of a free draining linear molecule should increase with $M$ raised to a power slightly greater than unity. Experimentally it may be shown that it is in fact less than predicted by a factor of 0.4 to 0.5, and therefore casts doubt on the free draining approximation.

This led Flory (54,62) to propose his model of the impermeable coil in which solvent in the interior of the molecule moves with the polymer beads as though it were part of the polymer. The average extension of the molecular coil is the same in every direction and the impermeable coil can be regarded as an equivalent hydrodynamic sphere of radius $R_e$, impenetrable to solvent, and having the same frictional coefficient, $f_o$, as the actual polymer molecule, which is

$$f_o = 6\pi \eta_0 R_e \quad \ldots \ldots (2.81)$$

According to Einstein’s viscosity equation

$$\frac{\eta - \eta_0}{\eta_0} = 2.5 \left( \frac{n_2}{V} \right)^{1/3}$$

where $n_2/V$ is the number of molecules per unit volume and $V_e = (4\pi/3)R_e^3$. Or putting $n_2/V = cN/100M$ where $c$ is the concentration in g/dl, we find

$$[\eta] = 0.025 \times \frac{N}{M} \times \frac{4}{3} \pi R_e^3 \quad \ldots \ldots (2.82)$$

Assuming that $R_e$ is proportional to the average size of the polymer molecule e.g. $(s^2)^{1/2}$, then in the absence of volume effects $R_e$ is proportional to $M^{1/4}$ and therefore so too is the intrinsic viscosity.
\[ [\eta] \propto M^3 \] 

Taking volume effect into account, \( R_e \) and therefore \([\eta]\) should increase more rapidly than \( M^3 \) in accordance with experimental observations.

As a result neither equations (2.80) or (2.83) are strictly true. In fact equation (2.74) with 'a' taking a value between 0.5 and 1.0 holds for most long flexible chains. Kirkwood and Riseman (78) and Debye and Bueche (79) suggested that a real polymer molecule will have large frictional interactions and will be intermediate between the permeable and impermeable model, consequently variations in 'a' were thought to be due to partial permeability. Their treatment is to consider again a stationary polymer molecule in a moving solvent with the shape of the coil remaining undisturbed. The innermost segments of the coil are considered to be shielded so that solvent flow near the centre is very nearly stationary, but on moving outwards its velocity increases. Therefore a transition region occurs at some distance from the centre of the molecule, where the velocity of the solvent relative to the molecule increases from zero to a value approaching its external value. The position of this region will depend on the number and distribution of the beads and on the frictional coefficient \( F \) of a bead. In fact the variable \( F/\eta_o \) is a more useful one to use being independent of \( \eta_o \). It can be varied by altering the diameter of a bead, though at the same time keeping the number of beads and their distribution fixed. If \( F/\eta_o \) is decreased solvent flow will penetrate closer to the centre, leading eventually to the free draining model. If \( F/\eta_o \) is increased solvent penetration will decrease, and, if sufficiently large, only the outer fringes of the molecule will be permeated by the flow.
Any further increase in $F/\eta_o$ will not cause much change in the penetration of solvent. Therefore the frictional coefficient, $f_0$, of the molecule, at fixed $\eta_o$, should become independent of the frictional coefficient, $F$, of a bead, at sufficiently large $F/\eta_o$. It depends in general on the size of the molecule, represented by the root mean square distance $(s^2)^{1/2}$ of a bead or segment from the centre of gravity; the number of beads, $x$; the nature of their distribution; and $F/\eta_o$. Since it is directly proportional to the viscosity of the medium the dependence of $f_0/\eta_o$ on these variables as given by Flory (34) is

$$f_0/\eta_o = \frac{(s^2)^{1/2}}{\Phi} \left( F/\eta_o, x, (s^2)^{1/2} \right) \quad \ldots \ldots \left(2.84\right)$$

$\Phi$ is a dimensionless function of the above variables with an upper asymptotic limit as $F/\eta_o$ and $x$ increase while $(s^2)^{1/2}$ remains constant. Since the effects of $F/\eta_o$ and $x$ are similar they may be replaced by their product having the dimensions of length. Since the function $\Phi$ must be dimensionless it may be assumed to depend on the variable $xF/\eta_o(s^2)^{1/4}$, and equation (2.84) becomes

$$f_0/\eta_o = \frac{(s^2)^{1/4}}{\Phi} \left( xF/\eta_o (s^2)^{1/4} \right) \quad \ldots \ldots \left(2.85\right)$$

The molecular frictional coefficient should depend only on the size and not otherwise on the nature of the polymer, hence

$$f_0/\eta_o = p' (s^2)^{1/4} \quad \ldots \ldots \left(2.86\right)$$

$p'$ is the limiting value of the function $\Phi$. It should be the same for all polymers in all solvents providing they are Gaussian.
i.e., their segment spatial distributions are similar. Equation (2.86) can also be written

\[ \frac{f_0}{\eta_0} = \frac{3}{16} \bigg( \frac{a}{\eta_0} \bigg)^2 \frac{X^2}{M} \]

(2.87)

since for a randomly coiled chain \( s^2 = \frac{r^2}{6} \) which would give

\[ \eta_0 = \frac{P}{(6)^{\frac{1}{2}}} \]

Returning to the Kirkwood Riseman (78) model of the partially permeated coil, the molecule rotates with an angular velocity \( \omega = q/2 \), assuming it to behave as if rigid. Solvent within the molecule will have the velocity of the chain segments, and permeation of the molecule by surrounding liquid is less the greater \( P/\eta_0 \). Also the greater the disturbance in the solvent caused by increasing \( P/\eta_0 \) is compensated for by a decrease in the number of segments subjected to the counterflow of the solvent. Their theory leads to

\[ [\eta] = \left( \frac{\pi}{6} \right)^{\frac{3}{2}} \times \frac{1}{100} \frac{X^2}{M} \]

\[ \frac{X}{\eta_0} \frac{(r^2)^{\frac{1}{4}}}{M} \]

(2.88)

where \([\eta]\) is in d1/g and

\[ X = \left( \frac{\pi^3}{6} \right)^{\frac{1}{4}} \frac{P}{\eta_0} \frac{(r^2)^{\frac{1}{4}}}{M} \]

and \( Y(X) \) is a function of \( X \). The intrinsic viscosity depends primarily on the ratio \( \frac{(r^2)^{\frac{1}{2}}}{M} \). Secondarily it depends on a function \( Y(X) \) similarly to that in the function \( \frac{f_0}{\eta_0} \) of equation (2.85) for the frictional coefficient \( f_0 \). At large \( X \), that is if \( X/\eta_0 \) is sufficiently large, \( XY(X) \) approaches the asymptotic limit 1.588, which leads to the conclusion that for polymers with molecule weight greater than about 10,000, \( XY(X) \) should be at or near the limiting value. Then, in analogy with equation with equation (2.85)
\[ [\eta] = \bar{\eta} \left( \frac{r^2}{x} \right)^{\frac{3}{2}} M^\frac{1}{4} \alpha^3 \] .......(2.89)

where
\[ \bar{\eta} = 0.01588 \left( \frac{\pi}{6} \right)^{\frac{3}{2}} \mathcal{N} = 3.6 \times 10^{21} \] .......(2.90)

Like \( P \) above \( \bar{\eta} \) is independent of the characteristics of the given chain molecule apart from it being spatially arranged as a randomly coiled chain molecule. In analogy to equation (2.86) we may write
\[ [\eta] = \bar{\eta}' \left( \frac{r^2}{x} \right)^{\frac{3}{2}} M \] .......(2.91)

and \( \bar{\eta}' = 6^{\frac{3}{2}} \bar{\eta} \).

According to Kirkwood and Riseman, the intrinsic viscosity is considered to be proportional to the ratio of the effective volume of the molecule in solution, divided by its molecular weight. Possibly the best theory to date of molecular weight dependence on viscosity of dilute polymer solutions is that of Flory and Fox (55). They pointed out that the excluded volume so far neglected could result by itself in 'a' taking any value from 0.5 to 1.0. The quantity \( \left( \frac{r^2}{x} \right)^{\frac{3}{2}} \) was split into its component factors \( \left( \frac{r^2}{x} \right)^{\frac{3}{2}} \) and \( \alpha^3 \). Equation (2.89) rewritten then becomes
\[ [\eta] = \bar{\eta}_0 \left( \frac{r^2}{x} \right)^{\frac{3}{2}} \left( \frac{r^2}{x} \right)^{\frac{3}{2}} M^\frac{1}{4} \alpha^3 \] .......(2.92)

Since \( \frac{r^2}{x} \) is independent of \( M \) for a linear polymer of a given unit structure (see section 2.3), we may write
\[ [\eta] = kM^\frac{1}{4} \alpha^3 \] .......(2.93)
where

\[ K = \frac{1}{\phi_0} \left( \frac{r_o^3}{M} \right)^{\frac{3}{2}} \]  

\text{......(2.94)}

Equation (2.94) is obviously the same as equation (2.46), the term \( \frac{1}{\phi_0} \) merely representing the universal constant when the polymer has its unperturbed dimensions, as denoted by the subscript zero.

Originally, the Kirkwood Riseman treatment, equation (2.90) gave a value of \( 3.6 \times 10^{21} \) for the universal constant, where \( r \) is expressed in cms., \( M \) in units of molecular weight and intrinsic viscosity in decilitres per gram. This has since been corrected by Kirkwood, Zwanzig and Ploct (80) to give \( 3.36 \times 10^{21} \). Flory (54), collected at the time, the available data of several workers, and found \( \phi \) values ranging from \( 1.95 \times 10^{21} \) to \( 2.6 \times 10^{21} \) with a mean at \( 2.1 \pm 0.2 \times 10^{21} \). At the same time he pointed out that it is important to use well fractionated samples otherwise there is uncertainty in the nature of the averages of the measured quantities \( \frac{1}{\phi} \left( \frac{r^3}{M^2} \right) \) and \( M \). As a result he suggested that the value \( 2.1 \times 10^{21} \) should be 15 - 20\% greater and proposed the figure \( 2.5 \times 10^{21} \). This was later obtained from experimental data by Flory et al (81).

According to more recent theoretical calculations of Auer and Gardner (82) and Zimm (83), the asymptotic limit of the function \( XYZ(X) \) in equation (2.88) has the value \( 1.259 \) which leads to a theoretical value of \( \phi \) of \( 2.87 \times 10^{21} \). It is this value that has been used in the subsequent calculations.
2.7 Osmometry

Osmotic pressure is, next to viscosity, perhaps the most widely measured property of polymer solutions. It is used to obtain either molecular weights or information on the thermodynamic properties of the solution (84).

If a solution is covered with a layer of pure solvent then the two layers will gradually mix by diffusion until the solute concentration is uniform throughout the system. With osmosis, however, we are dealing with a system in which the solution is separated from pure solvent by a barrier permeable only to solvent molecules. The activity of the solvent in the solution is less than the activity of solvent in pure solvent, thus, the thermodynamic basis of osmotic pressure can readily be seen. There results a spontaneous tendency for the solvent to move from the relatively high free energy state of the pure solvent to the relatively low free energy state of the solution, until equilibrium is reached and the solutions either side the membrane are at the same chemical potential. This can only occur by pressure build up on the solution side.

Experimentally, equilibrium can be attained more rapidly by applying an external pressure to oppose the liquid flow through the membrane. If the pressure is applied on the side of the solution the activity of the solvent in the dilute solution may be restored to that of the pure solvent. The pressure that will just do this so that there is no movement across the membrane is equal to the osmotic pressure \( \Pi \). The change in activity with pressure is given by

\[
\left( \frac{\partial \ln a_i}{\partial P} \right)_{T, x_1} = \frac{V_1}{RT}
\]
where $V_l$ is the partial molar volume of the solvent, which for the dilute solution may be replaced by the molar volume $V_l$ of the pure solvent, and $x_l$ is its mole fraction. Thus, at osmotic equilibrium

$$
\int_{a_l}^{1} \text{d} \ln a_l = \int_0^{\pi} \frac{(V_l/RT)}{dP}
$$

$V_l$ is independent of pressure for the minute pressures involved

$$
-\ln a_l = \pi \frac{V_l}{RT}
$$

For an ideal solution, which is sufficiently dilute, solvent activity is equal to the mole fraction, $a_l = x_l$ and since $x_l$ is very near unity

$$
-\ln x_l \approx 1 - x_l = x_2 \approx c \frac{V_l}{M}
$$

On substituting equation (2.96) into (2.95)

$$
\frac{\pi}{c} \approx \frac{RT}{M}
$$

$M$ is the molecular weight of the solute and $c$ its concentration in g/cc. At infinite dilution, this leads to van't Hoff's limiting law for osmotic pressure

$$
\left( \frac{\pi}{c} \right)_0 = \frac{RT}{M}
$$

The particular average molecular weight obtained from this measurement requires definition. For a mixture of macromolecules
with molecular weights $M_2$, $M_3$, .... etc., present at concentrations $c_2$, $c_3$, .... etc., the right hand side of equation (2.98) becomes

$$RT \sum_i c_i / M_i$$

or, where $c = \sum_i c_i$ is the total macromolecular concentration in g/cc

$$\left( \frac{\pi}{c} \right) c = 0 = \frac{RT \sum_i c_i / M_i}{\sum_i c_i}$$

Since $c_i$ is proportional to $N_i M_i$ where $N_i$ is the number of moles of the $i$th solute we have

$$\left( \frac{\pi}{c} \right) c = 0 = \frac{RT \sum_i N_i M_i}{\sum_i N_i M_i} = \frac{RT}{M_n}$$ ....(2.99)

hence osmotic pressure is a measure of the number average molecule weight.

If the solutions behaved ideally, Van't Hoff's law, equation (2.99), would apply and $\pi/c$ should be independent of $c$. However, due to the large effective size of the polymer molecules in solution, and the interactions which set in between them at low concentrations, the solutions cease to behave ideally and $\pi/c$ increases with $c$. It is therefore necessary to extrapolate to infinite dilution for the determination of molecular weight. Several workers (85,86,87) have shown how osmotic pressure may be expressed as a function of concentration

$$\frac{\pi}{c} = RT \left( \frac{1}{M} + A_2 c_2 + A_3 c_2^2 + \ldots \right)$$ ....(2.100)

where $A_2$, $A_3$ etc., are the second, third etc., virial coefficients and are given by equation (2.23) according to the Flory-Huggins theory.
2.8 **Dielectric constant and dipole moment**

Since molecules comprise of charged units, much of the behaviour of molecules is understandable in terms of electrical interactions. Quantum mechanics reveal the electron distribution of a molecule and can deduce how an assembly of charges making up a molecule would react with other molecules, or with the surrounding medium, or with an electric field. However, such applications of quantum mechanics cannot be made except for the simplest systems. Experimentally, the investigation of dielectric properties provides an important approach to an understanding of the structure of matter by employing classical mechanics.

The dielectric constant of a medium is a measure of its polarizability, that is, the polarization produced in the medium by the action of an electric field. It is interpreted at molecular level, the polarizability being attributed to an average contribution \( \alpha \) from each molecule. It is a complementary function being made up from the distortion of the charge distribution within the molecule, from the orientation of the permanent dipoles within a molecule and in an ionic media an additional contribution due to the displacement of ions relative to one another. We shall only be concerned with the use of dielectric measurements to measure dipole moment, that is the first and second of the three phenomena given above.

A relationship known as the Clausius-Mosotti equation has been derived (88) which relates polarizability \( \alpha \) to the dielectric constant of the material

\[
\frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d} = \frac{4}{3} \pi N \alpha
\]

\(\ldots..(2.101)\)
where \( d \) is the density, \( d/N \) is the number of moles per c.c. and \( (d/N)^{1/3} \) the number of molecules per c.c. \( \epsilon \) is the dielectric constant and may be defined by

\[
\epsilon = \frac{C}{C_0}
\]

.....(2.102)

where \( C_0 \) is the capacitance of the condenser in vacuum and \( C \) the capacitance with dielectric material.

Debye (89) went further by showing that the polarizability was made up of the permanent and induced effects such that

\[
\chi = \chi_o + \frac{\chi^2}{3kT}
\]

.....(2.103)

Then a more general expression than equation (2.101) is obtained by substituting equation (2.103)

\[
\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} = \frac{4\pi \chi}{3} \left( \chi_o + \frac{\chi^2}{3kT} \right)
\]

.....(2.104)

This is known as the Debye equation and a derivation of it is given by Smyth (90).

The limitations of the Debye equation have been shown (91-93) in that moments calculated from gas dielectric constants and from solution dielectric constants differ. The application of the Debye equation to dilute solution is an approximation since polarization cannot be treated as linearly dependent upon field strength as Debye suggested. The interaction of a molecule with its environment must be taken into account.

Development of the theory by Onsager (94) took into account
the long range dipolar interaction between molecules. His equation
based on the assumptions of spherical molecules and negligible
short range interactions is

\[
\frac{(\theta_0 - \theta_n)(2\theta_0 + \theta_n)}{\theta_0(\theta_0 + 2)^2} = \frac{4N}{9kT} \frac{\mu^2}{z} \quad \text{......(2.105)}
\]

where \(N\) is the number of molecules/cc as defined above, \(\theta_0\) is the
limiting low frequency dielectric constant as found experimentally
from equation (2.102), \(\theta_\infty\) is the limiting high frequency dielectric
constant and \(z\) the degree of polymerisation. At high frequency,
where the dielectric constant is independent of the permanent dipoles
it can be measured directly as the square of the refractive index of
the material. Hence

\[
\theta_\infty = n^2 \quad \text{......(2.106)}
\]

Guggenheim (95) has developed an equation whereby solution
moments are calculated from polarization values obtained by extra-
polating to infinite dilution the variations of dielectric constant
and refractive index with concentration. Smith (96) took
Guggenheim's equation one step further and showed that since
solutions are usually made up by weight, the simplest form of
expressing the concentration is by weight fraction \(w_2\) of solute.
This eliminates the measurement of solution densities and allows
the Guggenheim-Smith equation to be written as follows

\[
\frac{\mu^2}{z} = \frac{27kT}{4\pi \mathcal{N}} \frac{N}{d_1} \left[ \frac{\omega}{(\theta_0 + 2)^2} - \frac{\psi}{(n_1^2 + 2)^2} \right] \quad \text{......(2.107)}
\]
where $d_1$ and $n_1$ are the density and refractive index of solvent

$M_0$ is molecular weight which for a polymer is the molecular weight of the repeat unit and

$$
\alpha = \frac{d\theta}{dw_2} \quad \text{and} \quad \nu = \frac{dn}{dw_2} \quad \ldots \ldots (2.108)
$$

where $\alpha$ and $\nu$ represent the variation of refractive and dielectric constant of the solution with concentration.

This method can be applied to large and small molecules, but the correction for distortion polarization contained in the second term in the bracket, is probably less accurate than in the Onsager method.
3.1.1 Sample synthesis

Szwarz (87) has shown within the last 15 years that certain polymerisation reactions, involving carbanions as active species, exhibit a complete absence of chain termination. These systems are therefore unique, in that each growing chain will continue to add monomer units as long as there is monomer left to do so and hence the chain length is determined by the ratio between the total number of monomer units polymerised and the number of active chains present. This condition will only apply in the absence of any component which can react with these carbanions e.g., water, acids, alcohol etc.

Cyclic oxides have been shown to polymerise via cationic centres in this type of system and it is with members of the poly (ether) series that we are concerned with here. They are

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Polymer</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxacyclobutane</td>
<td>$\text{--CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{O} \quad \text{--}_n$</td>
<td>P.Tri.M.O.</td>
</tr>
<tr>
<td>tetrahydrofuran, T.H.P.</td>
<td>$\text{--(CH}_2)_4 \quad \text{--O} \quad \text{--}_n$</td>
<td>P.Tetra.M.O.</td>
</tr>
<tr>
<td>tetrahydropyran, T.H.P.</td>
<td>does not homopolymerise</td>
<td>P.Penta.M.O.</td>
</tr>
</tbody>
</table>
Two members of the series under investigation are P.Tri.M.O. and P.Tetra.M.O. A wide range of samples of both polymers have been prepared and studied and their synthesis is described below. Attempts were also made to obtain P.Penta.M.O. and P.Hexa.M.O.

3.1.2 High vacuum apparatus

Very rigorous experimental conditions are required in polymerisation work in order to obtain quantitative data. An apparatus is required with which it is possible to remove all impurities that can react with either the initiator or the growing polymers produced. Some impurities such as water can be removed by ensuring thorough drying of reactants. However for the reaction studied here traces of carbon dioxide, water and oxygen from the air must be excluded. A high vacuum apparatus permits these rigorous experimental conditions. The vacuum system employed (98) is shown in Fig.2. It is basically composed of an oil pump, A, capable of giving a vacuum of the order $10^{-1}$ to $10^{-2}$ mm of mercury. This pump acts as a backing pump for the mercury diffusion pump, B, which reduces the pressure in the system to better than $10^{-5}$ mm of mercury pressure. A liquid nitrogen trap, C, is used to condense any condensable gases so that the pressure measured by the gauge, E, is that of the noncondensable gases. In the absence of appreciable amounts of noncondensable gases a volatile material can be rapidly transferred from one region to another, provided the second region is colder than the first. This ability of a volatile material to distil to a colder region is used in order to transfer monomer etc., within the vacuum line.

All materials employed were therefore degassed prior to any
HIGH VACUUM APPARATUS

A BACKING PUMP
B DIFFUSION PUMP
C COLD TRAP
D MAIN VACUUM LINE
E VACUUM GUAGE
subsequent operation such as drying or distilling. The degassing procedure is as follows. The flask containing the liquid to be degassed was connected to the vacuum line and cooled until frozen. After evacuating for 5 minutes it was allowed to thaw out to room temperature. The freeze, pump, thaw procedure was repeated until all gas had been pumped off as indicated by the vacuum gauge showing no change.

3.1.3 Poly(tetramethylene oxide), P.Tetra.M.O.

Tetrahydrofuran, T.H.F., polymerises to give a polymer called polytetrahydrofuran, or as noted above, P.Tetra.M.O. The method adopted is that of Dreyfuss and Dreyfuss (99) in which the polymerisation of T.H.F. is brought about by \( p \)-chlorophenyldiazonium hexafluorophosphate catalyst.

\[
\begin{align*}
\text{Cl} & \quad \text{Phosfluorogen A.} \\
\text{N} & = \text{N} - \text{PF}_6
\end{align*}
\]

The catalyst, referred to from now on as Phosfluorogen A, was obtained as a crude red brown material (100). It was purified by recrystallisation from water at 0°C and after pumping dry for 24 hours was obtained as white crystals, (melting point 152°C). T.H.F., and \( \alpha \) methyl styrene were stirred and stored over calcium hydride on the vacuum line for 2 days. After thoroughly degassing, as described above, the appropriate amount of methyl styrene was passed over onto a sodium-potassium (3 : 1) amalgam, such that amalgam was always in excess. The T.H.F. was then distilled over the sodium-potassium/\( \alpha \) methyl styrene complex where it was stirred for a further 24 hours as a final purification step. A known amount of catalyst was placed in the polymerisation ampoule and then transferred to the vacuum line and
evacuated. A middle fraction of pure monomer was then distilled into the polymerisation ampoule and the ampoule sealed off and separated from the apparatus. It was placed in a bath at 50°C for approximately 30 minutes and then thermostated at 25°C for the required polymerisation time. Both purification and polymerisation were carried out at pressures of $10^{-4}$ mm of mercury or better.

The polymer was obtained as a crude brown mass. It was dissolved up in THF containing 10% acetic acid, to terminate the reaction, and then precipitated with methanol and filtered off. This was redissolved in benzene. To ensure the polymer was free of monomer and catalyst, it was reprecipitated with methanol, filtered off again, dissolved up in benzene, and freeze dried for 3 days.

A series of samples covering a range of molecular weight were produced. Molecular weight is a function of the amount of catalyst used and by appropriate adjustment of catalyst concentration, variation in molecular weight is achieved.

As shall be discussed more fully in chapter 5, the polymerisation procedure was varied in an endeavour to obtain monodispersed polymers. Attempts were made to 'seed' the monomer, so called because catalyst was dissolved in the minimum amount of monomer required, thus forming many active growing centres of short chain length. Polymerisation proceeded when the rest of the monomer was transferred over.

3.1.4 Poly(trimethylene oxide), P.Tri.M.O.

The polymerisation of oxacyclobutane to give P.Tri.M.O. is similar to that above in so far as it is a cationic process initiated by Phosfluorogen A. Freshly recrystallised catalyst was used. Oxacyclobutane monomer was dried over calcium hydride before distilling onto the sodium-potassium/methyl styrene complex.
A middle fraction of pure monomer was then distilled into the polymerisation ampoule containing pre-calculated amount of catalyst. Since Phosfluorogen A is very soluble in oxacyclobutane, it was only necessary to hold the ampoule at 50°C for a short time. The ampoule was sealed, placed in a thermostat at 50°C for 5-10 minutes and left to polymerise at 0°C. A series of polymers were made with polymerisation times of up to 24 hours.

The polymer was separated from catalyst after the method of Rose (101). Crude P.Tri.M.O. was dissolved in a 10% acetic acid/diethyl ether solution to isolate the polymer and terminate the reaction. The ether extract was washed with 20% sodium hydroxide solution and then several times with water. It was then left to dry over potassium carbonate. The polymer was precipitated from the dried ether extract by cooling down to -80°C. It was filtered off in a nitrogen atmosphere and then redissolved in benzene. The pure polymer was finally obtained after freeze drying for 3 days.

3.1.5 Poly(pentamethylene oxide) and poly (hexamethylene oxide)

Attempts were made to synthesise P.Penta.M.O. and P.Hexa.M.O. from tetrahydropyran and oxacycloheptane respectively. Purification procedures were as before and initiation was undergone at 50°C for 30 minutes as in the case of T.H.P. Polymerisations were attempted over a wide range of temperature, -70°C to +55°C, but no high polymer was formed.

3.1.6 Poly (3-chlorostyrene) and Poly (4-chlorostyrene)

Both samples of poly (3-chlorostyrene) and poly (4-chlorostyrene) were used, as prepared by Dr. R.E. Wetton. They were obtained by heating respectively highly purified 3-chlorostyrene and 4-chlorostyrene to 80°C, until 20% polymerised. The polymers were freed of monomer by precipitation from benzene solution using methanol as precipitant, and dried under vacuum.
3.2 Light Scattering

3.2.1 The Instrument

A Sofica light scattering instrument was used throughout and full details of its design etc., are given in the manual (102). The essential features are shown in Fig. 3a.

Light is provided by the mercury lamp, A, and, after passing through a series of slits, prisms, lenses and filters is obtained as a narrow, parallel, sharply defined primary beam free from stray light. The light was unpolarized and a green filter was used to give light of wavelength 5461Å. The vat liquid, D, in which the cylindrical cell, E, is immersed, is dependent upon polymer solvent, but as far as possible is chosen to have a similar refractive index as the cell walls, so that no correction is needed for back reflection at the glass surface. The scattering cells, made from optical glass, are accurately cylindrical and polished. The cell rotates with the thermostat about the centre of the turntable. The vat liquid may be thermostated to within 0.1°C, for working at precise temperatures. For temperatures below room temperature coolant is passed around the vat via the coolant tubes, F.

The scattered beam is reflected upwards and then horizontally to a photomultiplier, G, by total-reflectance prisms, B. Any incident beam remaining after passing through the cell is absorbed in a glass filter placed at the end of the vat to reduce reflection at the trap end.

To eliminate the effect of fluctuations in the light source, the intensity of the scattered light as measured by the photomultiplier, G, is compared to the intensity of a portion of the incident beam, measured by an ordinary vacuum photocell, C. The ratio of the currents is measured by passing them in opposite directions through a potentiometer.
LIGHT SCATTERING APPARATUS

A MERCURY LAMP WATER COOLED
B REFLECTANCE PRISMS
C STANDARD PHOTOTUBE
D SOLVENT VAT
E SOLUTION CELL
F VAT COOLANT TUBES
G MEASURING PHOTOTUBE
Scattering was measured at various preselected angles ranging from $0^\circ - 150^\circ$ to the incident beam. For a given angle the cell was rotated and the scattering obtained as the average of several readings. This, it is hoped, would eliminate any errors due to imperfections in the cell walls.

### 3.2.2 Clarification of solutions

The complete removal of extraneous matter is an essential for good light scattering results. Polymer solutions will contain contaminants of varying size, all of which will cause erroneously high scattering values and consequently false results.

A.R. grade solvents were used and these were further purified by doubly distilling and drying over sodium. They were then rendered dust free by filtering under pressure through two Oxoid membrane filters (standard grade 3.1 mm. grid) placed either side a sintered glass filter. All glassware was thoroughly cleaned then washed with dust free solvent. Several workers\(^\text{(103-105)}\) have gone into great detail over the cleaning procedures necessary for solution and glassware in light scattering work. A simplified version of Thurmond's (103) solvent spray was designed for removing the final traces of dust from the scattering cell. Polymer solutions, made up from dust free solvents, were centrifuged in a Janetski T 24 high speed centrifuge at 10,000 r.p.m. for 2 hours. The top portions were then transferred by dust free pipette to the scattering cell. All subsequent dilutions were made in situ by adding the appropriate amount of solvent and stirring with a dust free glass stirrer.

### 3.2.3 Calibration

Light scattering is an absolute method of measuring molecular weight, however the Sofica instrument does not give absolute intensities since there is no direct monitoring of $I_0$, the initial light intensity, and a calibration procedure is necessary. The scattering of benzene has been very widely studied and its Rayleigh ratio, $R_{80}$,
has now been precisely given (106). The angular scattering intensity of a benzene sample was checked against the calculated values obtained from the Einstein equation

\[ I_\theta = I_{90} \left[ 1 + \frac{(1 - P_u)}{(1 - P_u) \cos^2 \theta} \right] (\sin \theta)^{-1} \]  

(3.1)

where \( P_u \) is the depolarisation ratio as defined in section 2.5, and the two values are compared in Table 3.1.

Table 3.1 Angular scattering intensities of benzene

<table>
<thead>
<tr>
<th>( \theta )</th>
<th>( I_\theta ) (theoretical)</th>
<th>( I_\theta ) (expt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>260</td>
<td>235</td>
</tr>
<tr>
<td>142.5</td>
<td>210</td>
<td>202</td>
</tr>
<tr>
<td>135</td>
<td>170</td>
<td>168</td>
</tr>
<tr>
<td>120</td>
<td>127</td>
<td>126</td>
</tr>
<tr>
<td>105</td>
<td>106.5</td>
<td>106</td>
</tr>
<tr>
<td>90</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>75</td>
<td>106.5</td>
<td>106.5</td>
</tr>
<tr>
<td>60</td>
<td>127</td>
<td>126</td>
</tr>
<tr>
<td>45</td>
<td>170</td>
<td>167</td>
</tr>
<tr>
<td>37.5</td>
<td>210</td>
<td>203</td>
</tr>
<tr>
<td>30</td>
<td>260</td>
<td>260</td>
</tr>
</tbody>
</table>

For routine operation this is an inconvenient method of checking the calibration of the instrument. In practice a simple method was to use the glass standard as supplied with the instrument, for all further measurements.
3.2.4 Treatment of data

The data was subjected to the double extrapolation method due to Zimm (73). $Kc/R_\theta$ is plotted against $sin^2 \frac{\theta}{2} + kc$ where $k$ is a constant chosen to make the concentration term comparable with $sin^2 \frac{\theta}{2}$. It is better to extrapolate the lines of constant angle to zero concentration before extrapolating the lines of constant concentration to zero angle, because of the uncertainty present with the lower angles. This produces a grid like graph, the two limiting lines of which $(Kc/R_\theta)_0 = 0$ and $(Kc/R_\theta)_\theta = 0$ on extrapolation should meet at the same intercept. The value of this intercept is equal to the reciprocal of the weight average molecular weight.

From the slope of the line of zero angle is calculated the second virial coefficient, $(A_2)_z$, as defined in equation (2.62). The mean square radius of gyration of the polymer chain is found from the limiting slope of the $c = 0$ line since

$$s^2 = \text{Slope (c = 0)} \frac{3 \frac{M_w}{M}}{16 \pi^2 \left( \frac{\lambda_0}{n_0} \right)^2}$$

......(3.2)

and by equation (1.1) the mean square end to end distance follows. Dimensions are also quoted in terms of the characteristic ratio

$$C = \frac{x^2}{n_0 l^2}$$

......(3.3)

where $l^2$ is the mean square bond length, $n$ is the total number of bonds, which is simply the product of the degree of polymerisation and the number of bonds per monomer. As explained in section 2.5 it is the $z$ average end to end distance which is obtained from light scattering. Consequently, when using the characteristic ratio,
n must be calculated with respect to the $z$ average molecular weight. This was done using the Benoit (75) treatment of polydispersity on the angular distribution of light. In equation (2.66), see below, the initial slope and the slope of the asymptote of the $c = 0$ line may be determined from the Zimm plot, and, knowing the weight average degree of polymerisation the $z$ average degree of polymerisation may be calculated.

$$\frac{S_0}{S_\infty} = \frac{2}{3} \frac{N_z}{N_w}$$

From this $n$ readily follows.
3.3 Differential Refractometry

The determining factor for accurate light scattering work is in the accuracy of the evaluation of the refractive index increment, \((\text{dn}/\text{dc})\). Any fractional error here is immediately doubled since it appears as the square in Debye's equation. A P.C.L. differential refractometer was used for these determinations similar to that devised by Brice and Halwer (107) and a diagrammatic sketch of the optical system is shown in Fig. 3b. It comprises essentially a lamp housing containing a mercury lamp projecting its beam via a slit and monochromatic filter through a differential cell of the double prism type and finally via a projector lens onto a microscope fitted with micrometer eyepiece. The eyepiece is fitted with a 10 mm. fixed scale and a drum divided to 0.01 mm. All parts are carefully aligned on an optical bench. The cell is enclosed in a constant temperature unit which allows solutions to be precisely thermostated and the cell holder can be rotated about a vertical axis through 180°.

The two cell compartments were filled with solution and solvent respectively, solution always being put into one particular compartment of the cell since refractive index deviations may be positive or negative depending on solvent. After allowing time for temperature equilibrium, with the cell in the 0° position, \(d_2^{0°}\) the scale reading of the slit image was determined by focussing the microscope and centering the cross-wire on the slit image. Subscript 2 denotes solution. The determination was repeated about six times. The cell was then turned through 180° and the new position \(d_2^{180°}\) of the slit image determined in a similar manner. Both compartments were then filled with solvent and the slit image positions \(d_1^{0°}\) and \(d_1^{180°}\) determined in the same way. The total displacement \(\Delta d\) for a given solution is
DIVIDED CELL MOUNTED ON TURNTABLE

DIFFERENTIAL REFRACTOMETER
\[ \Delta d = (d_1^0 - d_1^{180}) - (d_2^0 - d_2^{180}) \quad \ldots (3.4) \]

The measured deviation, \( \Delta d \), is related to the refractive index difference, \( \Delta n \), by the relationship

\[ \Delta d = 2l \tan \alpha/2 (\Delta n) \quad \ldots (3.5) \]

where \( \alpha \) is the angle of the dividing wall and \( l \) is the distance from cell to eyepiece. Since the refractive index between solution and solvent is proportional to \( \Delta d \) then,

\[ \Delta n = K \Delta d \quad \ldots (3.6) \]

\( K \) the proportionality constant can be evaluated from solutions of known refractive index. In the present work sucrose solutions were used on which refractive index differences have been carefully measured (108). Sucrose, of concentration 3.5g/100g of sucrose solution, has a \( \Delta n \) of 0.0050030 using light of wavelength \( 5461\AA \).

This allows \( \Delta n \) to be determined for different polymer solutions, and, knowing their concentration \( \Delta n/ \Delta c \) follows.
3.4 Viscometry.

Viscosities were measured in a capillary flow viscometer of the Ubbe10hde suspended level type. The advantage of this type of viscometer is that measurements are independent of the volume of liquid, provided there is a certain minimum volume present. Dilutions can be made in the viscometer and viscosities at a whole series of concentrations can be measured with a single sample. The time taken for the level of solvent or solution to pass between two fixed marks is determined. The flow time, $t$, is proportional to viscosity since

$$\eta \propto \frac{\rho}{t}$$

where $\rho$ is the density of the liquid. In dilute solutions, therefore, where the density is not significantly different from that of solvent and $t_0$ is flow time of solvent,

$$\eta_R = \frac{t}{t_0}$$

The measurement of viscosity ratios is obtained with greater relative accuracy than that from absolute measurements since any instrument errors will be the same for solution and solvent. The dimensions of the instrument need not be known. The factors influencing accuracy are temperature and timing.

In practice the viscometer was clamped in a thermostat bath which could be regulated to within $0.02^\circ$C. Once in position the viscometer was not moved again since all dilutions were simply made by adding the appropriate amount of solvent. The flow times were measured with a stop watch and the mean of several readings taken. Intrinsic viscosities were calculated by the graphical method explained in section 2.6.
Initially, the shear stress of the viscometer was checked. Experimental determinations were made at several different values of the mean velocity gradient (rate of shear) and the calculated intrinsic viscosities extrapolated to zero velocity gradient. The viscometer was found to be of low shear stress and shear variations were less than 1%, consequently shear corrections were ignored.
3.5 Osmometry.

A Hewlett-Packard Model 502 high speed membrane osmometer was used for measuring osmotic pressure, details of which may be found in the manual (109). Fig 4 shows the apparatus in diagrammatic form. An optical system is used for detecting flow of solvent through the membrane. The light beam is able to focus at either the top or bottom of an air bubble introduced into the capillary on the solvent side of the membrane. Any movement of solvent through the membrane will cause the bubble to move, this will vary the amount of light falling on the detector and hence activate the servo motor. This automatically adjusts pressure by varying the height of the elevator reservoir so preventing net flow. Since practically no flow of solvent is needed to establish osmotic pressure, the whole process takes only minutes, and causes no dilution of the solution on the other side of the membrane.

Number average molecular weights, see section 2.7, can be measured on this instrument over the range 20,000 to more than 1,000,000. It may be thermostated at any temperature from room temperature up to 65°C. The cellulose membranes used in the instrument are packaged in an aqueous solution and must be converted for use in organic solvents. The membrane was first rinsed with distilled water and then successively soaked in

1. 50-50 solution of water-isopropanol
2. isopropanol
3. 50 50 solution of isopropanol-toluene
4. toluene

for a minimum of 4 hours in each but generally overnight. To transfer from toluene to another organic solvent the membrane was soaked in a 50-50 solution of toluene and the solvent concerned and then transferred
1) SYPHON VALVE
SAMPLE STACK
-MEMBRANE CHAMBER-
CAPILLARY
LIGHT SOURCE
BUBBLE
DETECTOR

SERVO MOTOR
READING
ELEVATOR RESERVOIR

HIGH SPEED MEMBRANE OSMOMETER.
to the new solvent.

In operation, the sample stack (see Fig. 4.) is first filled with solvent, the syphon valve opened and solvent drained through until the syphon system is operating effectively. A series of polymer solutions are then fed into the instrument in order of increasing concentration. Having established the solvent level, solvent is replaced by the most dilute solution. This is introduced into the sample stack and rinsed through by opening the syphon valve. Since the total volume of solution needed to fill the membrane chamber and sample stack to the reference mark is only 0.3 ml., a total volume of 1 - 2 mls., of solution is adequate. Two measurements were made at each concentration, the osmometer being rinsed through between measurements. Most membranes adsorb polymers from solution to a greater or less extent and the purpose of the rinsing is not only to remove traces of solution remaining from the previous measurement but also to ensure that the solution is in equilibrium with the membrane.

The limiting value of $\pi/c$ at infinite dilution has been shown to be a true measure of the molecular weight of the polymer, irrespective of size, shape or nature of solvent used. The accuracy of the molecular weight determination depends considerably on the extrapolation of the experimental measurements to infinite dilution (110). Two approaches are possible. Firstly the curves predicted by the lattice or dilute solution theories are taken as guides and the experimental points fitted to them in order to make the extrapolation. Or, secondly, extrapolate on an empirical basis drawing the best curve through the experimental points. The osmotic head can be measured to 0.01 cm, greater accuracy is required for curve fitting. Consequently empirical extrapolations of linear, or nearly linear $\pi/c$ versus $c$ plots were used. As can be seen from equation (2.100) the slope of this graph allows the osmotic second virial coefficient to be determined.
3.6. Dipole Moments in Solution

3.6.1 Apparatus

The dipole moments of P.Tri.M.O. and P.Tetra.M.O. were studied in solution using a Marconi Dielectric Test Set Type TF 704C (111). Measurements can be made at any frequency over the range $5 \times 10^4$ Hz. to $10^8$ Hz. The method of measurement and the design of the test jig incorporated in the apparatus are due to Hartshorn and Ward (112). A simplified circuit diagram is shown in Fig. 5. The amplitude of the oscillator output is controlled by an arrangement of coarse and fine resistors. One of two oscillators could be plugged into the circuit depending on whether the frequency of operation was in the lower or upper half of the range of the instrument. The oscillator circuit is coupled to a tuned circuit of various interchangeable coils, $L$, and two parallel plate condensers. The condensers are both precisely calibrated with micrometer adjustments. The larger of the two adjustable capacitors, $C_1$, could be used to hold the sample when dealing with a bulk specimen. The smaller micrometer capacitor, $C_2$, serves as a fine control for obtaining a sharp resonance point. The mirror voltmeter, $V$, is used as a resonance indicator. $C_1$ and $C_2$ are suitably adjusted until the light beam of $V$ shows maximum deflection. At this point we have resonance and $f_r = 1/(LC)^{1/2}$, where $L$ and $C$ are the total inductance and capacitance in the resonant circuit, and $f_r$ is in radians/second.

Cell

For solution work, an external Marconi cell was used, see Fig. 6. This consists of two concentric stainless steel metal cylinders insulated from one another by a quartz spacer. The external cylinder is hollow of internal radius 3.0 cms, while the internal cylinder of radius 2.6 cms, when in position, leaves a gap of 2mm's. between its walls and the outer cylinder. A small overflow pipe in the external
FIG. 5

Measuring Circuit

HIGH FREQUENCY DIELECTRIC TEST CIRCUIT.
FIG. 6.

HIGH FREQUENCY DIELECTRIC TEST CELL.
wall ensures that the cell is filled to exactly the same level for each reading. The volume of liquid required to fill the gap between the two walls of the cell is 15 mls. The whole cell can be placed in a thermostat which can be regulated to within 0.02°C.

The cell was placed in parallel to $C_1$ and $C_2$ by connecting to points $T_1$ and $T_2$ of the circuit, Fig. 5. The connecting wires were stiff, to retain a fixed position throughout the run, and as short as possible to cut down stray capacitance and inductance.

The principle of the apparatus is to equate the capacitance of the solution between the two walls of the cell, with that of a measured air gap. In effect the capacitance of the solution is exactly anulled by opening or closing the plates of the capacitors $C_1$ and $C_2$, until the capacitance of the air gap is the same as that of the solution, as indicated by full scale deflection of the light voltmeter.

**Sources of Error and Cell Modifications**

Errors are likely to arise during the course of a run for a number of reasons and may be due to :-

a) Changes in the stray capacitance of the cell, and its leads.

b) Incorrect filling of the cell due to the trapping of air bubbles. The filling and emptying of the cell must be as easy as possible.

c) Changes in capacitance due to reseating the top of the cell after a filling operation.

Point c) was found to be a very serious source of error and a means of emptying and filling the cell without disturbing it in any way was devised. A hole was bored in the base of the cell and a connecting tube led off to a separating funnel, which acted as a solution reservoir. By putting solution in the reservoir the cell
was filled simply by raising the separating funnel and allowing solution to run through under the action of gravity. As soon as the excess solution appeared out of the overflow pipe, the tap on the separating funnel was closed leaving the cell filled to its upper limit. In order for this method of filling to be successful it was necessary to tilt the cell to eliminate the possibility of air bubbles being trapped below the internal cylinder. A special clamp was made in which the cell was permanently fixed at an angle of 15° to the vertical, the maximum possible angle to still allow the central cylinder to be completely covered by solution (Fig. 6). If the overflowing solution is collected and returned to the reservoir, then dilutions of the solution in situ can be made simply by adding the appropriate amount of solvent. By lowering the reservoir the cell will empty, the solution can be mixed, and then the cell refilled.

In practice the oscillator was set at relatively high frequency (in the region 9.0 x 10^5 Hz.), chosen to avoid any conductivity effects. The measuring circuit was then tuned in to resonance. The capacitance due to the leads was measured with the cell out of circuit. The course capacitor, C1, was adjusted until maximum deflection of the light voltmeter was obtained. This was repeated with the empty cell in circuit, and then with the cell full of solvent. The most concentrated solution was then put in the cell and resonance achieved as before, but this time obtaining as precise a balance as possible with the fine adjustment capacitor, C2. The small changes in capacitance with dilution can only be measured with the fine tuner, and several readings were taken at each concentration and then averaged. At the same time the whole run was done as quickly as possible to minimise any effects of oscillator drift.

3.6.2 Treatment of data.

For the Marconi cell we may write
\[ C_M^O = C_o + C_s \quad \ldots \ldots (3.9) \]

where \( C_M^O \) is the measured capacitance between the terminals, \( C_o \) is the capacitance of the cell and \( C_s \) is the additional stray capacitance. The capacitance \( C_M^L \) is measured with liquid in the cell and we may write

\[ C_M^L = C_o e^L + C_s \quad \ldots \ldots (3.10) \]

\[ C_M^O = C_o e^O + C_s \quad \ldots \ldots (3.11) \]

where \( e^L \) and \( e^O \) are the dielectric constants of pure solvent (benzene = 2.274, cyclohexane = 2.052 and 1-hexene = 2.073) and air \((e^O = 1.000)\). Solving equations (3.10) and (3.11) gives the values of \( C_o \) and \( C_s \), constants for the cell. The capacitance \( C_M \), subsequently measured with the cell containing solution is related to the true capacitance since

\[ C = C_M - C_s \quad \ldots \ldots (3.12) \]

and, as given by equation (2.102), the dielectric constant

\[ e = \frac{C}{C_o} \]

The variation of dielectric constant was plotted as a function of concentration and from the slope, \( \alpha \), in equation (2.107) was obtained.

The variation of refractive index with concentration, \( \gamma \), was obtained from the differential refractometry results used in light scattering. From \( dn/dc \) we know the change in refractive index as
concentration changes and therefore we know the value of $\frac{dn^2}{dc}$ over the same concentration range since, at very low concentration, $c_2$,

$$n_2 = n_1 + \frac{dn}{dc} c_2 \quad \ldots \ldots (3.13)$$

$$n_2^2 = n_1^2 + 2n_1 \frac{dn}{dc} c_2 + \left( \frac{dn}{dc} c_2 \right)^2 \quad \ldots \ldots (3.14)$$

where subscript 1 denotes solvent and 2 solution. Assuming that the final term in equation (3.14) is trivial then

$$\Delta n^2 = n_2^2 - n_1^2$$

$$= 2n_1 \frac{dn}{dc} c_2$$

and

$$\frac{\Delta n^2}{\Delta \varepsilon} = \frac{\Delta n^2}{c_2} = 2n_1 \frac{dn}{dc} \quad \ldots \ldots (3.15)$$

Assuming $dn/dc$ is constant over the concentration range $0 \rightarrow c_2$ then from equation (3.15) we obtained the required $\frac{dn^2}{dc}$ ratio. $w$, is the weight fraction of polymer and assuming that the density of the solution is equal to that of the solvent, $dn^2/dc$ converts to $dn^2/dw$ simply by multiplying by the solvent density.

Dipole moment was then determined using the Guggenheim-Smith equation (2.107) from section 2.8.
3.7 Dipole moments of bulk sample.

3.7.1 Apparatus

Low frequency dielectric apparatus was used for determining dipole moments of the bulk samples. The cell, shown in Fig. 7 was a three terminal Wayne Kerr Permittivity Jig D321 and had been specially modified by Fielding-Russell (113).

The polymer samples were required in the form of a disc. A mould of diameter 5.1 cms and approximate thickness 2 mm was used for compression moulding the samples of P.Tri.M.O. and P.Tetra.M.O. The polished faces of the mould were covered with tin foil to prevent polymer adhering to them and an appropriate weight of polymer introduced, depending on required thickness. The mould was heated to 55°C for a short time then allowed to cool to room temperature and the sample removed.

The moulded disc fitted between the two electrodes $E_1$ and $E_2$. They form the two plates of a condenser across which measurements are made. $E_1$ is insulated by a guard ring of epoxy resin, while $E_2$ could be raised or lowered vertically by a micrometer screw gauge. Discs of tin foil were stuck to the faces of the sample with a thin smear of vaseline ensuring good contact. The third electrode is the earth. Mounted on one of the vertical cell supports it was arranged, when in position, to press onto the wall of the cell jacket. The cell, in its jacket, could be evacuated to $10^{-2}$ mm of mercury pressure.

The apparatus consisted of an oscillator, a waveform analyser and a Schering test bridge. The oscillator was set at the desired frequency which in this case was 10 KHz, and a Rohde and Schwarz tunable indicating amplifier adjusted until it was finely tuned in to the applied frequency, as indicated by maximum galvanometer deflection. The capacitance across the specimen was measured by balancing the bridge until a minimum deflection on the amplifier galvanometer. The
Specimen was withdrawn and the capacitance of the evacuated cell measured. Data on amorphous samples of P.Tri.M.O. and P.Tetra.M.O. being taken at room temperature.

3.7.2 Treatment of data.

The dielectric constant of the specimen was calculated from equation (2.102)

\[ \varepsilon = \frac{C}{C_0} \]

where stray capacitance terms are eliminated in the same manner as described with the Hartshorn and Ward apparatus.

Dipole moment is related to dielectric constant by Onsager's equation (2.105) see section 2.8

\[ \frac{4 \pi N_1}{9kT} \left( \frac{\mu^2}{z} \right) = \frac{(\varepsilon_0 - \varepsilon n^2)}{\varepsilon_0} \left( \frac{2\varepsilon_0}{\varepsilon_0 + \varepsilon n^2} \right) \left( \frac{\varepsilon_0 + \varepsilon n^2}{n^2 + 2} \right)^2 \]
3.8 Theta Solvents

Theta solvents for P.Tetra.M.O. and P.Tri.M.O. are required which are single solvents, and not solvent mixtures, and at the same time non polar because of the requirements for subsequent dipole moment studies. Solvent mixtures cause several undesired effects not least of which are the additional experimental difficulties which are discussed further in chapter 3. The method of precipitation was adopted with a variety of solvents and of the seven tested, one was successful for each polymer. The solvents were

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Density (g/ml)</th>
<th>B.pt (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>0.7791</td>
<td>81.4</td>
</tr>
<tr>
<td>Cycloheptane</td>
<td>0.8099</td>
<td>118.1</td>
</tr>
<tr>
<td>Cyclooctane</td>
<td>0.8349</td>
<td>148.5</td>
</tr>
<tr>
<td>n Hexane</td>
<td>0.6603</td>
<td>69.0</td>
</tr>
<tr>
<td>n Heptane</td>
<td>0.6837</td>
<td>98.4</td>
</tr>
<tr>
<td>1 - Hexene</td>
<td>0.6732</td>
<td>63.4</td>
</tr>
<tr>
<td>1 - Heptane</td>
<td>0.6969</td>
<td>93.6</td>
</tr>
</tbody>
</table>

A solvent was sought in which the polymer was partially soluble at a temperature between 10°C and 50°C. At temperature extremes experimental difficulties arise. Solubility was observed on a small scale in a test-tube. The polymer, in the appropriate solvents was first held at 25°C for a period of time. Should the polymer remain insoluble the temperature was raised in steps of 5°C. If, as the temperature increased, the polymer in a particular solvent dissolved, it was cooled slowly and observed for precipitation. Using this procedure theta conditions can be found approximately within ±2°C. Working on the principle of zero second virial
coefficient at theta conditions exact theta temperatures were located from light scattering or osmometry.

A variety of mixed and single theta solvents have been found for P.Tetra.M.O. and these have been listed by Dreyfuss and Dreyfuss (114). Of the mixed solvents only the cyclohexane/n-heptane system of Wetton and May (115) was studied further. The polymer was dissolved in varying ratios of good solvent (cyclohexane) and non solvent (n-heptane) mixture and the effect of an increasing proportion of non solvent on the second virial coefficient, studied osmotically.
CHAPTER 4

RESULTS

4.1 Poly (tetramethylene oxide)

4.1.1 Sample preparations

A series of six P.Tetra.M.O. samples were made with varying amounts of catalyst and varying polymerisation times as detailed in Table 4.1.

Table 4.1 Polymerisation of P.Tetra.M.O. in bulk at 25.0°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Catalyst Concentration</th>
<th>Polymerisation Time</th>
<th>% yield of polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.47 x 10^-2 M</td>
<td>48 hrs</td>
<td>42</td>
</tr>
<tr>
<td>B</td>
<td>1.44 x 10^-2</td>
<td>10 days</td>
<td>67</td>
</tr>
<tr>
<td>C</td>
<td>1.17 x 10^-2</td>
<td>10 days</td>
<td>30</td>
</tr>
<tr>
<td>D</td>
<td>0.99 x 10^-2</td>
<td>10 days</td>
<td>61</td>
</tr>
<tr>
<td>E</td>
<td>0.84 x 10^-2</td>
<td>48 hrs</td>
<td>62</td>
</tr>
<tr>
<td>F</td>
<td>0.62 x 10^-2</td>
<td>24 hrs</td>
<td>64</td>
</tr>
</tbody>
</table>

4.1.2 Molecular weight determinations

Intrinsic viscosities of the samples were determined in benzene at 25.0°C and plots of $\eta_{sp}/c$ and $\ln \eta_{R}/c$ versus concentration are shown in Fig. 8. Viscosity average molecular weights were calculated using the K and 'a' values of Dreyfuss and Dreyfuss (89).

Using the relationship $\left( \frac{\eta}{c} \right)_0 = \frac{RT}{M_n}$ as described in section 2.7, number average molecular weights were determined by high speed membrane osmometry. Four of the samples were measured in toluene at 25.0°C and the plots of $\eta/c$ versus $c$ are shown in Fig. 9. Weight average molecular weights were determined by the Zimm method as the common intercept of $\left( \frac{Kc}{\theta R} \right) \theta = 0$ versus conc. $+ \sin^2 \frac{\theta}{2}$ as discussed in sections 2.5 and 3.2.4. The plot obtained for sample A is shown in Fig. 22. Table 4.2 summarises the molecular weights obtained.
FIG 8
INTRINSIC VIS COS IT IES OF P.TETRA, M.O. SAMPLES

SAMPLE A

SAMPLE B

SAMPLE C

SAMPLE D

SAMPLE E

SAMPLE F
FIG. 9

MID DETERMINATION OF P.TETRA. M O SAMPLES
Table 4.2 Molecular weights of P.Tetra.M.O. samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\overline{M}_n)</th>
<th>(\overline{M}_v)</th>
<th>(\overline{M}_w)</th>
<th>(\frac{\overline{M}_v}{\overline{M}_n})</th>
<th>(\frac{\overline{M}_w}{\overline{M}_n})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>350,000</td>
<td>520,000</td>
<td>630,000</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>B</td>
<td>435,000</td>
<td>570,000</td>
<td>850,000</td>
<td>1.4</td>
<td>1.75</td>
</tr>
<tr>
<td>C</td>
<td>620,000</td>
<td>680,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>490,000</td>
<td>690,000</td>
<td>850,000</td>
<td>1.4</td>
<td>1.75</td>
</tr>
<tr>
<td>E</td>
<td>510,000</td>
<td>680,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>800,000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.1.3 Second virial coefficients

The osmotic second virial coefficients were determined for 4 of the P.Tetra.M.O. samples as \(A_2 = \frac{S}{RT}\) where \(S\) is the slope of the graphs in Fig. 9. The light scattering second virial coefficient, \((A_2)'\), for sample A was determined from the slope of the line \(\left(\frac{Ke}{R \theta}\right)\) versus \(5 \times 10^3 \times \text{conc}\) shown in Fig. 22. Their variation with molecular weight is shown in Table 4.3

Table 4.3 Second virial coefficients of P.Tetra.M.O. samples in benzene at 25.0°C.

| Sample | \(\overline{M}_n\) | \(\overline{M}_w\) | \(A_2\) (cc. mole. g\(^{-2}\)) |
|--------|-----------------|-----------------|------------------|------------------|
|        |                 |                 | Osmotic          | Light scattering |
| A      | 350,000         | 630,000         | \(9.7 \times 10^{-4}\) | \(8.0 \times 10^{-4}\) |
| B      | 433,000         |                 | \(8.8 \times 10^{-4}\) |                  |
| C      | 490,000         |                 | \(8.8 \times 10^{-4}\) |                  |
| E      | 510,000         |                 | \(6.9 \times 10^{-4}\) |                  |

4.1.4 Dispersity studies

The molecular weights of the samples A - F so far polymerised...
have a broad distribution. By suitable adjustment of polymerisation times a study of the polymerisation procedure was made in an effort to obtain a sample with a narrow molecular weight distribution. The effects of polymerisation time on percentage conversion into polymer are shown in Table 4.4. As far as possible the catalyst concentration was kept the same.

Table 4.4 P.Tetra.M.O. polymerisations to low conversion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of Catalyst</th>
<th>Polymerisation Time</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>$4.2 \times 10^{-2}$ M</td>
<td>15 hrs</td>
<td>28.1</td>
</tr>
<tr>
<td>b</td>
<td>$4.5 \times 10^{-2}$ M</td>
<td>5 hrs</td>
<td>10</td>
</tr>
<tr>
<td>c</td>
<td>$4.7 \times 10^{-2}$ M</td>
<td>3.5 hrs</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Sample b, polymerised for 5 hours, gave a 10% conversion into polymer. This was repeated (sample d) using greater quantities, in order to study all three molecular weight averages. The molecular weights of sample d compared with those determined for a, b, and c are shown in Table 4.5.

Table 4.5 Molecular weights of low conversion P. Tetra.M.O. samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_v$</th>
<th>$\bar{M}_w$</th>
<th>$\bar{M}_w / \bar{M}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>500,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>250,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>200,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>220,000</td>
<td>350,000</td>
<td>400,000</td>
<td>1.8</td>
</tr>
</tbody>
</table>

All subsequent studies of P.Tetra.M.O. were conducted on the samples A - F.
4.2 Poly (trimethylene oxide)

4.2.1 Sample preparations

Details of the P.Tri.M.O. systems synthesised with 'Phosfluorogen A' catalyst are shown in Table 4.6.

Table 4.6 Polymerisation of P.Tri.M.O. in bulk.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of Catalyst</th>
<th>% yield</th>
<th>Polymerisation Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Time (hours)</td>
</tr>
<tr>
<td>I</td>
<td>excess</td>
<td>15</td>
<td>6</td>
</tr>
<tr>
<td>II</td>
<td>$7.0 \times 10^{-2}$</td>
<td>55</td>
<td>18</td>
</tr>
<tr>
<td>III</td>
<td>$6.15 \times 10^{-3}$</td>
<td>62</td>
<td>16</td>
</tr>
<tr>
<td>IV</td>
<td>$4.0 \times 10^{-3}$</td>
<td>87</td>
<td>16</td>
</tr>
<tr>
<td>V</td>
<td>$3.0 \times 10^{-3}$</td>
<td>70</td>
<td>21</td>
</tr>
<tr>
<td>VI</td>
<td>$2.46 \times 10^{-3}$</td>
<td>70</td>
<td>16</td>
</tr>
<tr>
<td>VII</td>
<td>$3.70 \times 10^{-4}$</td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>

4.2.2 Molecular weight determinations

Number average molecular weights were again determined by high speed membrane osmometry in toluene at 25.0°C. The appropriate plots of $\bar{M}$ versus $c$ are shown in Fig. 10. Weight average molecular weights, by light scattering, were determined on selected samples in toluene at 25.0°C and the Zimm plots obtained are shown in Figs. 11 - 13 and 21a. The results obtained are given in Table 4.7.

Table 4.7 Molecular weights of P.Tri.M.O. samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w$</th>
<th>$\frac{\bar{M}_w}{\bar{M}_n}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>25,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>106,000</td>
<td>190,000</td>
<td>1.8</td>
</tr>
<tr>
<td>III</td>
<td>160,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>228,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>237,000</td>
<td>350,000</td>
<td>1.5</td>
</tr>
<tr>
<td>VI</td>
<td>327,000</td>
<td>495,000</td>
<td>1.5</td>
</tr>
<tr>
<td>VII</td>
<td>755,000</td>
<td>1,200,000</td>
<td>1.6</td>
</tr>
</tbody>
</table>
FIG. 10

Mn DETERMINATION OF P. TRIM.O. SAMPLES
P.Tri.M.O. SAMPLE \( \overline{V} \)

\[
\frac{Kc}{Re} \times 10^6
\]

\[
\text{Sin}^2 \theta + 5000 \text{ Conc}
\]

\( \theta = 150^\circ \)

\( \theta = 90^\circ \)

\( \theta = 30^\circ \)

\( \theta = 0^\circ \)
P. Tri.M.O. SAMPLE VII

\[ \frac{K_c}{R_0} \times 10^6 \]

\[ \sin^2 \theta + 5000 \text{ Conc} \]

- \( C = 0 \)
- \( \theta = 150^\circ \)
- \( \theta = 90^\circ \)
- \( \theta = 30^\circ \)
- \( \theta = 0^\circ \)

**Fig. 12.**
$\frac{K_c}{R_e} \times 10^6$

$\sin^2 \frac{\theta}{2} + 5000 \text{ Conc}$

$\theta = 0^\circ$
$\theta = 30^\circ$
$\theta = 90^\circ$
$\theta = 150^\circ$

FIG 13.
4.2.3 Second virial coefficients

Second virial coefficients of the P.Tri.M.O. samples in toluene at 25.0°C, from osmometry and light scattering, vary with molecular weight as shown in Table 4.8.

Table 4.8 Second virial coefficients of P.Tri.M.O. samples in toluene at 25.0°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Osmotic, $A_2$ (cc. mole g$^{-2}$)</th>
<th>light scattering, $(A_2)_2$ (cc. mole g$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$4.08 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>$9.09 \times 10^{-4}$</td>
<td>$3.75 \times 10^{-4}$</td>
</tr>
<tr>
<td>III</td>
<td>$6.95 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>$8.54 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>$5.07 \times 10^{-4}$</td>
<td>$2.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>VI</td>
<td>$4.50 \times 10^{-4}$</td>
<td>$2.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>VII</td>
<td>$2.16 \times 10^{-4}$</td>
<td></td>
</tr>
</tbody>
</table>

4.2.4 Intrinsic viscosity - molecular weight relationship

Intrinsic viscosities of the seven P.Tri.M.O. samples were determined in toluene at 25.0°C. A double logarithmic plot, shown in Fig. 14, of intrinsic viscosity versus number average molecular weight yielded

$$ K = 7.08 \times 10^{-5} $$

$$ a = 0.81 $$

hence

$$ [\eta] = 7.08 \times 10^{-5} M_v^{0.81} \quad \ldots \ldots (4.1) $$

in the molecular weight range $(\overline{M}_n)$, 25,000 - 755,000.
DOUBLE LOGARITHMIC PLOT
INTRINSIC VISCOSITY V MOLECULAR WEIGHT
OF P. TRI.M.O. IN TOLUENE
4.2.5 Kurata - Stockmayer (K-S) and Stockmayer - Fixman (S-F)

Treatments

The two treatments, expressed by equations (2.47) and (2.49), have been applied to intrinsic viscosities measured for the P.Tri.M.O. samples. Treatments have been approached both on a number average molecular weight and a viscosity average molecular weight basis. Viscosity average molecular weights were determined using equation (4.1). For the Kurata - Stockmayer plot the procedure as described in section 2.3 was followed. The Kurata - Stockmayer and Stockmayer - Fixman calculations are shown in Tables 4.9 and 4.10, respectively.

Table 4.9 Kurata - Stockmayer calculations

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\frac{2}{3}[\eta]^3 \times 10^2)</th>
<th>(\frac{2}{3}[\eta]^3 \times 10^2)</th>
<th>(\alpha\eta)</th>
<th>(g(\alpha\eta))</th>
<th>(\frac{2}{3}M_n g(\alpha\eta))</th>
<th>(\frac{2}{3}M_v g(\alpha\eta))</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.66</td>
<td>1.53</td>
<td>1.293</td>
<td>1.172</td>
<td>1.430</td>
<td>1.693</td>
</tr>
<tr>
<td>II</td>
<td>2.16</td>
<td>1.97</td>
<td>1.469</td>
<td>1.24</td>
<td>2.755</td>
<td>3.315</td>
</tr>
<tr>
<td>III</td>
<td>2.14</td>
<td>2.06</td>
<td>1.463</td>
<td>1.238</td>
<td>3.38</td>
<td>3.67</td>
</tr>
<tr>
<td>IV</td>
<td>2.61</td>
<td>2.33</td>
<td>1.614</td>
<td>1.29</td>
<td>3.795</td>
<td>4.74</td>
</tr>
<tr>
<td>V</td>
<td>2.68</td>
<td>2.38</td>
<td>1.638</td>
<td>1.285</td>
<td>3.82</td>
<td>4.87</td>
</tr>
<tr>
<td>VI</td>
<td>2.59</td>
<td>2.43</td>
<td>1.611</td>
<td>1.285</td>
<td>4.55</td>
<td>5.25</td>
</tr>
<tr>
<td>VII</td>
<td>3.42</td>
<td>3.02</td>
<td>1.850</td>
<td>1.34</td>
<td>6.28</td>
<td>8.07</td>
</tr>
</tbody>
</table>
Table 4.10 Stockmayer - Fixman Calculations

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n^{1/2}$</th>
<th>$M_v^{1/2}$</th>
<th>$[\eta]/M_n^{1/2} \times 10^3$</th>
<th>$[\eta]/M_v^{1/2} \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>157</td>
<td>179</td>
<td>2.16</td>
<td>1.895</td>
</tr>
<tr>
<td>II</td>
<td>325.6</td>
<td>374</td>
<td>3.165</td>
<td>2.76</td>
</tr>
<tr>
<td>III</td>
<td>400</td>
<td>424</td>
<td>3.125</td>
<td>2.95</td>
</tr>
<tr>
<td>IV</td>
<td>475.4</td>
<td>562</td>
<td>4.21</td>
<td>3.56</td>
</tr>
<tr>
<td>V</td>
<td>486.8</td>
<td>583</td>
<td>4.40</td>
<td>3.67</td>
</tr>
<tr>
<td>VI</td>
<td>571.8</td>
<td>633</td>
<td>4.18</td>
<td>3.78</td>
</tr>
<tr>
<td>VII</td>
<td>868.9</td>
<td>1,000</td>
<td>6.34</td>
<td>5.50</td>
</tr>
</tbody>
</table>

The appropriate graphs are shown in Figs. 15 and 16. From the intercepts of these graphs the following values of $K_\theta$ have been determined, see Table 4.11.

Table 4.11 $K_\theta \times 10^3$ values of P.Tri.M.O. in toluene

<table>
<thead>
<tr>
<th>Method</th>
<th>$K - S$</th>
<th>$S - F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_n$ basis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_n$</td>
<td>1.24</td>
<td>1.30</td>
</tr>
<tr>
<td>$M_v$</td>
<td>1.20</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Table 4.12 gives the polymer - solvent interaction parameter, B, calculated from the slopes of the plots.
STOCKMAYER-FIXMAN PLOT

\[ \frac{[\eta]}{M} \times 10^3 \]

\[ \frac{1}{M^2} \]

Mn DETERMINATIONS

Mv DETERMINATIONS

FIG. 16.
Table 4.12 Interaction parameters calculated for P.Tri.M.O. - toluene

<table>
<thead>
<tr>
<th>M,W. basis</th>
<th>B x $10^{28}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K - S</td>
</tr>
<tr>
<td>$M_n$</td>
<td>40.0</td>
</tr>
<tr>
<td>$M_v$</td>
<td>28.3</td>
</tr>
</tbody>
</table>

4.3 Higher poly (ethers)

Attempts were made to synthesise both poly (pentamethylene oxide) and poly (hexamethylene oxide) by ring opening of the appropriate cyclic ethers. Phosfluorogen A was used in both cases but no other catalyst was tried. Catalyst concentration, temperature and time of polymerisation were varied over wide limits but the monomer involved did not ring open. Attempts to polymerise them in a suitable solvent, propylene oxide, also failed.
4.4 Determination of theta solvents

The known theta solvent mixture of cyclohexane - n heptane, Wetton and May (115), was used initially for P.Tetra.M.O.. Polymer was dissolved in solvent mixture of varying proportions, and, keeping the temperature constant at 25.0°C, the theta properties followed by measuring osmotic second virial coefficient. The osmometry plots so obtained are shown in Fig. 17 and Table 4.13 shows the effect of solvent proportions on second virial coefficient.

Table 4.13 :- Variation of $A_2$ with solvent proportions

<table>
<thead>
<tr>
<th>Proportion (Volume)</th>
<th>$\bar{M}_n$ (from intercept)</th>
<th>$A_2$ (cc. mole, g$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>n - heptane</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>n - heptane</td>
<td></td>
</tr>
<tr>
<td>80 20</td>
<td>700,000</td>
<td>$6.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>70 30</td>
<td>685,000</td>
<td>$5.35 \times 10^{-4}$</td>
</tr>
<tr>
<td>60 40</td>
<td>717,000</td>
<td>$3.40 \times 10^{-4}$</td>
</tr>
<tr>
<td>50 50</td>
<td>700,000</td>
<td>$2.57 \times 10^{-4}$</td>
</tr>
<tr>
<td>40 60</td>
<td>Insoluble</td>
<td>-</td>
</tr>
<tr>
<td>45 55</td>
<td>Insoluble</td>
<td>-</td>
</tr>
</tbody>
</table>

As will be discussed in chapter 5 no further work was done on the mixed theta solvent systems and attention was turned to finding a single theta solvent for both P. Tetra.M.O. and P.Tri.M.O.

To find a single theta solvent, the solubility of P. Tetra.M.O. was studied in a variety of solvents. The experimental observations are shown in Table 4.14.
FIG. 17.

P. TETRA.M.O. IN CYCLOHEXANE/N-HEPTANE AT 25°C
Table 4.14: Determination of a theta solvent

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Experimental Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C for 2 days</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Cycloheptane</td>
<td>2 hours swollen</td>
</tr>
<tr>
<td></td>
<td>20 hours nearly dissolved</td>
</tr>
<tr>
<td>Cyclooctane</td>
<td>20 hours soluble</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>2 hours swollen</td>
</tr>
<tr>
<td></td>
<td>20 hours separate layer</td>
</tr>
<tr>
<td>1-Heptene</td>
<td>Soluble in 2 hours</td>
</tr>
<tr>
<td>n Hexane</td>
<td>insoluble</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>n Heptane</td>
<td>insoluble</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cyclohexane, cycloheptane, cyclooctane, 1-hexene and 1-heptene all contained dissolved polymer at 50°C. When cooled to 15°C in all but 1-hexene polymer remained in solution. The separate polymer layer in 1-hexene solution was found to dissolve again at 50°C. Second virial coefficients were measured by light scattering (the Zimm plots are shown in Figs. 23 and 24) at 35.0°C and 44.8°C and in the latter case zero second virial coefficient was observed, as shown in Table 4.15.
Table 4.15: Variation of $A_2$ with temperature for P.Tetra.M.O. in 1-hexene.

<table>
<thead>
<tr>
<th>Light Scattering in</th>
<th>Temperature</th>
<th>$A_2$ (cc. mole. g$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-hexene</td>
<td>35.0°C</td>
<td>$-0.83 \times 10^{-4}$</td>
</tr>
<tr>
<td>1-hexene</td>
<td>44.8°C</td>
<td>0</td>
</tr>
</tbody>
</table>

Similarly for P.Tri.M.O., solubility tests of polymer in the same solvents as above were carried out. The observations are given in Table 4.16.

Table 4.16: P.Tri.M.O., determination of a theta solvent

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Experimental Conditions</th>
<th>25°C for 2 days</th>
<th>30°C for 3 days</th>
<th>40°C for 2 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>swollen and transparent partially dissolved</td>
<td>soluble</td>
<td>soluble</td>
<td></td>
</tr>
<tr>
<td>Cycloheptane</td>
<td>insoluble</td>
<td>partially soluble</td>
<td>soluble</td>
<td></td>
</tr>
<tr>
<td>Cyclooctane</td>
<td>insoluble</td>
<td>swollen and transparent</td>
<td>soluble</td>
<td></td>
</tr>
<tr>
<td>1-Hexene</td>
<td>insoluble</td>
<td>insoluble</td>
<td>insoluble</td>
<td></td>
</tr>
<tr>
<td>1-Heptene</td>
<td>insoluble</td>
<td>insoluble</td>
<td>insoluble</td>
<td></td>
</tr>
<tr>
<td>n Hexane</td>
<td>polymer remained completely inert</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n Heptane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

P.Tri.M.O. is not easily dissolved in any of the above solvents. At
25°C it was insoluble in all but cyclohexane where it appeared to be partially soluble. On raising the temperature polymer only dissolved in cyclohexane, cycloheptane and cyclooctane. Cooling to 20°C caused polymer to precipitate from these three solvents, though at varying rates. Precipitation was complete in 10 minutes from cyclooctane, 30 minutes from cycloheptane and 2 hours from cyclohexane. All three have theta properties, though that of cyclohexane is more conveniently nearer room temperature. Second virial coefficients, by osmometry, were measured to precisely ascertain theta conditions and the plots obtained are shown in Fig. 18. The variation of $A_2$ with temperature is given in Table 4.17.

**Table 4.17:** Variation of $A_2$ with temperature for P.Tri.M.O. in cyclohexane.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$A_2$ (cc. mole. g$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.0°C</td>
<td>$1.65 \times 10^{-4}$</td>
</tr>
<tr>
<td>28.5°C</td>
<td>$6.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>25.0°C</td>
<td>0</td>
</tr>
</tbody>
</table>
θ CONDITIONS
P, TRI, M, O, IN CYCLOHEXANE

FIG. 18.
4.5 Unperturbed dimensions of P.Tri.M.O. and P.Tetra.M.O. from intrinsic viscosities

Intrinsic viscosities for P.Tri.M.O. (sample VI) and P.Tetra.M.O. (sample A) were measured in a good solvent, which was taken as benzene at 25.0°C in each case, and in their respective theta solvents. Intrinsic viscosities were obtained as the common intercept of plots $\ln \eta_p/c$ and $\ln \eta_R/c$ versus conc. and those obtained for P.Tetra.M.O. are shown in Fig. 19 and those for P.Tri.M.O. in Fig. 20. The values obtained are given in Table 4.18.

**Table 4.18**: Intrinsic viscosities in good and theta solvents for P.Tri.M.O. and P.Tetra.M.O.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Temperature</th>
<th>$[\eta]_i (d1/g)$</th>
<th>$A_2$ (csm) (cc. mole. g$^{-2}$)</th>
<th>$M_v \times 10^{-5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.Tri.M.O.</td>
<td>Benzene</td>
<td>25.0°C</td>
<td>2.758</td>
<td>$4.5 \times 10^{-4}$</td>
<td>3.25</td>
</tr>
<tr>
<td></td>
<td>Cyclohexane</td>
<td>25.0°C</td>
<td>0.630</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>P.Tetra.M.O.</td>
<td>Benzene</td>
<td>25.0°C</td>
<td>4.000</td>
<td>$9.7 \times 10^{-4}$</td>
<td>5.70</td>
</tr>
<tr>
<td></td>
<td>1-Hexene</td>
<td>44.8°C</td>
<td>1.065</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

These results will be discussed in terms of perturbed and unperturbed dimensions in chapter 5.
FIG. 19.

INTRINSIC VISCOSITIES OF P. TETRA. M. O.

BENZENE 25.0°C

I-HEXENE 44.8°C
FIG. 20.

INTRINSIC VISCOSITIES OF P.TRI.M.O.

BENZENE 25.0°C

Cyclohexane 25.0°C
4.6 Dimensions of P.Tetra.M.O. and P.Tri.M.O. from light scattering

Light scattering studies were made in good and theta solvents for both P.Tri.M.O. and P.Tetra.M.O. The results were plotted by the method of Zimm (73) as Kc/Rg versus sin^2 \( \theta/2 \) + conc., and from them, the perturbed and unperturbed dimensions calculated. The refractive index increments required for each polymer-solvent system were measured and the mean of several determinations are shown in Table 4.19.

Table 4.19: Refractive index increments for P.Tri.M.O. and P.Tetra.M.O.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \frac{dn}{dc} ) (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P.Tri.M.O.</td>
</tr>
<tr>
<td>Benzene</td>
<td>-0.0366</td>
</tr>
<tr>
<td>Toluene</td>
<td>-0.0306</td>
</tr>
<tr>
<td>1 - Hexane</td>
<td>+0.155</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>+0.0389</td>
</tr>
</tbody>
</table>

The Rayleigh ratios, \( R_{90} \), for pure solvent, were calculated taking the value 16.3 \( \times 10^{-6} \) for pure benzene (106) and measuring the scattering intensities of the pure solvents at 90°, relative to that of benzene. The solution concentrations and scattering intensities at preselected angles from 30° - 150° were computed and the results plotted directly. The interpretation of the Zimm plots is explained in section 3.2.

The Zimm plots obtained for P.Tri.M.O. in toluene at 25.0°C and cyclohexane at 25.0°C are shown in Figs. 21a and 21b. The results obtained are summarised in Table 4.20 where the polymer dimensions are quoted as, \( \langle r^2 \rangle^{1/2} \), the root mean square end to end distance.
θ CONDITIONS

P Tri.M.O. SAMPLE VI IN CYCLOHEXANE
AT 25.0°C

\[ \frac{K_c}{R_\theta} \times 10^6 \]

\[ \sin^2 \frac{\theta}{2} + 5000 \text{ Conc} \]

- \( \theta = 0^\circ \)
- \( \theta = 30^\circ \)
- \( \theta = 90^\circ \)
- \( \theta = 150^\circ \)
### Table 4.20: Dimensions of P.Tri.M.O. from light scattering

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature</th>
<th>$\bar{M}_w$</th>
<th>$A_2$ (cc. mole. g$^{-2}$)</th>
<th>$\langle r^2 \rangle_z^0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>25.0°C</td>
<td>495,000</td>
<td>$1.5 \times 10^{-4}$</td>
<td>860</td>
</tr>
<tr>
<td>Cyclohexane (θ)</td>
<td>25.0°C</td>
<td>500,000</td>
<td>0</td>
<td>680</td>
</tr>
</tbody>
</table>

Figs. 22-24 show the Zimm plots obtained for P.Tetra.M.O. in benzene and 1-hexene. Table 4.21 summarises the results obtained.

### Table 4.21: Dimensions of P.Tetra.M.O. from light scattering

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature</th>
<th>$\bar{M}_w$</th>
<th>$A_2$ (cc. mole. g$^{-2}$)</th>
<th>$\langle r^2 \rangle_z^0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>25.0°C</td>
<td>625,000</td>
<td>$0.80 \times 10^{-3}$</td>
<td>1,030</td>
</tr>
<tr>
<td>1-Hexene (θ)</td>
<td>44.8°C</td>
<td>625,000</td>
<td>0</td>
<td>840</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>35.0°C</td>
<td>605,000</td>
<td>$-0.83 \times 10^{-4}$</td>
<td>745</td>
</tr>
</tbody>
</table>
P.Tetra.M.O. SAMPLE I IN BENZENE AT 25°C

FIG. 22.
P. Tetra. M. O. SAMPLE I IN 1-HEXENE AT 44.8°C

\[ \frac{Kc \times 10^6}{Re} \]

\[ \sin^2 \frac{\theta}{2} + 5000 \text{ Conc} \]
4.7 Dipole Moments of P.Tri.M.O. and P.Tetra.M.O.

4.7.1 Dilute solution determinations

The dipole moments of both P.Tri.M.O. and P.Tetra.M.O. were measured under good solvent conditions, in benzene at 25.0°C, and also under their respective theta conditions. Dipole moments were determined using the Guggenheim - Smith equation as explained in section 3.6.

Table 4.22 gives the refractive indices, n₁, of the pure solvents as measured on an Abbe refractometer and also their dielectric constants, ε_L. The latter values were taken from the literature except for 1-hexene which was measured. This required the evaluation of the cell constants C₀ and Cₛ in equations (3.10 and 3.11) using solvents of known dielectric constant, and then calculating ε_L from equation (3.10).

Table 4.22: Physical properties of solvents needed in dipole moment studies

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature</th>
<th>n₁</th>
<th>ε_L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>25.0°C</td>
<td>1.5014</td>
<td>2.274</td>
</tr>
<tr>
<td>1-hexene</td>
<td>44.8°C</td>
<td>1.3821</td>
<td>2.117</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>25.0°C</td>
<td>1.4290</td>
<td>2.052</td>
</tr>
</tbody>
</table>

For a particular system, the change of capacitance with dilution was measured, converted to dielectric constant, and plotted against concentration of solution, where the concentration is expressed as the weight fraction of polymer in the solution. In Fig. 25 the plots obtained of the variation of dielectric constant with concentration for P.Tri.M.O., in both a good solvent and at theta conditions, are
shown. Similarly in Fig. 26 the same plots are given for P.Tetra.M.O. In Table 4.23 are given the gradients of these plots, which show the variation of dielectric constants with concentration, $\partial \varepsilon / \partial \omega^2$, represented by $\alpha$.

Table 4.23 Variation of dielectric constant with concentration for P.Tri.M.O. and P.Tetra.M.O.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>P.Tri.M.O.</td>
</tr>
<tr>
<td>Benzene</td>
<td>25.0°C</td>
<td>2.17 ± 0.05</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>44.8°C</td>
<td>1.62 ± 0.05</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>25.0°C</td>
<td>1.05 ± 0.05</td>
</tr>
</tbody>
</table>

The variations of the squares of the refractive indices with concentration were calculated from $dn/dc$ values obtained from differential refractometry, as explained in section 3.3. They are given in Table 4.24 where $\psi$ represents $\partial n^2/\partial \omega^2$.

Table 4.24 Variation of refractive index with concentration for P.Tri.M.O. and P.Tetra.M.O.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature</th>
<th>$\psi$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>P.Tri.M.O.</td>
</tr>
<tr>
<td>Benzene</td>
<td>25.0°C</td>
<td>-0.095</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>44.8°C</td>
<td>+0.320</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>25.0°C</td>
<td>+0.088</td>
</tr>
</tbody>
</table>

Knowing $\alpha$ and $\psi$ dipole moment, follows from the Guggenheim-Smith equation (2.107). The calculated values for P.Tri.M.O. and P.Tetra.M.O. in both good and bad solvents are given in Table 4.25.
FIG. 25.

P.TRI.M.O. VARIATION OF DIELECTRIC CONSTANT WITH SOLUTION CONCENTRATION

a) CYCLOHEXANE AT 25.0°C

$\varepsilon$

$2.060$

$2.055$

$2.050$

$W_2 \times 10^{-3}$

$0$

$1.0$

$2.0$

$3.0$

b) BENZENE AT 25.0°C

$\varepsilon$

$2.295$

$2.290$

$2.285$

$W_2 \times 10^{-3}$ [WEIGHT FRACTION OF POLYMER]
FIG. 26.

P.TETRA.M.O. VARIATION OF DIELECTRIC CONSTANT WITH SOLUTION CONCENTRATION

\( \varepsilon \)

\( W_2 \times 10^{-3} \) [WEIGHT FRACTION OF POLYMER]

(a) 1-HEXENE AT 44.8°C

(b) BENZENE AT 25.0°C
The ratio $\frac{\mu^2}{z}$ is the mean square dipole moment per degree of polymerisation.

Table 4.25: Dipole moments of P.Tri.M.O. and P.Tetra.M.O. from dilute solution data.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\frac{\mu^2}{z}$ (D$^2$)</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.Tri.M.O.</td>
<td>1.20 ± 0.03</td>
<td>0.64 ± 0.05</td>
</tr>
<tr>
<td>P.Tetra.M.O.</td>
<td>1.43 ± 0.04</td>
<td>1.30 ± 0.10</td>
</tr>
</tbody>
</table>

4.7.2 Bulk polymer determinations

Dipole moment data of the bulk amorphous polymer was obtained for both P.Tri.M.O. and P.Tetra.M.O. The dipole moments are again expressed by $\frac{\mu^2}{z}$, which was obtained via the Onsager relation equation (2.105). The alternative columns of $\frac{\mu^2}{z}$ in Table 4.26 represent different estimates of the limiting dielectric constant, $\varepsilon_{\infty}$, as discussed in section 2.8. In the first column $\frac{\mu^2}{z}$ is calculated from the limiting dielectric constant extrapolated from low temperature high frequency data (2.55 for P.Tri.M.O. and 2.50 for P.Tetra.M.O.) whilst the second column shows the dipole moment calculated from the refractive index squared plus a 10% allowance for nuclear distortion terms (2.34 for P.Tri.M.O. and 2.26 for P.Tetra.M.O.).

Table 4.26: Dipole moments of bulk amorphous polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temperature</th>
<th>$\varepsilon_0$ (10 KHz)</th>
<th>$\frac{\mu^2}{z}$ (D$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.Tri.M.O.</td>
<td>21°C</td>
<td>4.90</td>
<td>0.83 0.97</td>
</tr>
<tr>
<td>P.Tetra.M.O.</td>
<td>20°C</td>
<td>4.93</td>
<td>1.04 1.25</td>
</tr>
</tbody>
</table>
4.8 Poly (chlorostyrenes). Molecular weights and dimensions

Two samples, poly (3 chlorostyrene) and poly (4 chlorostyrene) were investigated. Their molecular weights were measured and their dimensions calculated under different conditions.

The number average molecular weights were measured by osmometry in benzene at 25.0°C. The $M_n$ values and second virial coefficients are given in Table 4.27.

**Table 4.27.** $M_n$ values of substituted poly (styrene) samples.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (co. mole. g )</th>
<th>$(A_2)_{osm}$ (cc. mole. g⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly (3 chlorostyrene)</td>
<td>360,000</td>
<td>$1.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>poly (4 chlorostyrene)</td>
<td>535,000</td>
<td>$0.646 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Light scattering studies were conducted on both polymers. Poly (4 chlorostyrene) with the lower osmometry second virial coefficient was measured at lower temperatures and the Zimm plots obtained in benzene at 20.5°C and 15.0°C are shown in Figs. 27 and 28 respectively. Table 4.28 summarises the results obtained. The dimensions are expressed as the root-mean-square end to end distance.

**Table 4.28.** Dimensions of poly (4 chlorostyrene) from light scattering

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature</th>
<th>$\bar{M}_w$</th>
<th>$(A_2)_z$ (cc. mole. g⁻²)</th>
<th>$\bar{r}^2$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>20.5°C</td>
<td>674,000</td>
<td>$2.63 \times 10^{-5}$</td>
<td>720</td>
</tr>
<tr>
<td>Benzene</td>
<td>15.0°C</td>
<td>690,000</td>
<td>0</td>
<td>670</td>
</tr>
</tbody>
</table>

Poly (3 chlorostyrene) was initially measured at 9.5°C. Benzene with a freezing point of 5.5°C cannot safely be taken lower and still
POLY [4 CHLOROSTYRENE] IN BENZENE AT 20.5°C

\[ \frac{K_0 \times 10^6}{Re} \]

\[ \theta = 150° \]

\[ \theta = 90° \]

\[ \theta = 30° \]

\[ \theta = 0° \]

\[ \sin^2 \frac{\theta}{2} + 5000 \text{ Conc} \]
POLY [4 CHLOROSTYRENE] IN BENZENE AT 15.0°C

\[ \frac{K_c \times 10^6}{R_b} \]

\[ \text{Sin}^2 \theta = 5000 \text{ Conc} \]
give reproducible results. In an endeavour to attain theta conditions, the freezing point of the benzene was lowered by adding cyclohexane as solute. This allowed the working temperature of the light scattering to be dropped by a further $5^\circ C$. Working on the principle of depression of freezing point, it was calculated that to lower the freezing point of benzene by $5^\circ C$ i.e. from $5.5^\circ C$ to $0.5^\circ C$, the addition of 9.3 mls of cyclohexane per 100 mls of benzene was needed. Cyclohexane was chosen due to its similarity in physical properties and since it was expected to be a poor solvent for the polymer. Table 4.29 summarises the results obtained for poly (3 chlorostyrene).

Table 4.29 Dimensions of poly (3 chlorostyrene) from light scattering

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature</th>
<th>$\overline{M}_w$</th>
<th>$(A_2)z$ (cc. mole. g$^{-2}$)</th>
<th>$(r^2)\overline{z}$ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>9.5°C</td>
<td>$1.2 \times 10^6$</td>
<td>$1.95 \times 10^{-4}$</td>
<td>2000</td>
</tr>
<tr>
<td>Benzene</td>
<td>5.2°C</td>
<td>$1.3 \times 10^6$</td>
<td>$1.41 \times 10^{-4}$</td>
<td>1840</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Zimm plots obtained for poly (3 chlorostyrene) in benzene at $9.5^\circ C$ and in benzene/cyclohexane mixture at $5.2^\circ C$ are shown in Figs. 29 and 30.

The $dn/dc$ values used in these determinations were measured as previously and are given in Table 4.30.

Table 4.30 Refractive index increments for 3 chloro and 4 chloro poly (styrenes).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$dn/dc$ Benzene</th>
<th>$dn/dc$ Cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly (3 chlorostyrene)</td>
<td>+ 0.08200</td>
<td>+ 0.08377</td>
</tr>
<tr>
<td>poly (4 chlorostyrene)</td>
<td>+ 0.08151</td>
<td>-</td>
</tr>
</tbody>
</table>
POLY[3 CHLOROSTYRENE] IN BENZENE AT 9.5°C
CHAPTER 5.

DISCUSSION.

5.1 POLYMERISATION OF CYCLIC ETHERS

Polymerisability

The polymerisation of ring monomers is energetically favourable provided there is strain in the ring. As a result, the polymerisation of the three membered cyclic ether and its substituent compounds was first discovered over a century ago (116), whereas the polymerisation of T,H,F. was not accomplished until the 1930's (117). Free energy of polymerisation $\Delta G_p$, of which the heat of polymerisation, $\Delta H_p$, is the main contributor, may be expressed as a function of ring size. This has been done by Dainton et al (118,119) for cycloalkanes and by Small (120) for heterocyclic compounds. Small showed that the free energy change occurring on polymerisation shows a maximum in the polyether series for the six membered ring, tetrahydropyran. The differences in $\Delta H_p$ are caused mainly by changes in ring strain and by a certain amount of steric conflict between adjacent hydrogen atoms. The polymerisation of three and four membered cyclic oxides, ethylene oxide and oxacyclobutane, is accompanied by a large negative heat of polymerisation of about -20 k. cal. mole$^{-1}$, as shown in Table 5.1., and polymerisation occurs readily, probably due to ring strain. T,H,F. polymerises less readily than the three and four membered rings because of a smaller heat of polymerisation (-3.5 k. cal. mole$^{-1}$), whilst its polymerisability probably results from the repulsion of eclipsed hydrogens. In either case heats of polymerisation are such that for both oxacyclobutane and T,H,F. there are no experimental difficulties in polymerising them.

In this work attempts to polymerise 6 and 7 membered rings proved to be completely unsuccessful. This is not entirely unexpected
in the case of tetrahydropyran as it has a positive free energy of polymerisation, as shown in Table 5.1. Oxacycloheptane is in a similar position to T.H.P., in that it is the opposite side of the peak caused by the positive $\Delta G_p$ of tetrahydropyran, with a similar $\Delta G_p$ to T.H.P. There are no reports of its polymerisation in the literature although with a $\Delta G_p$ of -1.4 it has a favourable free energy of polymerisation. In this respect we must look further for the reasons for non polymerisation of oxacycloheptane. The cause may possibly lie in the non favourable kinetics of the system, the problem being in the mechanism rather than the free energy.

The three thermodynamic parameters, $\Delta H_p$ heat of polymerisation, $\Delta S_p$ the entropy change on polymerisation and $\Delta G_p$ free energy change on polymerisation are linked by equation 5.1, and are tabulated for the various monomers in Table 5.1.

$$\Delta G_p = \Delta H_p - T \Delta S_p$$

Table 5.1 : Thermodynamic parameters involved in the polymerisation of cyclic ethers at 298°C.

<table>
<thead>
<tr>
<th>Ring Size</th>
<th>Monomer</th>
<th>$\Delta S_p$ (e.u.)</th>
<th>$\Delta H_p$ (K.cal.mole$^{-1}$)</th>
<th>$\Delta G_p$ (K.cal.mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>ethylene oxide</td>
<td>-18.7</td>
<td>-22.6</td>
<td>-17.0</td>
</tr>
<tr>
<td>4</td>
<td>oxacyclobutane</td>
<td>-15.9</td>
<td>-19.3</td>
<td>-14.6</td>
</tr>
<tr>
<td></td>
<td>oxetane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>trimethylene oxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,3 -epoxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>oxacyclopentane</td>
<td>-10.2</td>
<td>- 3.5</td>
<td>- 0.5</td>
</tr>
<tr>
<td></td>
<td>tetrahydrofuran</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>tetramethylene oxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,4 -epoxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>oxacyclohexane</td>
<td>- 1.1</td>
<td>+ 1.3</td>
<td>+ 1.6</td>
</tr>
<tr>
<td></td>
<td>tetrahydropyran</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>pentamethylene oxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,5 -epoxide</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Substituted 4 membered rings have been studied by several workers (121-124) however the polymerisation of oxacyclobutane itself has received far less attention. Rose (101) successfully polymerised oxacyclobutane using \( \text{BF}_3 \) as catalyst and obtained a polymer of molecular weight \( 3 \times 10^4 \), as too did Yamamoto et al (24) using the same method.

Phosfluorogen A, the catalyst employed by Dreyfuss and Dreyfuss (99, 125) for ring opening T,H,F. has also been used in this work for ring opening oxacyclobutane. The resulting polymer, P.Tri.M.O. has been obtained over a wide range of molecular weight as shown in Table 4.7. Molecular weights of the order of \( 10^5 \) have been achieved and this is the first report of high molecular weight P.Tri.M.O.

The ability to produce high molecular weight P.Tri.M.O. is probably due to the extra stability of the \( \text{PF}_6^- \) gegenion, present in phosfluorogen A catalyst. From a chemical standpoint this is considerably more stable than say \( \text{BF}_4^- \) or \( \text{SbCl}_6^- \), commonly used catalysts which are often responsible for termination, or a combination of transfer and termination within the polymerisation reaction.

**Mechanism of Polymerisation**

It is believed (99,125) that the propagating species in the cationic polymerisation of T.H.F is the tertiary oxonium ion

\[
\text{CH}_2\text{CH}_2\text{O}^- + \text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}^- \rightarrow \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}^- + \text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}^-
\]

Propagation occurs via a nucleophilic attack of the monomer oxygen at an \( \alpha \) carbon atom to the positive oxygen. A new tertiary oxonium ion is formed but one monomer unit longer.
Similarly depropagation would occur by a nucleophilic attack by the penultimate oxygen atom followed by expulsion of monomer. At monomer-polymer equilibrium the rates of propagation and depropagation become equal.

Oxacyclobutane polymerises cationically and it is proposed that it proceeds in a similar way to T.H.F. Dreyfuss and Dreyfuss (99) suggest initiation by phosphorogen A, occurs via a hydride ion abstraction and that the expected product of hydride ion abstraction, chlorobenzene, is formed in the decomposition of p-CIC₆H₄N⁺PF₆⁻.

Therefore, by analogy

\[
\begin{align*}
\text{oxonium ion} & \quad \text{Nucleophilic attack of monomer oxygen at the } \alpha \text{ carbon atom of the oxonium ion then proceeds as before}
\end{align*}
\]
In any polymerisation process, successive additions of monomer units to a growing polymer chain (propagation) will continue either until a termination reaction takes place, until equilibrium is established, or until the supply of monomer is exhausted. In the latter case Szwarz (126) has given the name 'living' to the polymer system. Dreyfuss and Dreyfuss (99) have shown that T.H.F. may polymerise without any appreciable termination and consequently the system is an example of a 'living' polymer.

Within a 'living' system, eventually a steady state is attained and the rate of propagation becomes equal to the rate of depolymerisation, although in most practical situations the equilibrium is such that depolymerisation is trivial. For T.H.F about 3.0M of monomer remain in equilibrium with polymer (99) at a polymerisation temperature of 25°C. This compares with for example styrene where under normal polymerisation conditions the amount of monomer in equilibrium is very small (10^-6 - 10^-5 M) (127) but for α-methylstyrene is 0.75 and 7.5M at 0°C and 60°C respectively (128). T.H.F. is therefore more similar to the anionic α-methylstyrene case.

If a system containing 'living' polymers is at equilibrium at one temperature and the temperature is then altered, the steady state is destroyed and either polymerisation or depolymerisation will occur until a new steady state is established. Addition of further monomer to a polymerisation at equilibrium will cause

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polymerisation to continue until equilibrium is again reached at a higher molecular weight. If another monomer is added a block copolymer should result. Conversely, if additional growing centres are introduced to the polymerisation at equilibrium, propagation of the new chains will occur at the expense of depropagation of existing chains and a lower molecular weight polymer results. All of these phenomena take place in the T.H.F. polymerisation system catalyzed by Phosfluorgen A.

From the work of Dainton and Ivin (119) on reversible polymerisations, the concept of a polymerisation ceiling temperature has been defined. That is for reversible polymerisations there is a temperature above which the formation of long chain polymer from monomer is less favoured than depolymerisation and below which polymerisation is the more favoured process. This temperature is termed the ceiling temperature, $T_c$. It may also be defined as the temperature at which the free energy of polymerisation is zero and hence

$$T_c = \frac{\Delta H_p}{\Delta S_p} \quad \ldots \ldots (5.2)$$

and also

$$\Delta G_p = -RT\ln K$$
$$0 = RT\ln K$$
$$K = 1.$$ 

where $K$ is the polymerisation - depolymerisation equilibrium constant and $R$ the gas constant. The $T_c$ of T.H.F. is thought to be about 85°C (99,129).

**Polymer dispersity**

Miyake and Stockmayer (130) say that for batch polymerisation
of a living system, where neither initiator or monomer is added after the start, and with an irreversible polymerisation stage, the ratio of chain lengths, determined by weight and number averages \( \bar{X}_w / \bar{X}_n \), will pass through a maximum of about \( \sim 1.3 \) soon after the start before falling to unity at long polymerisation times. Further, Miyake and Stockmayer have also stated that for reversible living polymers, where the depolymerisation reaction is involved, \( \bar{X}_w / \bar{X}_n \) reaches a Poisson distribution fairly rapidly \( \sim 1.3 \) but ultimately approaches 2.0, the value for the 'most probable' equilibrium or Schulz distribution.

The P.Tetra.M.O. samples synthesised in this work have a molecular weight distribution \( \bar{M}_w / \bar{M}_n \) of about 1.8, as shown in Table 4.2. A high value is not unexpected as demonstrated in the kinetics of the system. In the presence of PF₆⁻ gegenions the propagation-depropagation equilibrium is very mobile and polymerisation can readily be reversed. Consequently the system is reversible and as predicted, ultimately a value of 2.0 should be obtained.

In view of the additional problems caused when conducting dimensional studies on polydispersed samples, the possibility of producing a narrower molecular weight distribution polymer was looked into.

One important consequence of a 'living' polymer is that the molecular weight of a polymer isolated from such a system depends only on the number of growing centres and the amount of monomer available for polymerisation. It would therefore seem that for monodispersity short polymerisation times and low conversion to polymer are the necessary conditions.

Accordingly a series of P.Tetra.M.O samples were polymerised following these conditions, and the dispersity of the samples obtained compared with previous samples. Instead of using polymerisation times from 1 - 10 days, periods of \( 3\frac{1}{2} \) to 5 hours were allowed. The catalyst was first dissolved in a minimum amount of monomer. In this way it was hoped that a system containing short chains with
active growing centres could be obtained. These would all have equal abilities to continue growing on addition of the rest of the monomer. Even with such elaborate methods these samples were found to have dispersities, $\frac{M_w}{M_n}$ of about 1.8, as shown in Table 4.5, which is identical to the previous P.Tetra.M.O. samples.

The P.Tri.M.O samples produced in this work are not monodispersed either, and as shown in Table 4.7 have molecular weight ratios $\frac{M_w}{M_n}$ lying between 1.5 and 1.8, with an average of about 1.8.

Contrary to the T.H.F./P.Tetra.M.O. system in which depolymerisation and polymerisation kinetics are similar, for oxacyclobutane/P.Tri.M.O., the depolymerisation rate is presumed much slower than that for the polymerisation stage. Indeed, theoretically, it is unlikely that the polymerisation of the four-membered ring is measurably reversible at room temperature. Knowing that the free energy changes for the polymerisation of T.H.F to P.Tetra.M.O and oxacyclobutane to P.Tri.M.O are respectively about $-2 \text{ K. cals. mole}^{-1}$ and $-22 \text{ K. cals. mole}^{-1}$, the equilibrium concentration of the four-membered ring is calculated to be extremely small, $< 10^{-13}$ at 0°C or 25°C, compared with the 20-30% of T.H.F present at equilibrium with its polymer. Since the reaction is not measurably reversible according to Miyake and Stockmayer the molecular weight distribution should fail to unity. However the P.Tri.M.O samples produced do not agree with this prediction being of the order of $\frac{M_w}{M_n} \approx 1.8$ as mentioned above.

There are however other factors which may cause polydispersity. In particular any impurities not eliminated from the system, despite the rigorous conditions described in chapter 3, can cause premature termination of the polymer chains, resulting in a broader distribution of molecular weight. Secondly there is the possibility of chain transfer.

During the course of the polymerisation the oxonium ion reacts with monomer oxygen and penultimate polymer chain oxygen. In addition
to this it should also be capable of reacting with other ether oxygens. Polymer ether oxygens are always present and intermolecular reaction is possible as shown

$$Z \sim \text{CH}_2\text{CH}_2\text{O} + \text{CH}_2\text{CH}_2 \sim X + \text{CH}_2 \sim Y \rightarrow Z \sim \text{CH}_2\text{CH}_2\text{O}(\text{CH}_2)_3 \sim O \sim \text{CH}_2 \sim X + \text{CH}_2 \sim Y$$

Although this mechanism has been written with respect to oxacyclobutane, the same applies within T.H.F. polymerisations. The overall result of such a reaction is to alter the molecular weight distribution of the product and clearly any such reaction taking place would have a direct bearing on the final dispersity of the sample, although the $M_n$ value would not be altered.

Bearing in mind Szwarc's definition of the living polymer Dreyfuss and Dreyfuss (89) in discussing the kinetics of polymerisation of T.H.F. to P.Tetra.M.O propose that if there is a direct relationship between the amount of catalyst charged and the number of growing centres formed, and the system is living, then there is a linear relationship between $\log [\eta]$ and $\log$ [catalyst]. This there undoubtedly is, as there also is with the P.Tri.M.O samples synthesised in the present work. The fact that they use this as evidence of a 'living polymer' is another matter since not only is this relation true of the systems being described here but in general many other types of polymerisation can also have a linear variation of $\log [\eta]$ with $\log$ [catalyst or initiator]. In fact Szwarc et al. (131,132) in his work with 'living polymers', shows that a linear
relation exists between log $[\eta]$ and log $[M/\gamma C]$ where $M$ represents monomer and $C$ catalyst concentration. The $\gamma$ arises since Szwarz is polymerising styrene by anionic polymerisation using a naphthalene $^-/Na^+$ complex. Dimerisation of the primarily formed species produces polymer with both ends living, consequently for each mole of catalyst used two growing centres are formed. Thus, the polymer molecular weight is dependent on $[M]/\gamma[C]$, a far more discerning test than that proposed by Dreyfuss.

Arguing along the same lines in the present work, if each catalyst molecule initiates one living chain, the theoretical molecular weight is given by the expression in equation (5.3).

$$\text{Theoretical molecular weight} = \frac{[M]}{[C]} \times M_o \quad \ldots \ldots (5.3)$$

where $[M]$ and $[C]$ are defined as before and $M_o$ is the monomer molecular weight. Table 5.2 compares the theoretical and experimental values obtained.

**Table 5.2**: Comparison of experimentally determined and theoretically calculated molecular weights.

<table>
<thead>
<tr>
<th>P.Tri,M.O. sample</th>
<th>Catalyst Concentration</th>
<th>$\overline{M}_n$</th>
<th>Theoretical $M,W.$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>excess</td>
<td>25,000</td>
<td>-</td>
</tr>
<tr>
<td>II</td>
<td>$7.0 \times 10^{-2}$ M</td>
<td>106,000</td>
<td>25,000</td>
</tr>
<tr>
<td>III</td>
<td>$6.15 \times 10^{-3}$</td>
<td>160,000</td>
<td>140,000</td>
</tr>
<tr>
<td>IV</td>
<td>$4.0 \times 10^{-3}$</td>
<td>226,000</td>
<td>220,000</td>
</tr>
<tr>
<td>V</td>
<td>$3.0 \times 10^{-3}$</td>
<td>237,000</td>
<td>290,000</td>
</tr>
<tr>
<td>VI</td>
<td>$2.46 \times 10^{-3}$</td>
<td>327,000</td>
<td>360,000</td>
</tr>
<tr>
<td>VII</td>
<td>$3.70 \times 10^{-4}$</td>
<td>755,000</td>
<td>2,400,000</td>
</tr>
</tbody>
</table>
The agreement obtained between theoretical and calculated molecular weights is excellent and apart from samples II and VII which shall be discussed later, are well in line with the above prediction for a living polymer. On this evidence it would suggest that oxacyclobutane polymerisation with phosfluorogen A catalyst is an example of a living system. Fig. 31 represents a graphical treatment of these results and shows a plot of $1/M_n$ versus $[C]/[M]M_o$. This in effect is a reciprocal plot of experimentally determined versus theoretically calculated molecular weight. For a living system this should have a slope of unity and should pass through the origin. This is approximately so, but in fact the best graphical fit has a slope of $\sim 0.8$ and misses the origin. The reason for this is probably chain transfer.

Polymer chain length is given by equation (5.4)

$$\frac{1}{x_n} = \frac{1}{(x_n)_o} + K_{tr} \frac{[M]}{[M]} \quad \ldots \ldots (5.4)$$

where $x_n$ represents actual chain length, $(x_n)_o$ is the theoretical chain length (eg $[M]/[C]$) and $K_{tr}$ is the chain transfer constant. The transfer term represents a number of possibilities and clearly these may all occur in the same system. Oxonium ion reacting with ether oxygens has been dealt with earlier where growing polymer reverts to dead polymer and the overall effect is a broadening of molecular weight distribution but a retention of the same average molecular weight. This has been omitted in the transfer term of equation (5.4). A further possibility is for growing polymer to go to monomer (there is no solvent present) and a possible mechanism is proposed for this below.

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FIG 31.
VARIATION OF EXPERIMENTAL MOLECULAR WEIGHT WITH THEORETICAL FOR P.TRI.M.O. SAMPLES.
The sudden termination of the growing polymer chain proposed here will have the effect of lowering molecular weight the result being dead polymer and monomer.

The sum total of transfer effect is to cause the plot shown in Fig. 31 to have a positive intercept, as a limit is being placed on the infinite molecular weight that can theoretically be achieved.

Whereas the proportion of chain transfer may not vary, at high molecular weight it assumes a greater significance, and it is thought that this is the reason for the observed lowering of molecular weight. For instance P.Tri.M.O sample VII has $M_n$ of 755,000 but theoretically its molecular weight is calculated to be 2,400,000. Although this appears erroneous it is explained by chain transfer and in fact lies on the graph shown in Fig. 31.

Further, P.Tri.M.O samples III to VII show an average 75% yield for monomer to polymer conversion, as shown in Table 4.6. Allowing for polymer losses, if the catalyst is only some 80% efficient this too will assume a greater importance when it is being used to the limits of its efficiency to produce high molecular weight polymer.

Returning to the results of Dreyfuss and Dreyfuss (99), instead of
plotting log [η] versus log [C] for the P.Tetra.M.O samples as they have done but plotting log [Mv] versus log [C], then if the system is a living one molecular weight should vary as [C]⁻¹. Fig. 32 shows the appropriate plot and from it the slope does in fact tend to a slope of -1 at low catalyst concentrations. A curious feature however is that as catalyst concentration increases the slope rapidly falls off and tends to zero. The kinetics of polymerisation cannot be as easily explained as Dreyfuss and Dreyfuss suggest.

Here it is believed the problem lies in the initiation stage. For polymerisation to occur monomer must react with catalyst to form an ionic species as follows.

\[ \text{CH}_2 - \text{CH}_2 \rightarrow \text{CH}_2 \rightarrow 0 + \text{Cl} \rightarrow \text{N} = \text{NPPF}_6 \rightarrow \text{CH}_2 - \text{CH}_2 \leftarrow \text{CH}_2 \rightarrow 0 \]

\[ \text{N} \rightarrow \text{O} \rightarrow \text{Cl} \]

From this the oxonium ions are provided for subsequent polymerisation. If with increasing catalyst concentration this reaction is upset then the number of oxonium ions being produced will diminish. This we believe is the cause of the anomalous behaviour at high catalyst concentrations. If the limiting solubility of the ionic species occurs before that of the coordinate species then equation (5.5) is best described as an equilibrium reaction with ionic species going to coordinate species being represented by the right to left reaction.

Not only does this explain Dreyfuss's observations but also the fact that P.Tri.M.O sample II synthesised in the present work has \( M_n \) of 106,000 but theoretically should have a molecular weight of 25,000. Concentration of catalyst is high enough for there to be a right to left reaction occurring in equation (5.5). The number of
FIG 32

EFFECT OF CATALYST CONCENTRATION ON MOLECULAR WEIGHT FOR THE P.TETRAM-O. SAMPLES OF DREYFUSS AND DREYFUSS (99) POLYMERISED IN BULK AT 25°C.
ionic species present is below that expected, consequently less growing centres are formed. A higher $\bar{M}_n$ is observed because there are less polymer chains present than theoretically predicted, but those that are, are longer.

On this account a limiting stage should be reached whereupon any further increase in catalyst concentration produces no corresponding increase in the number of active growing centres. This is exactly what has been observed. Using an excess of catalyst (P.Tri.M.O. sample I) a limiting molecular weight of 25,000 was found at the low end of the scale.

5.2 POLYMER SOLUBILITY

Solubility parameters

The interaction that arises when dissolving an amorphous polymer in a liquid is similar to that between two liquids. Solubility will occur if the free energy of mixing, $\Delta G$, given in equation (5.6) is negative.

$$\Delta G = \Delta H - T\Delta S$$

The partial molar entropy of mixing, $\Delta S$, of solvent is usually large and positive in a non-aqueous system so that the sign of $\Delta G$ is determined by the sign and magnitude of $\Delta H$, the heat of mixing. There are two possible situations. If there is some kind of positive interaction between polymer and liquid, so that $\Delta H$ is negative, then solution will occur. The so called 'good' solvents for a particular polymer belong to this group. Or, when interaction involves only dispersion forces, $\Delta H$ being positive, then the magnitude of $\Delta H$ is the critical factor in determining whether or not solution will occur. Hildebrand (133) in his work on the solubility of non-electrolytes, showed that the heat of mixing per unit volume, when only dispersion forces are involved, is
\[ \Delta H_1 = v_1 v_2 (s_1 - s_2)^2 \] ......(5.7)

where \( v_1 \) and \( v_2 \) are the volume fractions of solvent and polymer, and \( s_1 \) and \( s_2 \) are the solubility parameters of solvent and polymer, given by

\[ s = \left( \frac{\Delta E}{V} \right)^\frac{1}{3} \] ......(5.8)

\( \Delta E/V \), the energy of vapourisation per unit volume is called the cohesive energy density (CED). For \( \Delta H \) to be minimal \( s_1 \) and \( s_2 \) should be close in magnitude. Therefore if the solubility of a polymer in a particular solvent is approached via solubility parameters, in the absence of specific interaction effects, it will dissolve if the CED of the polymer is close to that of the solvent. This method of determining polymer solubility is not always successful however. In many cases interaction effects can dominate the heat of mixing. This may cause, for instance, a polymer to dissolve in a solvent where their CED's are far removed from each other.

**Theta solvents**

As explained in chapter 2 the interaction between solvent and polymer molecules will cause the polymer chain to be extended to a greater or lesser degree. The mean end to end distance of the polymer chain will thus be greater than that predicted for an identical unperturbed chain. This chain extension is characterised by the expansion factor \( \alpha \). As the solvent is made less good, (e.g. by lowering the temperature), the configuration of the chain molecule approaches that of a random coil. This is accompanied by \( \alpha \) approaching unity and becoming equal to unity at a certain temperature, the theta temperature. At this point the polymer in solution is at the point of phase separation. In quoting a theta temperature a unique
characteristic of a polymer and solvent are being given.

A theta solvent can be a single solvent or a mixture of two, three or more solvents and non-solvents. A good solvent can be made into a theta solvent by adding non-solvent (precipitant) until the polymer is just at the point of precipitation. However the use of mixed solvents immediately raises further problems. It is possible for the composition of the solvent mixture within the domains of the polymer molecules to differ slightly from that outside owing to selective absorption of solvent in preference to the non-solvent. This will result in a non homogeneous system, although in sufficiently dilute solution this may be overcome. Neither can the mixed solvent be considered a single solvent with regard to polymer precipitation, since nonsolvent-solvent ratios differ markedly for the two phases in equilibrium.

Phase separation techniques will always be molecular weight dependent with higher molecular weight polymer tending to come out of solution first. This is not ideal in the thermodynamic sense since unless \( \chi = \frac{1}{2} \) in the Flory-Huggins equation (2.18) or \( \frac{\theta}{T} = 1 \), i.e. \( 1 - \frac{\theta}{T} = 0 \), in the dilute solution theory equation (2.30), theta conditions are not exact. The corresponding condition for a mixed solvent is phase separation of a species at infinite molecular weight. Thus the single solvent will always be preferable to a mixed solvent.

At the theta temperature the polymer solution behaves as an ideal, or at least a pseudo-ideal solution. In a truly ideal solution both the enthalpy of dilution and the excess entropy of dilution are zero. The thermodynamic behaviour described above results from the fact that intermolecular attraction terms just compensate for molecular size, so that the excluded volume becomes zero.

Deviations from ideality observed in dilute polymer solutions can be traced by evaluating the second virial coefficient. This quantity
depends on a large number of factors and the work described here has shown its dependence on solvent, molecular weight and temperature.

The decrease of $A_2$ with increasing molecular weight is shown in Fig. 33 for the series of P.Tri.M.O samples synthesised in the present work. The dotted line in the same figure is the theoretical variation predicted from Flory's dilute solution theory with additional approximations. The theoretical line was deduced from the expression given in equation (5.9) as described below (54).

$$A_2 = \frac{J}{N} P(J^3) \quad \ldots \ldots (5.9)$$

$A_2$ is the second virial coefficient and $N$ Avogadro's number. The quantity $J$ represents various thermodynamic parameters and $J^3$ is obtained from the very simple relation shown in equation (5.10)

$$J^3 = 2(\kappa^2 - 1) \quad \ldots \ldots (5.10)$$

The function $F(X)$ (with $X$ replacing $J^3$) varies as the series expansion

$$F(X) = 1 - \frac{X}{2!} + \frac{X^2}{3!} - \ldots$$

A combination of equations (2.44) and (2.46) gives

$$[\eta_g] = \Phi_0 \left( \frac{r_o^2}{M} \right)^{3/2} \quad \ldots \ldots (5.11)$$

The ratio $(r_o^2/M)^{1/2}$, which is independent of molecular weight, has been calculated to be 0.728 for P.Tri.M.O as given in Table 5.8. Hence from equation (5.11), $[\eta_g]$ for each polymer sample is known and using equation (2.43) $\alpha$, the chain expansion parameter follows. Hence knowing $\alpha$, $P(J^3)$ can be calculated. A value of $J$ in equation (5.9) was found by taking a known $A_2$ for one of the P.Tri.M.O samples from
Fig 33.

Variation of second virial coefficient with molecular weight for P.Tri.M.O. in toluene at 25°C.

Experimental.

Theory.
Table 4.8. Thus having fixed a value of $J$ by trial, $A_2$ values were calculated for the series and plotted as a function of molecular weight.

Flory (54) has observed and indeed the same has been found here that there is a significantly larger decrease in $A_2$ with $M$ than is predicted by theory. Whereas theory predicts a slope of $-0.1$ in practice $-0.8$ is obtained. Inaccuracies in the theory may arise since the polymer chain is thought of as a cloud of chain segments and when segment interactions are estimated they are done so without taking into account the continuity of the chain from one segment to the next.

Simple excluded volume theory can also be used to predict a molecular weight dependence for $A_2$ since from equation (2.28) we have the relationship $A_2 = N u / 2M^2$ where $u$ represents excluded volume. Very simply, if the excluded volume of the polymer chain is taken as the volume of an equivalent sphere of radius $R_0$, its volume, $u$, will be given by $4/3 \pi R_0^3$. Assuming the radius of the sphere is proportional to the end to end distance of the polymer chain i.e. $R_0 \propto (r^2)^{1/2}$, then since $r^2 \propto n \ell^2$ where $n$ is the number of bonds per polymer chain and $\ell^2$ the mean square bond length, it follows that $r^2$ is directly proportional to molecular weight since $n$ is directly dependent on $M$. Hence we may write

$$u \propto \frac{4}{3} \pi \left( \frac{r^2}{M^2} \right)^{3/2}$$

and

$$u_i \propto \frac{4}{3} \pi M^{3/2}$$

and

$$A_2 \propto \frac{4}{3} \pi M^{3/2} \cdot \frac{1}{M^2}$$

$$\therefore A_2 = KM^{-1/2}$$
K is a constant including the proportionality constant. From this approach $A_2$ is shown to have a dependence on molecular weight to the $-\frac{1}{2}$.

Thus the simple excluded volume theory outlined above shows a greater $M$ dependence of $A_2$ than is predicted by Flory's dilute solution theory and is more in line with the slope $\sim -0.8$ observed in Fig. 33. However, the main objection to this theory is that when the sphere expands (i.e. $M$ increases) it does so faster than Gaussian chain statistics predict. Therefore $\rho^2$ is not really proportional to $M$ but to some higher power of $M$ (i.e. $\rho^2 \propto M^{(1 + x)}$), in a good solvent. This dependence of $M$ is the same as the 'a' value calculated in the relationship $[\eta] = KM^a$. For P.Tri.M.O. in toluene at 25°C it was calculated, as shown in section 4.2.4, to have a value of 0.81. Consequently $x$ has a value of $\sim 0.3$. This has the effect of lowering molecular weight dependence on $A_2$, as given by equation (5.12), and brings it more in line with dilute solution predictions.

However it still does not account for an experimental variation of $\sim -0.8$. In addition there must be some term that causes a lowering of molecular weight dependence on excluded volume. Possibly, with chain expansion causing a lowering of segment density, exclusion for a given sphere will become less rigorous. Molecular weight dependence on excluded volume will now be powered by some fractional power $y$. Thus $u \propto M^{(\frac{3}{2} - y)}$. The present results show a molecular weight dependence of $\sim -0.8$ with $A_2$. In order to fit experimental results to prediction, and bearing in mind $M$ also has an additional positive dependence given by $x$, the value $y$ is required to take is $\sim 0.6$.

So, $u$ must vary as $M^{0.9}$.

The decrease in $A_2$ observed in a transfer from good to poor solvent is shown in Tables 4.20 and 4.21 for both P.Tri.M.O. and P.Tetra.M.O. Similarly it was also pointed out in section 2.2 that temperature should have a pronounced effect on the value of $A_2$. 
particularly in poor solvents. Tables 4.15 and 4.17 show how $A_2$ falls with decreasing temperature until at $25.0^\circ C$ for P.Tri.M.O. in cyclohexane and at $44.8^\circ C$ for P.Tetra.M.O. in 1-hexane, the polymers are at their respective theta conditions and zero $A_2$.

This method was used to find theta conditions for the two polymers. The critical miscibility temperature was first crudely determined and then the theta temperature exactly located from $A_2$ data. Other methods, such as cloud point titration, are available for determining theta conditions, but were not used here.

A search of the literature shows that there are theta solvents for P.Tetra.M.O. already known. Evans and Huglin (22) have shown that isopropanol at $44.6^\circ C$, diethyl malonate at $33.5^\circ C$ and a mixture of ethyl acetate/n-hexane (22.7/77.3 wt. %) at $30.4^\circ C$ are all suitable. Also, Kurata et al. (21) have quoted the same mixed solvent in exactly the same proportions to be a theta solvent for P.Tetra.M.O. at $31.8^\circ C$. However, none of these are suitable in the present study as a non-polar solvent for dielectric measurements is required. May and Wetton (115) have said that cyclohexane/n-heptane is a theta solvent for P.Tetra.M.O. but the precise conditions have not been ascertained. Due to the non-polar nature of both components, this prompted initial investigations for a theta solvent. Osmometry was used for determining second virial coefficients of polymer solutions made of varying cyclohexane/n-heptane proportions. This yielded anomalous results in that over a wide variation of solvent composition, $A_2$ values below $10^{-4}$ could not be obtained, in spite of the fact that polymer was on the verge of precipitating from solution on occasions. A further feature of the $T/C$ versus $C$ plot was a high degree of curvature for some of the lines (see Fig. 17).

The anomalous behaviour of the mixed theta solvent is not an unknown phenomena. Oee (134) and Scott (135) have written that
preferential absorption of one component by the polymer coils may occur, resulting in the ratio of solvent to non-solvent in the two compartments of the osmometer being slightly different at equilibrium. The time required for final equilibrium may be prolonged as a result of the disproportionate movement of the two solvent components across the membrane.

Because of the additional complications arising with mixed solvents attention was diverted into finding a suitable single theta solvent.

1-hexene at 44.8°C was found to be a theta solvent for P.Tetra.M.O. Although not strictly non-polar the amount of polarity caused by the double bond ($\mu = 0.09 D$), is insufficient to complicate subsequent dipole moment measurements.

As mentioned earlier, the P.Tri.M.O. prepared in this work is the first recorded high molecular weight polymer to be obtained. Cyclohexane at 25°C was found to be a theta solvent (136). Cycloheptane and cyclooctane show suitable theta solvent properties, although P.Tri.M.O. requires progressively higher temperatures to dissolve in them. However, as Table 4.16 shows it is soluble in all of these solvents at 40°C. With cyclohexane being both the most suitable and readily available it was not necessary to study the P.Tri.M.O./cycloheptane or P.Tri.M.O./cyclooctane systems further. It is clear though that the theta temperature for these two solvents lies between 25 - 40°C.

5.3 UNPERTURBED DIMENSIONS

5.3.1 The method of light scattering

The precision with which measurements can be obtained from light scattering depends greatly on the accuracy of measurement of the change in refractive index with concentration, because this later appears as a squared term in the Debye equation. For the greatest accuracy it is preferable for this quantity to be as large
as possible but it is usually in the range 0.03 to 0.2 cc/g. The dn/dc values used in this work (see Table 4.19) all lie within this range although P.Tri.M.O. in toluene at -0.0306 gives the lowest value. In fact P.Tri.M.O. in various solvents shows far smaller refractive index increments (varying between -0.03 and -0.04) than does P.Tetra.M.O. (varying between +0.13 and +0.16).

The differential method employed in this instrument holds the great advantage of being fairly insensitive to small temperature changes. Ambient temperature for instance, need not be closely controlled since the temperature coefficient of the difference in refractive index between a solution and its solvent is much smaller than that for the refractive index of solution or solvent alone. It is essential, however, that solution and solvent in the differential cell are at the same temperature and therefore all solutions were allowed to attain equilibrium before subsequent measurements were taken. Tests performed with sucrose solutions in water showed that with the cell lid and cell-housing in position, no detectable change in observed values of d occurred over a period of two hours. With a highly volatile solution such as 1-hexane, however, a significant drift of Δd with time was noted. It was therefore necessary for readings to be taken rapidly. The time required for equilibrium was shortened by taking pre-thermostated solutions.

Both perturbed and unperturbed dimensions of P.Tri.M.O. and P.Tetra.M.O. obtained from light scattering are given in Tables 4.20 and 4.21. The values given are the root mean square end to end distance. For comparative purposes these distances are best quoted in terms of the characteristic ratio \( r^2/n \). \( r \) is the number of main chain bonds and is obtained as the product of the degree of polymerisation and the number of bonds per monomer unit (which is 4 in the case of P.Tri.M.O. and 5 for P.Tetra.M.O.). \( n^2 \) is the mean
square bond length and is calculated from the C - C and C - O bond lengths where $l_{c-c} = 1.53 \text{ Å}$ and $l_{c-o} = 1.43 \text{ Å}$.

Equation (2.62) shows that light scattering data can yield weight average molecular weight but z average end to end distance. Therefore in the conversion to $\frac{r^2}{n l^2}$, n must be in terms of the same average as $r^2$ i.e. as the z average number of bonds. This can be calculated from a knowledge of the z average molecular weight.

As explained in section 2.5, Benoit (75) has proposed a method of calculating the z degree of polymerisation, $N_z$, directly from the Zimm plot by using both the limiting tangent and the asymptote to the reciprocal intensity curve. The average $N_z$ for P.Tri.M.O. calculated from Zimm plots (Figs. 21a and 21b) is 27,800 and for P.Tetra.M.O. calculated from plots (Figs. 22-24) is 24,000. These values were used in calculating $\frac{r^2}{n l^2}$ values for perturbed and unperturbed dimensions of the two polymers and are shown in Table 5.3.

**Table 5.3:** z - average dimensions from Benoit treatment

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$\frac{r^2}{n l^2}$ P.Tri.M.O. ($N_z = 27,800$)</th>
<th>$\frac{r^2}{n l^2}$ P.Tetra.M.O. ($N_z = 24,000$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good solvent</td>
<td>3.04</td>
<td>4.00</td>
</tr>
<tr>
<td>$\theta$ solvent</td>
<td>119</td>
<td>2.7</td>
</tr>
</tbody>
</table>

These values are a lot lower than the theoretical ones calculated by Mark (42-44) shown in Table 2.2. The anomaly lies in the fact that the $N_z$ values as calculated from the Zimm plots are far too high when compared with their $N_w$ values, see Table 5.4.
Table 5.4: Comparison of weight average degree of polymerisation with Benoit z average

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Nw</th>
<th>Nz</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.Tri.M.O.</td>
<td>8620</td>
<td>27,800</td>
</tr>
<tr>
<td>P.Tetra.M.O.</td>
<td>8690</td>
<td>24,000</td>
</tr>
</tbody>
</table>

They show ratios of approximately 3 : 1 for $M_z : M_w$ which is highly unlikely if $\bar{M} : \bar{M}$ is 1.8 : 1. Whereas in theory the shape of the plot of $Kc/R_\theta$ versus $\sin^2 \theta/2$ should furnish the dispersion of the polymer, in practice it seems difficult to obtain data of sufficient precision to yield information on this point.

The dispersity of the polymers and hence $M_z$ can however be estimated from a knowledge of the ratio weight average molecular weight to number average molecular weight. For most molecular weight distributions encountered in polymer systems the averages of $M$ are related in good approximation to the heterogeneity defined according to the Schulz - Zimm distribution function, $U$, (73), where $U = M_w/M_n - 1$ and

$$M_n : M_w : M_z = 1 : (1 + U) : (1 + 2U)$$

$\cdots \cdots (5.14)$

From Tables 4.7 and 4.2, the average values of $M_w/M_n$ are 1.6 for P.Tri.M.O and 1.8 for P.Tetra.M.O, which would mean $U$ has the values 0.6 and 0.8 respectively. Table 5.5 shows the $M_z$ values that the two polymers would then have.
Table 5.5: Molecular weights from Schulz - Zimm distribution

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.Tri.M.O.</td>
<td>315,000</td>
<td>500,000</td>
<td>715,000</td>
</tr>
<tr>
<td>P.Tetra.M.O.</td>
<td>350,000</td>
<td>625,000</td>
<td>900,000</td>
</tr>
</tbody>
</table>

$N_z$ is given by $\frac{M_z}{m_o}$ where $m_o$ represents the monomer molecular weight, and $n$ is obtained from the product of this ratio and the number of bonds per monomer. The calculated $\bar{r}^2/nl^2$ values are given in Table 5.6.

Table 5.6: $z$ average dimensions from light scattering

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$\frac{\bar{r}^2}{nl^2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P.Tri.M.O.</td>
</tr>
<tr>
<td>Good solvent</td>
<td>6.9</td>
</tr>
<tr>
<td>$\theta$ solvent</td>
<td>4.3</td>
</tr>
</tbody>
</table>

From equation (2.3) the dimension of the hypothetical freely rotating chain are given by

$$\frac{\bar{r}^2}{r_{of}^2} = nl^2 \frac{(1 + \cos \theta)}{(1 - \cos \theta)}$$

$n$ and $l$ have the usual meaning, and $\theta$ is the bond angle. The conformational parameter is then the ratio of the mean square unperturbed end to end distance to the mean square end to end distance of the freely rotating chain

$$\sigma = \left( \frac{\bar{r}^2}{r_{of}^2} \right)^{\frac{1}{2}}$$

\[ \ldots (5.15) \]
From equations (2.3) and (5.15) it therefore follows that

\[
\frac{r^2}{\eta^2} = \frac{2}{\sigma^2} \frac{(1 + \cos \theta)}{(1 - \cos \theta)} \quad \ldots \ldots \ldots (5.16)
\]

Since the COC bond angles in ethers and related compounds are approximately tetrahedral, \( \theta \) was taken as 110\(^\circ\) and the following conformational parameters calculated from light scattering data were obtained for P.Tri.M.O. and P.Tetra.M.O. These will be discussed and compared with values obtained from other methods later.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Conditions</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.Tri.M.O.</td>
<td>Cyclohexane, 25.0(^\circ)C</td>
<td>1.47</td>
</tr>
<tr>
<td>P.Tetra.M.O.</td>
<td>1-hexene, 44.8(^\circ)C</td>
<td>1.60</td>
</tr>
</tbody>
</table>

One further measurement shown in Table 4.21 is the dimension of P.Tetra.M.O. in 1-hexene at 35.0\(^\circ\)C. This is below the theta temperature of 44.8\(^\circ\)C as confirmed by the Zimm plot (Fig. 24) having negative second virial coefficient. This end to end distance is also less than for the ideal polymer length at theta conditions. It would seem therefore that polymer should be precipitating, and this is in fact the case, as after the experiment some polymer was found separated out onto the cell walls of the light scattering instrument. As might be expected, the points on the Zimm plot show an appreciable amount of scatter and therefore no great emphasis can be placed on the quoted end to end distance.

5.3.2. The method of viscometry.

From equation (2.93) and (2.94), \( K_0 \) and hence the unperturbed dimensions can be calculated. \( \Phi_0 \) was taken as \( 2.87 \times 10^{21} \) with
concentration in g/dl. and other units as defined in section 2.6.

The dimensions obtained are directly dependent on the chosen value of \( \frac{1}{10} \). However, it is a problem that also arises when obtaining unperturbed dimensions from extrapolated data in good solvents and will be discussed at a later stage.

The calculated dimensions, given in Table 5.8, are quoted in terms of \((r_0^2/M)^{\frac{1}{2}}\), as the root mean square end to end distance \((r_0^2)^{\frac{1}{2}}\), and as the characteristic ratio \(r_0^2/n_1^2\).

**Table 5.8:** Viscosity unperturbed dimensions

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Conditions</th>
<th>(k_g \times 10^3) (dl/g)</th>
<th>((r_0^2)^{\frac{1}{2}}) (Å)</th>
<th>((r_0^2)^{\frac{3}{2}}) (Å)</th>
<th>(r_0^2/n_1^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.Tri.M.O.</td>
<td>Cyclohexane, 25.0°C</td>
<td>1.105</td>
<td>0.728</td>
<td>420</td>
<td>3.6</td>
</tr>
<tr>
<td>P.Tetra.M.O.</td>
<td>1-Hexene, 44.8°C</td>
<td>1.41</td>
<td>0.852</td>
<td>650</td>
<td>4.8</td>
</tr>
</tbody>
</table>

As before the conformational parameters \(\sigma\) for the two polymers may be calculated and they are shown in Table 5.9.

**Table 5.9:** Conformational parameters from viscosity data

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Conditions</th>
<th>(\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.Tri.M.O.</td>
<td>Cyclohexane, 25.0°C</td>
<td>1.35</td>
</tr>
<tr>
<td>P.Tetra.M.O.</td>
<td>1-Hexene, 44.8°C</td>
<td>1.55</td>
</tr>
</tbody>
</table>

The expansion factor, \(\alpha\), can be calculated from the viscosity data given in Table 4.19 since
\[ x^3 = \frac{[\eta]}{[\eta_0]} \] ......(5.17)

and the same quantity from light scattering data follows as

\[ x = \left( \frac{r^2}{r_0^2} \right)^{\frac{1}{2}} \] ......(5.18)

As a result we may compare the expansion factors for P.Tri.M.O. and P.Tetra.M.O., obtained from two independent sources. These values are shown on Table 5.10.

Table 5.10: Expansion factors for P.Tri.M.O. and P.Tetra.M.O.

<table>
<thead>
<tr>
<th>Method</th>
<th>Expansion factor, x</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P.Tri.M.O.</td>
</tr>
<tr>
<td>Viscometry</td>
<td>1.60</td>
</tr>
<tr>
<td>Light Scattering</td>
<td>1.285</td>
</tr>
</tbody>
</table>

From which it is seen that the light scattering values are lower and show an approximately 25% chain expansion in going from the unperturbed state to the perturbed dimension. Viscometry shows an expansion of between 50-60% in chain length. Although x from light scattering has been calculated via absolute values of chain dimensions it ultimately depends on the accuracy of the Zimm plots and the precision with which slopes can be determined. As has been outlined earlier these difficulties are enormous. Therefore the viscometry values of 1.60 and 1.55 for P.Tri.M.O. and P.Tetra.M.O. respectively, are probably the more accurate. Indeed they are in line with the viscometry values obtained by amongst others Flory and Fox (1,137,138) and Flory and Krigbaum (139) for poly(isobutylene) in cyclohexane and poly(styrene)
in benzene, using polymers of a similar molecular weight.

5.3.3 Theoretical treatments

The theoretical treatments of Kurata - Stockmayer (2) and Stockmayer - Fixman (3) have been used for the P.Tri.M.O. system in toluene. The graphical representations are shown in Figs. 15 and 16 respectively. From the graphs, $K_0$, from which the unperturbed dimensions are calculated, and $B$, a polymer-solvent interaction parameter, are obtained. The graphical procedures required in these two cases are described in detail in chapter 2.

Using the values of $K_0$ given in Table 4.11 and substituting into equation (2.46) the unperturbed dimensions of the polymer chain were obtained. They are given in Table 5.11 as the root mean square end to end distance and as the characteristic ratio $r_o/\eta_1^2$.

Table 5.11 P.Tri.M.O. unperturbed dimensions via K-S and S-F treatments

<table>
<thead>
<tr>
<th>Method</th>
<th>$\lambda$</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M, W, b, basis$</td>
<td>$\left(\frac{r_o}{\eta_1^2}\right)^\frac{1}{2}$</td>
<td>$\left(\frac{r_o}{\eta_1^2}\right)^\frac{1}{2}$</td>
</tr>
<tr>
<td>$\bar{M}_n$</td>
<td>435</td>
<td>3.83</td>
</tr>
<tr>
<td>$\bar{M}_v$</td>
<td>473</td>
<td>3.70</td>
</tr>
</tbody>
</table>

These values are once again dependent on the chosen value of the viscometry parameter $\phi_0$. Throughout this work $\phi_0$ has been taken as $2.87 \times 10^{21}$, the theoretical value for monodisperse polymers. This value comes from the Kirkwood-Riseman theory (78) of viscosity at the $0$ - point. This figure was obtained by neglecting segmental Brownian motion, but Zimm (83) has since verified that the error so introduced is only small ($\sim 1\%$). Brandrup and Immergut (140) list
\( \bar{\Phi} \) in terms of degree of fractionation and show it can take values down to \( 2.1 \times 10^{21} \). This is the empirical value originally recommended by Flory and Fox (55), and more recently Hearst (141) has obtained a theoretical value of \( 2.2 \times 10^{21} \) in good agreement with this. Banks and Greenwood (142) however working with amyllose acetate suggest that \( \bar{\Phi}_o \) is as low as \( 1.6 \times 10^{21} \). To date the value \( 2.87 \times 10^{21} \) seems to be the most widely accepted one, and since it has been used by other workers for P. Tetra. M. O. systems it has been used here to enable us to make direct comparisons.

For the graphical procedures of both the Kurata-Stockmayer treatment, shown in Fig. 15, and the Stockmayer-Fixman treatment, shown in Fig. 16, results have been plotted on a number average and viscosity average molecular weight basis. This has enabled a more precise value for the intercept and hence \( K_\Theta \) to be obtained in each case. It would be expected that the \( \bar{M}_n \) based plot would show a wider spread of points since any incorrect \( \bar{M}_n \) or viscosity value would be directly reflected in such a plot. Since viscosity average molecular weights were calculated from the \( K \) and \( a \) values obtained in this work there will be an element of self-consistency which is shown in the respective \( \bar{M}_v \) plots of the two treatments.

Although the \( \bar{M}_v \) based slopes and consequently the polymer-solvent interaction parameters are not in close agreement with those determined from \( \bar{M}_n \) based plots (see Table 4.12) for the two treatments they are both in good agreement with each other. That is to say polymer-solvent interaction parameters from \( \bar{M}_n \) based plots are in good agreement for the two treatments, as too are those obtained from the \( \bar{M}_v \) based plots. Disagreement comes in comparing \( \bar{M}_n \) and \( \bar{M}_v \) based values. The \( K_\Theta \) values obtained from the intercepts of the \( \bar{M}_n \) and \( \bar{M}_v \) based plots are in excellent agreement and consequently afford a direct check on each other. It is likely that the \( \bar{M}_v \) plots

-145-
will give the best results for the polymer-solvent interaction parameter. This is because in taking viscosity average molecular weight we are using the correct average for the calculations involved, also in the plots of Figs. 15 and 16 functions of viscosity are plotted against $\overline{M}_v$ and clearly the same errors will occur in each axis and to a certain extent will cancel each other.

Considering the methods whereby $K_\theta$ can be obtained, the graphs of the two theoretical functions shown in Figs. 15 and 16 emphasize the errors to which all current treatments are subjected. However the fact remains that even if a fairly accurate value of $K_\theta$ can be obtained, the unperturbed dimensions remain dependent of the value of the viscosity constant $\overline{\eta}_0$, for which there is no generally accepted value.

Once again the unperturbed dimensions obtained in this way can be expressed in terms of the conformational parameter $\sigma$. These are shown in Table 5.12

<table>
<thead>
<tr>
<th>Method</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\overline{M}_n$</td>
<td>K-S: 1.39</td>
</tr>
<tr>
<td>$\overline{M}_v$</td>
<td>K-S: 1.36</td>
</tr>
</tbody>
</table>

5.3.4 Comparison of methods

It may be true to say that polymer dimensions are most readily obtained from measurements of the limiting viscosity number, but the interpretation of such measurements necessitates a separation of the short and long range interactions. At the theta point the excluded volume effect vanishes and an estimate of unperturbed polymer dimensions (i.e. short range interactions only) may be made directly from
measurements at this point. The attainment of theta conditions is not easy and sometimes when it may be experimentally impossible it is then necessary to make use of one of the theoretical treatments.

In the present work the theories of Kurata-Stockmayer and Stockmayer-Fixman have been applied to a series of poly(trimethylene oxide) samples in toluene. The unperturbed dimensions obtained directly from experiment can thus be compared with those resulting from the theoretical separation of short and long range interactions, thus enabling an assessment to be made of the validity of the various theories.

Unperturbed dimensions were measured directly at theta conditions for P.Tri.M.O. and P.Tetra.M.O. using viscometry and light scattering. Once again viscosity data was the more easily obtained but the dimensions calculated are dependent on the value of $\phi_0$ chosen. Light scattering gives an absolute unperturbed dimension but unfortunately the experimental difficulties encountered are numerous. Also as shown earlier the polydispersity problem is not easily resolved when determining polymer dimensions, from light scattering. The dimension calculated is the z average and when expressing it as the characteristic ratio $\frac{2}{n^2}$, $n$ the number of bonds in the chain must be of the z average molecular weight. This work shows how z averages have been estimated via the Benoit treatment direct from the Zimm plots and via the theoretical treatments of Schulz and Zimm. The former case has proved to be highly inaccurate with the difficulty lying in the impossibility in determining relative slopes from the Zimm plot to any high degree of accuracy.

5.3.5 Configuration of Poly(ethers)

The P.Tetra.M.O. dimensions calculated in the present work show good agreement, with the viscosity method taking slightly the lower value. However both measurements fall between the limits calculated by Mark (20) all of which are shown in Table 5.13. They are therefore consistent with predicted values. Other workers (21,22) have obtained
unperturbed dimensions of P.Tetra.M.O. considerably higher than predicted, in each case though, their data comes solely from viscometry and the final result is always dependent on the particular value of $\phi$ chosen.

Dimensions of P.Tri.M.O. from light scattering, viscometry and the theoretical treatments of Stockmayer-Fixman and Kurata-Stockmayer are all shown in Table 5.13. The only work available for comparison is that of Yamamoto et al. (24) working with low molecular weight ($< 25,000$) P.Tri.M.O. Once again viscosity measurements determined here give a lower value than the corresponding light scattering dimension. The theoretical treatments are self consistent in this instant, showing $\frac{r^2}{n\lambda^2}$ values of $3.76$ and $3.8$, compared with viscometry and light scattering $3.6$ and $4.3$ respectively. The validity of the theoretical treatments for the systems under discussion does not seem in doubt, the values they produce falling directly between the absolute viscometry and light scattering values. Overall, the P.Tri.M.O. unperturbed dimensions calculated by the various independent methods, all lie within Mark's predicted range of $\frac{r^2}{n\lambda^2}$, of $3.4$ to $4.3$, showing a mean of $3.86$.

The flexibility of a polymer chain is expressed in terms of its conformational parameter $\sigma$, which is defined in equation (5.15) as the root mean square end to end distance of the chain in a theta solvent relative to its value which would be obtained if the hindrance to the rotation of successive bonds were absent except for the bond angle restrictions. It is of interest to compare the values of this parameter for polymers whose structural units vary in a systematic fashion. The polyethers with which we are dealing are a good example of this and we may represent the series by $\frac{1}{n}(\text{CH}_2)_m - 0 - 1/n$. Where $m$ is the number of $\text{CH}_2$ units per monomer up to the limiting value of $m = \infty$, which is poly(ethylene).
An overall picture of the present work can now be seen in the light of known data, and, that predicted, as compiled in Table 5.13.

Table 5.13: Comparison of $\bar{r}_o^2/nl^2$ and for poly(ethers) $-(CH_2)_m-O-\frac{1}{n}$

<table>
<thead>
<tr>
<th>Polymer</th>
<th>m</th>
<th>Literature</th>
<th>Present work</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\bar{r}_o^2/nl^2$</td>
<td>Ref</td>
</tr>
<tr>
<td>P.M.O.</td>
<td>1</td>
<td>11.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>P.E.O.</td>
<td>2</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>P.Tri.M.O.</td>
<td>3</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.4 - 4.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(calc)</td>
<td></td>
</tr>
<tr>
<td>P.Tetra.M.O.</td>
<td>4</td>
<td>5.6 - 6.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.6 - 5.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(calc)</td>
<td></td>
</tr>
<tr>
<td>P.Hexa.M.O.</td>
<td>6</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>P.Deca.M.O.</td>
<td>10</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>P.E.</td>
<td></td>
<td>6.67</td>
<td></td>
</tr>
</tbody>
</table>

* Calculated using $\bar{r}_o = 2.5 \times 10^{21}$

All values calculated at 25.0°C
The σ values quoted in Table 5.13 are best shown graphically as a variation of 1/n, where n represents the number of CH₂ groups per monomer. This is done in Fig. 34. Data for polyethylene has been included since this polymer may be regarded as the limiting case of the polyether series in which the number of carbon atoms between ether oxygen atoms becomes infinitely large.

From Table 5.13 and Fig. 34 it appears that P.M.O. and Poly(ethylene) (P.E.) the first and last member of the poly(ether) series have the highest polymer dimensions. For chains having equal skeletal bond angles, \[ \lim_{n \to \infty} \left( \frac{r_0^2}{n l^2} \right) = \infty \] for both the all trans form and the all gauche form of the same sign. Thus such chains will have large values of \( r_0^2/n l^2 \) if there is a marked preference for either trans or gauche states. Poly(ethylene) chains are in largely trans states and P.M.O. chains largely gauche which would explain their relatively high characteristic ratios. According to Mark the low value of the ratio predicted for P.Tri.M.O., and shown in experiment, reflects the fact that neither trans nor gauche states are expected to be in great predominance in this chain.

Data on higher poly(ethers) would enable a better appraisal of the series to be made and accordingly time was devoted in attempting to polymerise the 6 and 7 membered ring poly(ethers). These would produce P.Penta.M.O. and P.Hexa.M.O. The latter has, of course, been polymerised from n-hexamethylene glycol and dimensions have been published by Yamamoto et al (144), but this is only of very low molecular weight polymer and it is believed that high molecular weight polymer has not as yet been produced.

5.4 DIPOLE MOMENTS OF POLYETHERS

It has already been discussed in chapters 1 and 2 that polymers showing resultant dipole moments per monomer unit in the direction of the main chain axis, have an overall dipole vector proportional
$\sigma$ VALUES FOR THE POLYETHERS AS A FUNCTION OF $m$, THE NUMBER OF CH$_2$ GROUPS BETWEEN ETHER OXYGEN ATOMS, INCLUDING $m = \infty$ LINEAR POLY(ETHYLENE).

\[
\sigma = \left( \frac{r_0^2}{r_{of}^2} \right)^{\frac{1}{2}}
\]
to chain length and hence molecular weight dependent. Polymers such as the polyethers however, which exhibit a resultant dipole moment per monomer perpendicular to the main chain axis, do not show the same overall dipole moment dependence on molecular weight. In this instance, as the monomer dipole moment vector is not aligned to the chain length vector, the same molecular weight dependence does not arise. The dipole moment in this type of chain being dependent on local chain configuration. Therefore the problems which occurred in dimensional studies due to the polydispersity of the polymer samples do not arise here.

In conjunction with polymer dimensions in the perturbed and unperturbed state, dipole moments of P.Tri.M.O. and P.Tetra.M.O. measured in good and theta solvents in dilute solution have been compared with dipole moments obtained from the bulk amorphous polymer.

The quantities used for characterising dipole moment are $\overline{\mu^2}/z$ and $\mu^2/\text{nm}^2$. $z$ is the degree of polymerisation and hence $\overline{\mu^2}/z$ is the means square dipole moment per degree of polymerisation. $\overline{\mu^2}/\text{nm}^2$, the dipole moment characteristic ratio, is analogous to the dimensional term $r^2/nl^2$ with $n$ remaining the same and representing the number of bonds in the polymer, and $l^2$ the mean square bond moment. The dipole moment term ($\mu^2$) is obtained directly from the Guggenheim-Smith equation. The second quantity is derived from this using bond moments $m_c-o = m_c-c = 0.89\text{D}$ and $m_c-c = 0.06\text{D}$ (19,20).

The dilute solution dipole moments ($\overline{\mu^2}/z$) quoted in Table 4.25 are now converted to $\mu^2/\text{nm}^2$ and compared in Table 5.14 below, with dipole moment characteristic ratios of the bulk amorphous polymers and the calculated values determined by Mark (19,20).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Benzene at 25.0°C</th>
<th>9 Conditions</th>
<th>Bulk sample</th>
<th>Calculated values of Mark (19,20)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.Tri.M.O.</td>
<td>0.77 ± 0.07</td>
<td>0.41 ± 0.05</td>
<td>0.42 - 0.50</td>
<td>0.47</td>
</tr>
<tr>
<td>P.Tetra.M.O</td>
<td>0.74 ± 0.07</td>
<td>0.66 ± 0.05</td>
<td>0.53 - 0.64</td>
<td>0.5 - 0.6</td>
</tr>
</tbody>
</table>

The wide range in values of the bulk sample dipole moments reflects the difficulty in obtaining a value of the limiting high frequency dielectric constant of the bulk polymer sample as mentioned in section 4.6.2.

According to the work of Flory (40) there is evidence that long range interactions do not have a significant effect on the configuration adopted by a long chain molecule in the bulk amorphous state. Therefore any property measured on the bulk amorphous polymer should refer to unperturbed chain statistics. Thus the reported experimental data in this work can be used as a test of the calculations of Mark (20).

Bulk P.Tetra.M.O. samples give a dipole moment characteristic ratio 0.53 - 0.64 in excellent agreement with the range 0.5 - 0.6 predicted. Dilute solution data at theta conditions gives 0.66 ± 0.05 which within the limits shown is again in agreement with Mark’s predicted values, and also with the bulk sample data. Bulk P.Tri.M.O. gave experimentally a dipole moment characteristic ratio of 0.42 - 0.50, whilst at theta conditions a value of 0.41 ± 0.05 was obtained. The predicted value is 0.47 which is a good mean of the results obtained in the present work.

A further dipole moment measurement was made on both polymers in dilute solution in a good solvent. In benzene at 25.0°C, the
dipole moment characteristic ratio obtained for P.Tri.M.O. is markedly above the unperturbed and predicted values (which have an average value of 0.45). P.Tetra.M.O. on the other hand in the same solvent and at the same temperature gives a dipole moment of $0.74 \pm 0.07$, only slightly above unperturbed and predicted values.

Overall, the dipole moments of the unperturbed polymers both in the bulk and at theta conditions, are in agreement with the predicted values of Mark (20). An explanation for the dipole moment in good solvent conditions being above that predicted, particularly in the case of P.Tri.M.O., is proposed below.

The model of the P.Tetra.M.O. chain used here and shown in Fig. 1 was proposed by Mark (20). Various features are reliably established and they are: (i) for rotations about CH$_2$ - O and O - CH$_2$ bonds, and about CH$_2$ - CH$_2$ bonds which bring CH$_2$ groups into opposition, gauche states are of significantly higher energy than trans; (ii) rotations about CH$_2$ - CH$_2$ bonds which bring O atoms and CH$_2$ groups into proximity will cause the gauche state to be of equal or slightly lower energy than the trans; and (iii) g$^+$ - g$^-$ conformations with two CH$_2$ groups, separated by four bonds, coming into steric conflict are excluded, but similar conformations in which O atoms and CH$_2$ groups conflict are only suppressed.

The form of the P.Tetra.M.O. chain of minimum intramolecular energy is theoretically predicted as ttg$^+$-tg$^-$, as was discussed in section 2.1.2, with the bonds in the repeat unit labelled as in Fig. 1. The intramolecular energy difference between this form and the planar zigzag (ttttt) conformation is small, it is however the all trans form which prevails in the stable crystalline modification. This has been proved by Tadokoro et al (147) thus indicating intermolecular interactions may be of some consequence when more than one form is of low intramolecular energy. No other arrangements
of the chain are of comparable low energy. The dipole moments measured for P.Tetra.M.O, given in Table 5.14, are shown not to alter markedly under varying conditions. Consequently if the all trans form is of lowest energy, any small variations caused by solvent cannot be sufficient to significantly alter the population of the configurations.

The theoretically predicted conformation of lowest intramolecular energy (ttg\(^+\) g\(^-\)) for the sequence \(\text{CH}_2\text{-O-CH}_2\text{-CH}_2\) is the form adopted by the P.Tri.M.O. chain in its most usual crystalline modification. This is due to the preference of a \(\text{C-C}\) bond bearing a pendant oxygen for the gauche and of the \(\text{O-C}\) and \(\text{C-O}\) bonds for the trans conformation as shown diagrammatically in Fig. 1 by the occurrence of bonds \(1 - 1\) to \(1 + 2\). In addition, and quite differently from the P.Tetra.M.O. case, two other crystal forms of P.Tri.M.O. commonly occur. These have the respective conformations tttg\(^+\) and tttt and are predicted to have only slightly higher intermolecular energy than (ttg\(^+\) g\(^-\)) (in the order of 200 cal.Mole\(^{-1}\)). On the crystal conformation evidence the energy differences between these chain conformations is very small. There is therefore no reason to suppose that under varying conditions the chain will adopt the same configurational preferences. In fact from the dipole moment data presented here it would appear that the P.Tri.M.O. chain certainly does adopt significantly different local chain configurations under good solvent conditions than it does in the unperturbed state.

5.5. EXCLUDED VOLUME AND CHAIN EXPANSION

The discussion of the excluded volume of flexible polymer molecules presented so far has been entirely qualitative. For an exact quantitative treatment firstly the correct relation between excluded volume and \(\kappa\) must be established and secondly, both of these parameters must be related to suitable thermodynamic functions characterising polymer segment-solvent molecule interaction. This
problem has still not been completely solved and a number of theories including those of Zimm, Stockmayer and Fixman (58) and Orovino and Flory (148) have all tried with varying degrees of success to predict experimental behaviour of flexible polymers.

We shall use here the theory of Flory and Krigbaum (149) in which the interaction between segments and solvent molecules can be characterised by heat and entropy parameters \( \chi \) and \( \psi \). A positive value of \( \chi \) representing a poor solvent where segment-segment contacts are not energetically favoured, whereas a negative value indicates a good solvent. From this theory Flory and Krigbaum obtain an expression for \( u \), the excluded volume, in terms of the chain expansion, as shown in equation (5.19).

\[
 u = 2 \left( \frac{4 \pi}{3} \right)^{3/2} \left( \alpha^2 - 1 \right) \left[ \left( \frac{1}{r^2} \right)^{1/2} \right]^3 \left[ 1 - \frac{\chi}{2 \gamma \chi} + \frac{\chi^2}{3 \gamma \chi} \ldots \right]
\]

\[ \ldots..(5.19) \]

where \( \chi = 2(\alpha^2 - 1) \)

An expression for \( A_2 \) corresponding to this relation for the excluded volume is obtained by combining equations (5.19) and (2.28), whence equation (5.20) is obtained

\[
 A_2 = \frac{N}{2M^2} \cdot 2 \left( \frac{4 \pi}{3} \right)^{3/2} \left( \frac{r^2}{6 \gamma \chi} \right)^{3/2} \left( \alpha^2 - 1 \right) \left[ 1 - \frac{\chi}{2 \gamma \chi} + \frac{\chi^2}{3 \gamma \chi} \ldots \right]
\]

\[ \ldots..(5.20) \]

which simplifies to give

\[
 \frac{A_2 M^2}{(r^2)^{3/2}} \cdot \text{Const} = (\alpha^2 - 1) \left[ 1 - \frac{\chi}{5.656} + \frac{\chi^2}{31.18} \ldots \right]
\]

\[ \ldots..(5.21) \]

where \( \text{Const} = \frac{1}{3.517 \times 10^{23}} \)
The theory thus predicts that a plot of \( \frac{A_2 M^2}{(x^2)^3} \) const. versus \( f(\alpha) \) should be linear of slope unity. Here \( f(\alpha) \) represents the right hand side of equation (5.21) with higher terms of the series expansion neglected.

Unperturbed dimensions from light scattering have been determined for three polymers in the present work P.Tri.M.O., P.Tetra.M.O. and poly (4-chlorostyrene) (P.4 Cl.S.). The data available for these three polymers is presented in Table 5.15 and graphically, the agreement with theoretical prediction is shown in Fig. 35.

### Table 5.15: Collected light scattering and chain expansion data

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \langle \frac{x^2}{\bar{R}} \rangle )</th>
<th>( \langle \frac{r^2}{\bar{R}} \rangle )</th>
<th>( f(\alpha) )</th>
<th>( \langle A_2 \rangle_z ) (cc.mole.g(^{-2}))</th>
<th>( M_z \times 10^{-5} )</th>
<th>( A_2 M^2 \times 10^{-3} )</th>
<th>Const.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.Tri.M.O.</td>
<td>880</td>
<td>680</td>
<td>0.5000</td>
<td>2.0 \times 10^{-4}</td>
<td>7.0</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>P.Tetra.M.O</td>
<td>1030</td>
<td>840</td>
<td>0.4300</td>
<td>1.8 \times 10^{-4}</td>
<td>9.0</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>P.4 Cl.S.</td>
<td>720</td>
<td>670</td>
<td>0.1475</td>
<td>2.65 \times 10^{-5}</td>
<td>8.6</td>
<td>0.149</td>
<td></td>
</tr>
<tr>
<td>P.3 Cl.S.</td>
<td>2000</td>
<td></td>
<td></td>
<td>1.95 \times 10^{-4}</td>
<td>24</td>
<td>0.399</td>
<td></td>
</tr>
</tbody>
</table>

The end to end distance \( r \) is given in cms whilst in accordance with \( r \) and \( A_2 \) being \( z \)-average quantities \( M^2 \) is also expressed as its \( z \) average, determined via the Schulz Zimm distribution of equation (5.14).

The dotted line in Fig. 35 denotes theoretical variation whereas the full line is the experimentally obtained one. Agreement is excellent, within the limits of experimental accuracy. \( M_z \), the most difficult quantity to evaluate gives larger values when calculated by the highly inaccurate method of Zimm and the experimental line then falls above the theoretically predicted.

Using such a graph as given in Fig. 35 it is possible to determine the expansion factor and hence unperturbed dimension of any polymer if
FIG 35.

CORRELATION OF CHAIN EXPANSION TO GOOD SOLVENT PARAMETERS.

\[
\frac{A_2M^2}{[r^2]^{3/2}} \times \text{CONST}
\]

- EXPERIMENTAL.
- THEORY.

\[ f(\alpha) \]

P.4.C.I.S.

P. TRI.M.O.

P. TETRA.M.O.
its dimension and second virial coefficient are available from good solvent data. Also a measure of molecular weight dispersity is required, but nevertheless this provides a way of finding unperturbed dimensions from data that is far more easily gathered than the corresponding ones at theta conditions.

Using this technique the unperturbed dimension of poly (3-chlorostyrene) (P.3 Cl.S.) was calculated from light scattering data obtained in benzene at 9.5°C. Experimentally theta conditions had been unattainable even when the freezing point of the benzene had been lowered by adding cyclohexane, non solvent, and working at 5.0°C, hence the data in the single solvent was used.

Solving equation (5.21) for \( \alpha \) by successive approximations gave:

\[
P.3 \text{ Cl.S.} \quad \alpha = 1.24,
\]

and since \( (r^2) = 2000 \, \text{Å} \), then \( (r^2_0) = 1600 \, \text{Å} \).

The unperturbed dimensions of P.3.Cl.S. and P.4.Cl.S. are compared in Table 5.16, the two columns of \( r^2/nl^2 \) representing the two methods of determining \( n \), either from Benoit's treatment of light scattering data or the Schulz-Zimm distribution.

Table 5.16: - Unperturbed dimensions of P.3.Cl.S. and P.4.Cl.S.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \frac{r^2}{nl^2} )</th>
<th>Benoit</th>
<th>Schulz Zimm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.3.Cl.S.</td>
<td>11.7</td>
<td>31.0</td>
<td></td>
</tr>
<tr>
<td>P.4.Cl.S.</td>
<td>9.1</td>
<td>15.0</td>
<td></td>
</tr>
</tbody>
</table>

Previously, in the case of the poly(ethers), the data from the Schulz-Zimm distribution was taken, as opposed to the Benoit treatment, which was rejected, owing to the curvature of the Zimm plots and the
resultant inaccuracies in determining the initial and asymptote slopes, $S_0$ and $S_\infty$, of the $c = \infty$ line. In the present case however the Zimm plots obtained for the substituted poly(styrenes) are of a rectilinear nature, as shown in Figs. 27-30, such that the various slopes can be measured with some degree of accuracy. Correspondingly a fair agreement is obtained for the two methods in the case of P.4.Cl.S. This is not the case with P.3.Cl.S. however, with the Schulz-Zimm method leading to a curiously high value. Possibly this method of measuring molecular weight dispersity becomes less accurate as dispersity increases, and here the $\overline{M}_w/\overline{M}_n$ ratio in question is at 2.4, the highest encountered in the present work.

Taking $r_o^2/nl^2$ for P.4.Cl.S. as the mean of both measurements, the Benoit value is increased by some 30%. Giving the same allowance to P.3.Cl.S. the following sequence, shown in Table 5.17, when compared with poly(styrene) is obtained.

Table 5.17—Unperturbed dimensions of styrene and chlorostyrene polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\overline{r}_o^2/nl^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(styrene)</td>
<td>10.0</td>
</tr>
<tr>
<td>Poly(4-chlorostyrene)</td>
<td>12.0</td>
</tr>
<tr>
<td>Poly(3-chlorostyrene)</td>
<td>15.8</td>
</tr>
</tbody>
</table>

The value quoted for poly(styrene) is of atactic polymer at the limit of high chain length ($r_o^2/nl^2$) (40).

5.6 **DIMENSIONS AND CRYSTALLINE STRUCTURE OF POLY(CHLOROSTYRENES)**

Table 5.17 shows the sequence of end to end dimensions of poly(styrene) and the two substituted chloro compounds. The following attempts to relate this sequence to the local configuration of the polymer chain. In order to do this we are assuming that the structure
of the polymer at theta conditions is related to crystalline structures of the corresponding tactic chains.

The polymers under question are atactic samples consisting of a random arrangement of isotatic and syndiotactic portions. Birshtein and Ptitsyn (150) show that in such a sample of poly(styrene) a syndiotactic arrangement will always crystallise in the trans-form and the isotactic in a 3_1 helix. Information on the mono substituted poly(3-chlorostyrene) and poly(4-chlorostyrene) is not so abundant although data is available on the corresponding poly(methyl styrenes).

The chloro substituent is similar in size to the methyl group and it would be expected that the crystallisation behaviour of the chlorostyrenes would be similar to the corresponding methyl compounds. Assuming this to be so, Birshtein and Ptitsyn show that the presence of a bulky substituent in the phenyl ring close to the main chain, in the ortho position, leads to a 4_1 helix. On the other hand a substituent relatively remote from the main chain in the meta or 3 position, leads to the intermediate 11_3 or closely related 29_8 helix. Finally if the substituent is in the para or 4 position, remote from the main chain the chain has the structure of a 29_9 or 10_3 helix. These are closer to a 3_1 helix than the 29_8 or 11_3 helices. However the structure of 4 chloro or 4 methyl styrenes have not yet been resolved and consequently their crystal arrangement is unknown.

Table 5.18 indicates the helix form of poly(styrene) and its related chloro-compounds, along with the respective dimensions of the helices and the unperturbed dimensions of the polymer chains.
Table 5.18: Crystal structures and unperturbed dimensions of poly(chlorostyrene) series

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Helix Type</th>
<th>Identity Period ($\bar{A}$)</th>
<th>Increment per monomer ($\bar{A}$)</th>
<th>$\frac{2}{n_0^2}$ $ar{r}_0^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.S.</td>
<td>1</td>
<td>6.65</td>
<td>2.22</td>
<td>10.0</td>
</tr>
<tr>
<td>P.4.Cl.S.</td>
<td>-</td>
<td>12.9</td>
<td>-</td>
<td>12.0</td>
</tr>
<tr>
<td>P.3.Cl.S.</td>
<td>11 \text{ or } 29 \frac{2}{8}</td>
<td>21.74 or 57.0</td>
<td>1.98 or 1.97</td>
<td>15.8</td>
</tr>
<tr>
<td>P.2.Cl.S.</td>
<td>4 \frac{1}{2}</td>
<td>8.10</td>
<td>2.02</td>
<td>-</td>
</tr>
</tbody>
</table>

From Table 5.18 it is seen that the distance per monomer along the helix remains virtually constant at around 2.00 $\bar{A}$ per monomer. It would therefore seem that the isotactic or helical portions of the chain cannot be responsible for the variation in the unperturbed dimensions as is observed for the series.

The difference must either lie in the syndiotactic portions, or what is more likely, the length of the syndiotactic and isotactic portions. In general the longer the sequences of syndiotactic and isotactic polymer, the longer will be the polymer chain. It is only possible to say therefore that with $\frac{2}{n_0^2}$ increasing in the series P.S., P.4.Cl.S., P.3.Cl.S., it is likely that in going from P.S. to P.3.Cl.S. there is an increase in the lengths of isotactic and / or syndiotactic sequences.

5.7 LOW TEMPERATURE RELAXATIONS OF POLY(STYRENE) AND POLY(CHLOROSTYRENES)

To date several studies have been made of the dynamic mechanical properties of polymers down to about 4°K and various loss peaks have been found at temperatures between 4° - 50°K (151 - 155).

Dielectric measurements on poly(styrene) and poly(2,3 and 4 - chlorostyrenes) have been obtained by McCammon, Saba and Work (30) over the
temperature range 4 to \(300\,\text{K}\) and at frequencies ranging from 0.1 to 20 \(\text{KHz}\). Each of the samples exhibits a dielectric loss maximum in the range 15 - 50\(\text{K}\). McCammon et al. show that the temperature of the maximum loss, as reproduced in Table 5.19, decreases as the substituent lowers the symmetry of the pendant phenyl group.

Table 5.19: Temperature of loss maxima of P.S. and P 2,3 and 4 Cl.S., measured at 1 KHz

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(T_m) ((^\circ\text{K}))</th>
<th>Dielectric loss maxima (\varepsilon'') ((\times 10^6))</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.S.</td>
<td>46.0 ± 0.5</td>
<td>130</td>
</tr>
<tr>
<td>P.4.Cl.S.</td>
<td>47.5 ± 2</td>
<td>405</td>
</tr>
<tr>
<td>P.3.Cl.S.</td>
<td>17.5 ± 0.5</td>
<td>315</td>
</tr>
<tr>
<td>P.2.Cl.S.</td>
<td>32.7 ± 0.2</td>
<td>450</td>
</tr>
</tbody>
</table>

They explain this sequence by suggesting a model which allows two distinct modes of side group motions. Using substituted chlorostyrenes the directional feature of the dipole moment vector can be varied in a known way, and it was hoped that by making a dielectric study of these compounds it would be possible to elucidate the nature of the loss peak previously observed in P.S. at very low temperatures.

McCammon et al. observed loss peaks for P.S. and P.4.Cl.S reaching a maximum at almost the same temperature. They also calculated that their activation energies are similar, and reason that the same type of molecular motion is involved in the two polymers. On this basis they say that the low temperature peaks are related to motions of the phenyl side group.

Limited torsional oscillation or rotation of the pendant phenyl group around its bond to the main chain is frequently used to explain relaxation effects in low temperature nuclear magnetic resonance (n.m.r.)
and mechanical loss experiments in P.S. Such a motion by itself cannot produce a dielectric response in P.S. or P.4.Cl.S. because the dipole moment of the phenyl group lies along its assumed axis of rotation. In order to explain the observed losses McCammon et al. include an additional mode of side group motion. They suggest the phenyl group motion be described in terms of a local, fixed co-ordinate system. If the origin of such a system is at the carbon atom on the main chain to which the side group is attached, then orientation of the i th side group can be defined in terms of the polar angle $\Theta_i$, dependent on main chain rotation, the azimuthal angle, $\Phi_i$, of the bond that connects the side group to the main chain, dependent on side group 'wagging', and also on the rotation angle $\omega_i$ of the side group around an axis directed along its connecting bond.

In terms of this model McCammon et al. explain the differences in the loss peaks of the substituted poly(styrenes). The dielectric loss in P.S. and P.4.Cl.S. they say involves only $\Theta$ and $\Phi$ motions and hence the high temperature end of the spectrum is most heavily weighted. Substitution of the chlorine in the ortho position (P.2.Cl.S.) results in a dipole vector nearly perpendicular to the $\omega$ axis so the $\omega$ -motion contributions now become emphasized in the spectrum. The shift of the peak to a lower temperature ($32.7^\circ$K instead of $46^\circ$K) is then in accordance with the assumption of lower barrier for $\omega$-motions compared to $\Theta$ or $\Phi$ - motions. The loss peak in P.3.Cl.S. occurs at a still lower temperature ($17.5^\circ$K), reflecting less steric hindrance to $\omega$ -motion than P.2.Cl.S. In this case, they suggest the direction of the dipole vector is such as to weight the different components of motion almost equally and the loss peak represents as near a 'true' relaxation spectrum as possible.

temperature loss peaks. This is an interesting feature on two accounts. Firstly in that the type of substituent is not responsible for the observed results, a point also made by McCammon et al. (30) when they list the temperatures of the mechanical loss peaks of poly(2,3, and 4 methystyrenes), only to find a similar sequence to the chlorostyrenes. Secondly any explanation based on the dielectric effect of the chloro substituent cannot be valid if the same sequence is found in mechanical loss measurements, obviously insensitive to any variation to dipole direction.

Low temperature loss data by McCammon et al. and others (152-154, 30) on P,S. and poly(chlorostyrenes) has now been accurately tabulated and the system well characterised. However, since an explanation of these observations is still very much lacking a study of the dimensional aspect of the polymers was prompted. As a result unperturbed dimensions of P,S., P,3.Cl.S. and P,4.Cl.S. were measured, or, for P,S. taken from the literature (40). These are given in Table 5.18. As was discussed earlier the isotatic or helical segments of the chain do not appear to affect end to end distance, as initially thought by the author. Although the polymers adopt helices of varying size the chain length increments per monomer are virtually the same in each case, also shown in Table 5.18. In this aspect the dimensional results have not proved as helpful to structural elucidation as was hoped.

It is thought though, as was mentioned earlier, that the increased dimensions is due to a lengthening of syndiotactic and isotactic sequences within the chain.

The odd feature in the loss peak data is that P,2.Cl.S. should be out of sequence compared with P,3.Cl.S. and P,4.Cl.S. Unperturbed dimensions of P.S., P,4.Cl.S. and P,3.Cl.S. show an increase in that order. Unfortunately the fourth member P,2.Cl.S. was not available for determination. It would prove interesting to discover if its
unperturbed dimension is even larger than the other members of the series, or if in fact it reverts back nearer to that of P.S. and P.⁴.Cl.S. as does its low temperature relaxation.
CHAPTER 6

CONCLUSION

It has been possible in the present work to synthesise high molecular weight P.Tri.M.O. and P.Tetra.M.O. from their respective cyclic ring ethers using 'Phosfluorogen A' catalyst. The lower members of the polyether series, and indeed P.Tetra.M.O., have all been studied previously, but P.Tri.M.O. has only relatively recently been polymerised from the cyclic ring ether and that to only low molecular weight. The fact that Phosfluorogen A is capable of producing high molecular weight polymer is probably due to the stability of the PF₆⁻ geganion.

Although both initiation and polymerisation stages were varied in an effort to obtain monodisperse polymers, molecular weight distributions \( \overline{M_w}/\overline{M_n} \) of 1.8 for P.Tetra.M.O. and 1.6 for P.Tri.M.O. were typically obtained. The broadening of molecular weights is probably due to chain transfer effects. In the case of P.Tri.M.O. an additional catalyst solubility effect arises. It appears that at high catalyst concentration an equilibrium between coordinate and ionic catalyst species is established with the limiting solubility of ionic species tending to be lower than that for the coordinate species. This results in a limiting value of 25,000 being placed at the low end of the molecular weight range when using excess catalyst. Further, on the evidence obtained for the oxacyclobutane polymerisation, it is possible to conclude that the system is an example of a 'living' polymer, with chain transfer.

Second virial coefficients were seen to decrease with increasing molecular weight, although the rate of decrease was significantly larger than that predicted by theory. This is not uncommon and is due to certain inaccuracies in the theory as was discussed earlier.

Using the same catalyst, efforts to polymerise tetrahydropyran and oxacycloheptane proved negative.
Unperturbed dimensions of P.Tri.M.O. were determined in cyclohexane at 25.0°C, theta conditions for the polymer. \( \bar{r}_0^2/nl^2 \) from viscometry gave 3.6 whilst light scattering gave 4.3. Similarly unperturbed dimensions of P.Tetra.M.O. determined in 1-hexene at 44.8°C yielded 4.8 from viscometry and 5.1 from light scattering.

In addition P.Tri.M.O. unperturbed dimensions were determined via the theoretical treatments of Kurata-Stockmayer and Stockmayer-Fixman, which only require viscosities in a good solvent, of a series of polymer samples of known molecular weight. Excellent agreement was obtained between the two treatments and the dimensions obtained, averaging at 3.78 fall directly between the absolute values determined from viscometry and light scattering. Further agreement is obtained with theoretically calculated dimensions obtained via conformational energies and statistical weights assigned to the respective chains from rotational isomeric state theory.

Two problems arise from dimensional calculations. Firstly, from viscometry where all values depend on the chosen value of \( \bar{\eta}_0 \), the viscosity parameter. Although several values are available for this quantity, \( 2.87 \times 10^{21} \), the theoretical value for monodisperse polymers was used throughout. Secondly, since light scattering yields \( z \) average end to end distance, \( n \), the number of bonds in the characteristic ratio \( r^2/nl^2 \), must be quoted in terms of \( z \) average molecular weight polymer. This was estimated from the Zimm plots by the Benoit method and also from the theoretical treatments of Schulz and Zimm. The former method was highly inaccurate due to the difficulty in determining relative slopes from the Zimm plot. The Schulz-Zimm distribution, however, readily yields molecular weight distributions in good approximation to the heterogeneity, for \( M_w/M_n \) ratios up to 2.0, the "most probable" or Schulz distribution.

Poly(methylene oxide) and poly(ethylene), the first and last
members of the poly(ether) series have the highest characteristic ratios. Poly(ethylene) chains are in largely trans states and P.M.O. chains largely gauche and for such chains where skeletal bond angles are also equal \( \lim_{n \to \infty} \frac{r_n^2}{n^2} = \infty \). Consequently these two polymers will have relatively high characteristic ratios. All other members of the series have lower characteristic ratios. The average value for P.Tri.M.O. determined here is 3.6 and with P.E.O. is the lowest for the series. This is probably due to the fact that neither trans or gauche populations are expected to be in great predominance in this chain.

Complementary data was obtained from dipole moment measurements on P.Tri.M.O. and P.Tetra.M.O. in dilute solution and in bulk. There is evidence that long range interactions do not have a significant effect on the configuration adopted by a long chain molecule in the bulk amorphous state. If this is so bulk polymer properties should refer to unperturbed chain statistics. The results obtained here bear out this assumption with dipole moment data showing close agreement between bulk, theta conditions and theory. For P.Tri.M.O. \( \mu^2/nm^2 \) gave 0.42 ± 0.50 for bulk and 0.41 ± 0.05 for theta conditions and P.Tetra.M.O. 0.53 ± 0.64 and 0.66 ± 0.05 respectively.

Dipole moment of P.Tri.M.O. in a good solvent yields \( \mu^2/nm^2 \) of 0.77 ± 0.07 somewhat higher than unperturbed values, whilst P.Tetra.M.O. also in good solvent at 0.74 ± 0.07 is lower and still in line with unperturbed values. The most stable crystalline form of P.Tetra.M.O. has been shown to be the planar zigzag where the (ttttt) conformation prevails. Since no other arrangements are of comparable low energy, small energy differences caused by solvent are not likely to significantly alter the population of configurations. This is reflected in the similar moments measured for P.Tetra.M.O. under varying conditions.
For P.Tri.M.O. the situation is quite different. Although the most usual crystalline form is a \((-\text{gtg})^+\) conformation two others commonly occur \((-\text{gtg})^-\) and \((-\text{tgg})\). Since these are of only slightly higher intermolecular energy, varying conditions are likely to cause new configurational preferences, as seems to be the case here with P.Tri.M.O. in a good solvent. Thus, the dipole moment proves a sensitive test of local configurational changes in P.Tri.M.O. but not P.Tetra.M.O.

Unperturbed dimensions of P.4.Cl.S. gave \(r_0^2/\ell^2\) of 9.1 from theta conditions, in benzene at 15.0°C. Theta conditions for P.3.Cl.S. could not be attained in benzene. From a knowledge of the expansion parameters \(\alpha\), of P.Tri.M.O., P.Tetra.M.O. and P.4.Cl.S. a graphical correlation of \(\alpha\) to second virial coefficient was deduced. This enabled the unperturbed dimension characteristic ratio of P.3.Cl.S. to be calculated to be 11.7. From the sequence of unperturbed dimensions shown for polystyrene and P.3 and 4 Cl.S. explanations are offered for the varying crystalline structures observed for the series. It appears that it is not the isotactic or helical portions of the chain that are responsible for increased end to end distance in the series from P.S., P.4.Cl.S., P.3.Cl.S., to P.2.Cl.S. It is proposed that the increase in length is due to a lengthening either of the syndiotactic or isotactic elements within the chain. Also the behaviour of the low temperature (S) dielectric and mechanical relaxations of polystyrene and poly(chlorostyrenes) are viewed via their dimensions in an effort to explain the anomalous behaviour that occurs, but without any obvious correlations.
REFERENCES
1/ P. J. Flory and T. G. Fox, J. Amer. Chem. Soc., 73, 1904 (1951)
   and J. R. Schaefgen, ibid., 70, 2703 (1948)
2/ M. Kurata and W. H. Stockmayer, Fortschr. Hochpolym. - Forsch.,
   3, 196 (1963)
   63, 1964 (1967)
5/ N. G. McCrum, B. E. Read and G. Williams, 'Anelastic and
   Dielectric Effects in Polymeric Solids', Wiley (1967)
9/ J. E. Mark and P. J. Flory, ibid., 88, 3702 (1966)
   21, 313 (1956)
16/ G. Allen, C. Booth et al., Polymer, 8, 391 (1967)
33/ H. Eyring, Phys. Rev., 39, 746 (1932)
38/ W. Kuhn, Kolloid - Z., 76, 258 (1936)
ibid., 87, 3, (1939)
43/ J. E. Mark, J. Amer. Chem. Soc. 88, 3703 (1966)
48/ Lord Rayleigh, Phil Mag. [6], 37, 321 (1919)
49/ W. Kuhn, Kolloid - Z, 68, 2 (1934)
50/ E. Guth and H. Mark, Monatsh., 65, 93 (1934)
      c) J. Amer. Chem. Soc., 64, 1712 (1942)
55/ P. J. Flory and T. G. Fox, J. Amer. Chem. Soc., 73, 1904 (1951)
57/ E. Teramoto, Busseiron Kenkyu (Researches on Chemical Physics), 39, 1 (1951); 40, 18 (1951); 41, 14 (1951) Brief summary given by P. J. Flory, J. Polym. Sci., 14, 1 (1954)
67/ P. Debye, ibid., 17, 392 (1946)
69/ J. Carabannes, 'La Diffusion Moleculaire de la Lumiere Univ. France, Paris 1929.
71/ F. W. Peaker, 'Techniques of Polymer Characterisation'

ibid., 3, 763 (1948)


76/ M. L. Huggins, J. Amer. Chem. Soc., 64, 2716 (1942)


87/ W. R. Krigbaum and P. J. Flory, J. Polym Sci., 9, 503 (1952)


89/ P. Debye, 'Polar Molecules', Chem. Cat., New York 1929; and
'Dielectric Constant and Molecular Structure', Chem. Cat.,
New York 1931.

90/ C. Smyth, 'Dielectric Behaviour and Structure' McGraw-Hill,
London 1955.


93/ F. H. Müller, Physik Z., 34, 689 (1933)
100/ Ozark Mahoning Company, Tulsa, Oklahoma
102/ Sofica Light Scattering Manual.
103/ C. D. Thurmond, J. Polym. Sci., 8, 607 (1952)
109/ Hewlett-Packard High Speed Membrane Osmometer Handbook
111/ Marconi Dielectric Test Set Manual
119/ F. S. Dainton and K. J. Ivin, Quart. Revs., 12, 61 (1958)
123/ A. C. Farthing, J. Appl. Chem., 8, 186 (1958)
125/ M. P. Dreyfuss and P. Dreyfuss, Polymer, 6, 93 (1965)
130/ A. Miyake and W. H. Stockmayer, Markromol. Chem. 88, 90 (1965)
133/ J. Hildebrand and R. Scott, 'The Solubility of Non-Electrolytes', 3rd edition, Reinhold, 1949
136/ C. G. Richardson and R. E. Wetton, to be published.
138/ T. G. Fox and P. J. Flory, J. Amer. Chem. Soc. 73, 1915 (1951)
143/ W. H. Stockmayer and L.-L. Chan, unpublished data cited by
K. Yamamoto et al. in Ref. 24.
144/ K. Yamamoto and H. Fujita, Polymer, 7, 557 (1966)
145/ K. Yamamoto and H. Fujita, Polymer, 8, 517 (1967)
147/ H. Tadokoro, Y. Chatani et al., Progr. Polymer Phys., Japan, 6, 303 (1964)
150/ T. Birshtein and O. Ptitsyn, 'Conformation of Macromolecules'
Interscience, New York, 1966
154/ J. M. Crissman, J. A. Sauer and A. E. Woodward,
ibid., 3, 2693 (1965)