



**A PHYSICO-CHEMICAL STUDY OF ATACTIC AND ISOTACTIC
POLYSTYRENE SULPHONIC ACIDS**

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Doctor of Philosophy**

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SUMMARY

This thesis deals with the preparation and the physico-chemical properties of isotactic and atactic polystyrene sulphonic acids and their corresponding sodium salts.

Isotactic polystyrene was prepared by using the titanium tetrachloride-triisobutyl aluminium catalyst system and then fractionated from solution by addition of a non-solvent. Suitable fractions were characterised both by the determination of the degree of crystallinity from the X-ray diffraction patterns, melting points, specific volumes and infra-red spectra of oriented samples and by the determination of the molecular weights by viscometry and sedimentation. During the latter measurements the pressure dependence parameter of the sedimentation coefficient was calculated for the polystyrene-benzene system.

The polystyrene fractions were sulphonated using a liquid sulphur trioxide-triethyl phosphate complex. The degree of sulphonation was shown to be in excess of unity by determination of the equivalent weight of the vacuum-dried polyacid samples and the observation that the extinction coefficients of a polyacid and its corresponding sodium salt were the same. Narrow molecular weight atactic polystyrene samples were sulphonated in a similar way.

X-ray diffraction and infra-red spectral studies of solid samples of the two forms were conducted in an attempt to detect signs of crystallinity. Evidence for structural differences in solution was sought by spectral studies of proflavine-polyelectrolyte complexes,

by optical rotation studies of the quinine salts of the polyacids and by measurements of the temperature dependence of the reduced viscosity and optical density of salt-free aqueous solutions of the polyacids.

The extent of counterion binding of hydrogen ions and sodium ions to the polystyrene sulphonate ion was investigated by conductance-transference studies. In addition, measurements were made on electrochemical cells in which one half-cell was a glass electrode reversible with respect to hydrogen ions. In the latter series of experiments the results obtained by using a saturated calomel half-cell in conjunction with a saturated potassium chloride bridge were compared with those found by using a cell in which liquid junctions were eliminated by the use of a silver-silver chloride electrode in the presence of hydrochloric acid.

The partial molal volumes of the polysulphonic acids and their sodium salts were compared both for the effect of tacticity and for evidence of the nature of counterion binding to the polystyrene sulphonate ion.

To the best of my knowledge and belief, this thesis contains no material previously published or written by another person, nor any material previously submitted for a degree or diploma at any University, except where due reference is made in the text.

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CHAPTER IINTRODUCTION(a) Tactic and atactic polymers

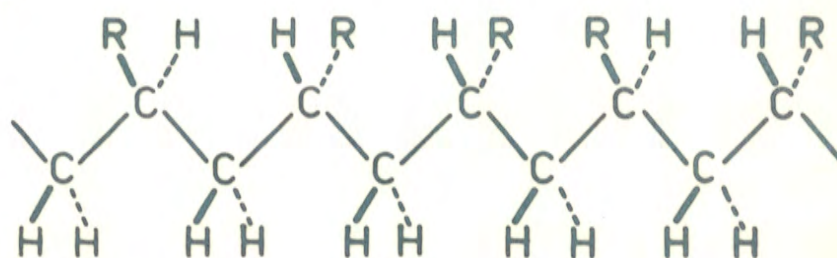
During the growth of a linear vinyl polymer the asymmetric centre which is created as each new monomer unit is added to the chain end during propagation, may have either the same or the opposite configuration to that of the preceding asymmetric centre.¹ There exists, therefore, the possibility of different structures in the resultant polymer depending on the relative positions of the main chain substituents. A convenient way of illustrating this point is to represent the carbon atoms of the chain backbone as lying in a plane and forming a zig-zag structure¹⁻⁴ corresponding to the maximum chain extension compatible with bond angles.

(i) If the preparation leads to the addition of monomer molecules with random d- and l-configuration the resultant polymer is described as atactic (Type I, fig. 1-1).

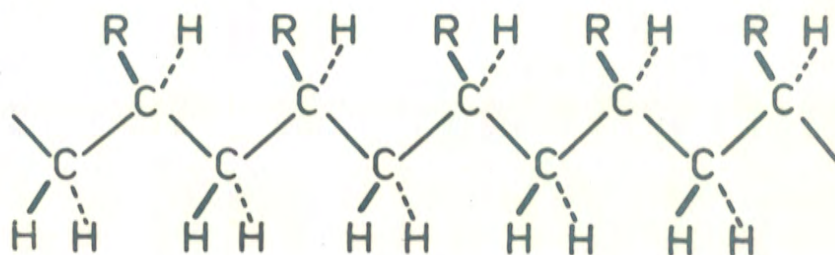
(ii) If the resultant chain backbone contains long sequences of monomer units in which the configuration of the carbon atoms carrying the chain substituents are all identical (either -dddd- or -llll-) then the polymer chains are described as isotactic (Type II, fig. 1-1). In actual fact any preparation of isotactic polymer almost certainly consists of blocks having all d-configurations over a certain length followed by a block having all l-configurations over the adjacent stretches and so on.

(iii) If the experimental conditions give rise to a stereo-

Type I



Type II



Type III

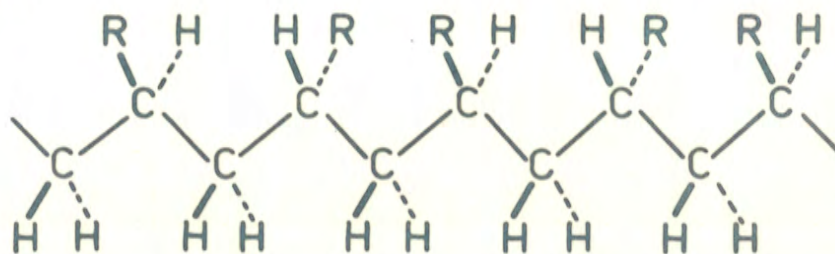


Figure 1-1. Diagrams representing sections of hypothetically extended zigzag chains of atactic (Type I), isotactic (Type II) and syndiotactic (Type III) vinyl polymers.²

regular chain in which there is a regular alternation of the configuration of pseudo-asymmetric carbon atoms (-dldldl-) then the stereoregular polymer is described as syndiotactic.

In addition, however, any polymer with a stereoregular structure can assume one of a number of different conformations¹⁻⁶ or spatial arrangements. Thus an isotactic polymer may assume an alternating trans-gauche conformation, so generating a helix, as this arrangement would result in least steric interference of side groups. On the other hand the most stable main chain conformation of a syndiotactic polymer is expected to be trans-trans resulting in a planar zig-zag structure for the main chain. The resultant component of the length in the direction of the chain per monomer unit may be therefore greater for a syndiotactic than an isotactic polymer with the value for the atactic form being intermediate between the two stereoregular forms.⁵

(b) Polyelectrolytes

Just as in classical chemistry a distinction can be made between uncharged molecules and simple electrolytes so polymer chemistry has its counterparts in uncharged macromolecules and charged macromolecules. The latter, referred to as polyelectrolytes, dissociate in ionizing solvents to give rise to multiply-charged macroions together with a sufficient number of simple ions of opposite charge (called counterions) to render the system electrically neutral.

The numerous linear polyelectrolytes which have been synthesized from vinyl monomers fall into two general classes as in the case of

simple electrolytes - they are distinguished as strong or weak depending on whether the repeating monomeric unit is strongly or weakly ionized. As a consequence the charge densities of the polyions arising from strong polyelectrolytes such as polystyrene sulphonic acid or polyvinyl sulphonic acid are high leading to considerable extension of the flexible polyions in solution as a result of mutual repulsion of the fixed charges on the polyion. At the same time the high local charge density on the polyion affects the properties of the simple ions in solution leading to what can be interpreted as a high degree of counterion binding. Although the charge densities of typical weak polyacids such as polymethacrylic acid and polyacrylic acid and weak polybases such as poly-4-vinyl pyridine, polyvinylamine and polyethylene imine are low, they can be increased at will by varying the degree of neutralization with simple strong acids and alkalis or the extent of quaternization with alkyl halides. When neutralization or quaternization is complete the resultant polysalts or polyquaternary ammonium halides can be classified as strong polyelectrolytes. They differ, however, in some respects to the strong polysulphonic acids in that they undergo hydrolysis in water and are affected by carbon dioxide to an extent which may increase the difficulty of both the experimental procedure in salt-free solutions and the interpretation of results.

Natta's discovery⁷ of the existence of stereoregular polymers eleven years ago has raised the possibility of preparing the stereoregular polyelectrolyte counterparts and observing whether the solid

state and solution state properties differ from those of the corresponding atactic variety.

(c) Comparative study of atactic and stereoregular polyelectrolytes

In contrast to the extensive research that has been carried out on the physico-chemical properties of uncharged stereoregular polymers, the study of the corresponding polyelectrolytes has received comparatively little attention. Apart from the optical rotation studies of the d-tartrates of isotactic and atactic poly-2-vinyl pyridine⁸ research in this field has been almost exclusively confined to a study of the potentiometric titration behaviour of isotactic, syndiotactic and atactic polymethacrylic acid⁹⁻¹² and polyacrylic acid and a comparison of the extent of copper ion^{9,10} and magnesium ion binding¹⁰ to polymethacrylic acid (see section 3-15). Recently measurements of the electrophoretic mobilities of conventional and isotactic polymethacrylic acid have been reported.¹³

For this reason a comparative study of properties of a strong stereoregular polyelectrolyte and its atactic counterpart was embarked upon in view of anticipated conformational differences. To avoid the troublesome effects that occur during the use of the salts of weak polyacids and polybases¹⁴ in very dilute solutions the polyelectrolytes chosen for the project were polystyrene sulphonic acids and their corresponding sodium salts. Almost all experiments were performed in the absence of salt.

(d) Structure of the thesis

Chapter 2 of this thesis deals with the characterisation of various fractions of isotactic polystyrene by determining the degree of crystallinity of oriented samples by X-ray diffraction, specific volume, melting point and infra-red spectral measurements. The molecular weights are reported from results obtained by viscometry and sedimentation.

In Chapter 3 an account is given of attempts to detect signs of crystallinity in solid isotactic polystyrene sulphonic acid by examination of X-ray diffraction patterns and infra-red spectra. Evidence of structural differences between the atactic and isotactic polysulphonic acids is reported as a result of spectral studies of the complex formed with proflavine and optical rotation studies of the quinine salts of the polyacids. In the latter part of the chapter the extent of counterion binding to the polystyrene sulphonate ion is discussed from the results of combined conductance-transference number experiments as well as from electromotive force measurements using suitable electrochemical cells. Details are given of the way in which electrochemical cells without liquid junction can be used to give values of the charge fraction. Before Chapter 3 concludes with a general discussion of results, the partial molal volumes of the different types of polyacids and their sodium salts are compared.

The final chapter of the thesis gives details of the preparation and fractionation of isotactic polystyrene, the preparation of the sulphonated polymer and the calculation of its degree of

sulphonation and details of the various experimental methods used in this investigation.

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CHAPTER IICHARACTERIZATION OF ISOTACTIC POLYSTYRENE FRACTIONSPart 1 - Solid State Characterization2-1 Introduction

Perhaps the most remarkable property of many tactic polymers is their ability to crystallize.¹ It is obvious, however, that the packing of a macromolecule into a crystal lattice must be limited by factors which need not be considered when mobile, simple molecules or ions form a crystal.

(a) Conditions for crystallization of polymers

As the definition of a crystal implies three dimensional order a linear polymer to be crystalline must at least show stereoregularity in its monomeric units.^{2,3,4} By assuming that these monomeric units in a crystal occupied geometrically equivalent positions with respect to each chain axis Natta and Corradini² concluded that there were only two regular sequences of vinyl head-to-tail polymers that could be expected to lead to crystallizable polymers. Polymers with isotactic configuration might be capable of assuming a helix-type crystalline structure while syndiotactic polymers would have to take up a glide plane structure in the crystalline state. Natta assumed that the conformation of the chain would not only approach that corresponding to the minimum potential energy of an isolated chain oriented along an axis but might also have to undergo slight modifications in order that the polymer chains might fill a

minimum of space as uniformly as possible.

In the case of isotactic polystyrene the bulky group makes a planar conformation impossible^{1,5} and a suitable accommodation of these side-groups can only be achieved in a helical structure by arrangement of successive monomeric units in a right or left-handed, three-fold helix.^{1,5} This structure of crystalline polystyrene was subsequently verified by Natta and his co-workers^{6,7} and later confirmed by Miller.^{8,9}

On the other hand because of these requirements it is obvious that atactic polymers cannot be crystallized. As excessive energy requirements¹⁰ rule out the possibility of rotation of monomer units about the chain axis it follows that the resultant wide spacing which would necessarily exist between parallel chains with randomly spaced side-groups, would be incompatible with the general structure of a crystalline solid.

(b) Orientation of crystallizable polymers

While the degree of crystallizability of a polymer depends on its intrinsic structure, the degree of crystallinity depends on the manner in which the sample is treated after its preparation.¹¹ The stretching of tactic polymers under suitable conditions, for example, tends to align extended, unentangled portions of polymer chains parallel to the direction of stretching thus producing crystalline regions¹² comprised of bundles of adjacent polymer chains with the unit cell direction parallel to the fibre axis. Other methods such as the slow cooling of a melt¹³ or annealing at a suitably high

temperature, often for a considerable time, may induce crystallization. It is also known that the heating of the crystallizable polymers in suitable non-solvents^{4,13} provides the necessary energy and swelling for the stereoregular chains in the meta-stable amorphous state to assume some degree of three-dimensional order.

Natta¹⁵ has pointed out, however, that tacticity alone is not a sufficient condition for crystallization. Stereoregular polymers of mono-para substituted polystyrenes, for example, are not crystallizable^{4,15} at all except when the size of the substituent is very small as in the case of a hydrogen or fluorine atom. Natta¹⁵ has suggested that crystallization will not proceed when a stereoregular polymer, due to the size and position of the side chain, leads to such a poor spatial filling that the density in the crystal phase is lower than that in the amorphous phase. On the other hand Miller³ proposes that the absence of crystallinity in these polymers may be merely a problem in crystallization kinetics rather than packing efficiency.

(c) Determination of stereoregularity

Most of the methods used to determine the tacticity of polymers are based on estimates of the degree of crystallinity of the sample under test. The magnitude of the crystallinity index, however, will depend upon both the extent to which the sample has been oriented^{14,16} and the sensitivity of the technique in detecting limited regions of crystallinity. Takeda and co-workers,¹⁶ for example, have reported crystallinities which varied from zero to 0.66

for differently treated samples of the same isotactic polystyrene and, in addition, they found that the value varied to some extent depending on the method used in its measurement. In this work, samples of each polystyrene fraction were oriented under similar conditions and the degree of crystallinity, determined by different methods, was used to obtain an indication of their isotacticity.

2-2 X-ray Diffraction Studies

(a) Estimation of tacticity

The determination of tacticity of polymers by X-ray methods¹ is limited because patterns can only be interpreted if a regular three dimensional order exists in the sample being investigated. For an accurate evaluation of tacticity it would be necessary to obtain the sample with a maximum degree of crystallinity by a suitable orientation procedure. In practice this is impossible so that any estimate of tacticity will always be a low approximation. It has been suggested¹⁴ for example, that the stable crystallites which must be present if crystallinity is to be detected by X-rays, can form only when segments of stereoregular molecules containing twenty or more monomer units become aligned parallel to each other. Tactic polymers with bulky side-groups cannot be investigated by the X-ray method owing to their inability to crystallize.^{15,17}

(b) Previously reported investigations using polystyrene

When Natta and his collaborators^{18,19} first reported the preparation of isotactic polystyrene the well-defined X-ray diffraction pattern was one of the physical properties used to distinguish their

product from atactic polystyrene. Shortly afterwards during the characterization of their Alfin-catalysed polystyrene, Williams and his co-workers¹³ found that suitably treated samples exhibited X-ray patterns with the same interplanar spacings and relative intensities of the seven strongest reflections previously reported by Natta. The Milan research group^{6,7,20} extensively studied the X-ray spectra of stretched and annealed fibres of isotactic polystyrene and as a result confirmed the predicted crystal structure.^{1,5}

In recent years efforts have been mainly directed towards determining the degree of crystallinity^{16,21} and indirectly, therefore, the approximate tacticity of the polystyrene samples. The method which involves a comparison of the X-ray diffractograms of oriented isotactic samples with those of the atactic variety (see section 4-3a), has been criticised by Yamada.²² More recently a considerably refined method which had been used previously for the characterization of polyethylene²³ and polypropylene,²⁴ has been described by Challa, Hermans and Weidinger.²⁵

(c) Crystallinity of isotactic polystyrene fractions

Since an accurate X-ray quantitative determination of the isotacticity of polymers is difficult and uncertain, requiring considerable refinements to techniques,^{25,26,27} no effort was made to characterize the oriented isotactic polystyrene fractions used in this study in the manner described by the Hermans group. The X-ray diffraction powder patterns of the parent isotactic polystyrene and the fractions F1 to F5 (see sections 4-2 and 4-3a) are shown in

figure (2-2.1) together with that of a sample of amorphous polystyrene. The diffractogram shown in figure (2-2.2) exhibits the typical maxima that have previously been reported^{16,21} for oriented isotactic polystyrene. Furthermore a comparison of the relative heights and sharpness of the (220) and (211) peaks lying between 2θ equal to 15° and 20° leads to the conclusion, based on the results of Takeda et al.,²⁶ that the crystallinity is high. Approximate values ($\pm 10\%$) of the degrees of crystallinity, calculated by measuring the crystalline and amorphous contributions to the X-ray diffraction pattern of isotactic samples by the method suggested by Natta²¹ and used by Takeda,¹⁶ are shown in table (2-2.1) and indicate that the isotacticity of each fraction is high.

Table 2-2.1

X-ray crystallinities of isotactic polystyrene fractions

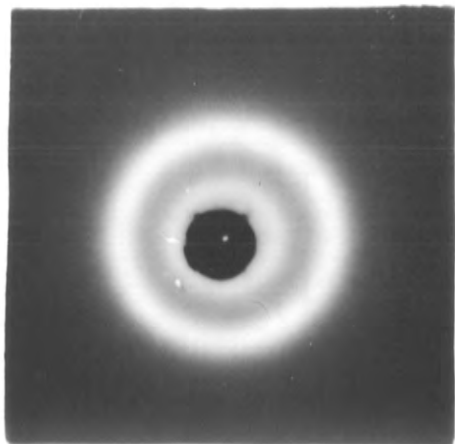
Fraction	F1	F2	F3	F4	F5
X_x	0.51	0.58	0.49	0.44	0.48

2-3 Melting Point Determinations

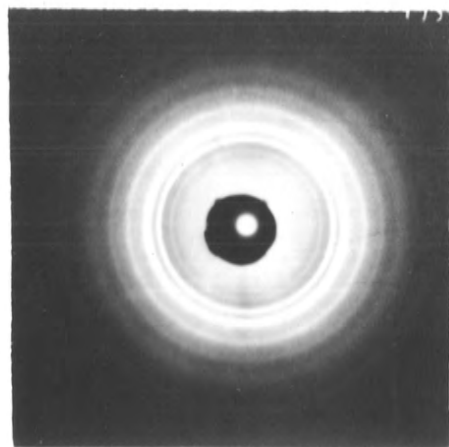
(a) Effect of crystallinity

During the orientation of crystallizable polymers small crystallites become embedded in an amorphous medium consisting of entangled polymer chains. When the polymer is subsequently heated it is the melting of these crystallites²⁷ over a narrow temperature

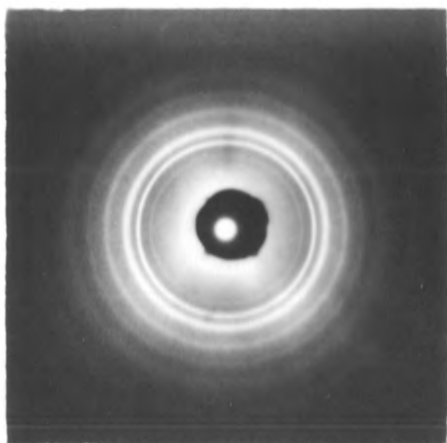
Figure 2-2.1. X-ray diffraction patterns of isotactic polystyrene fractions, F1-F5, and atactic polystyrene, S108.



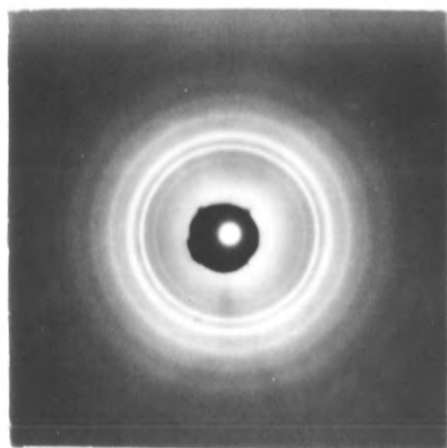
S108



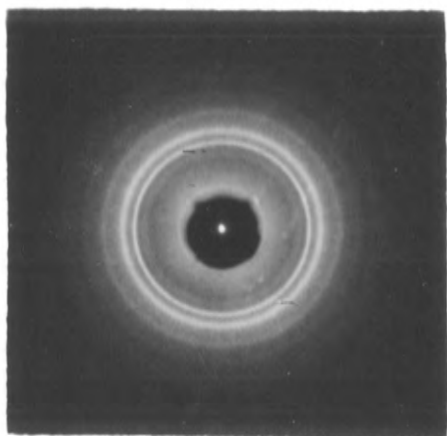
F1



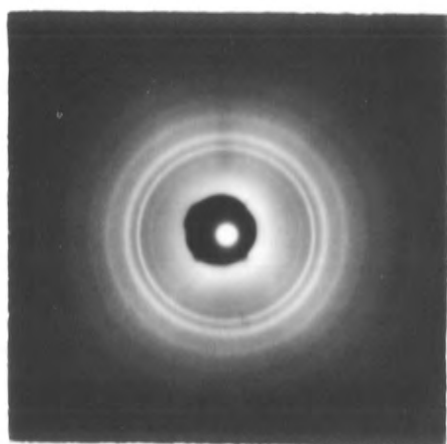
F2



F3



F4



F5

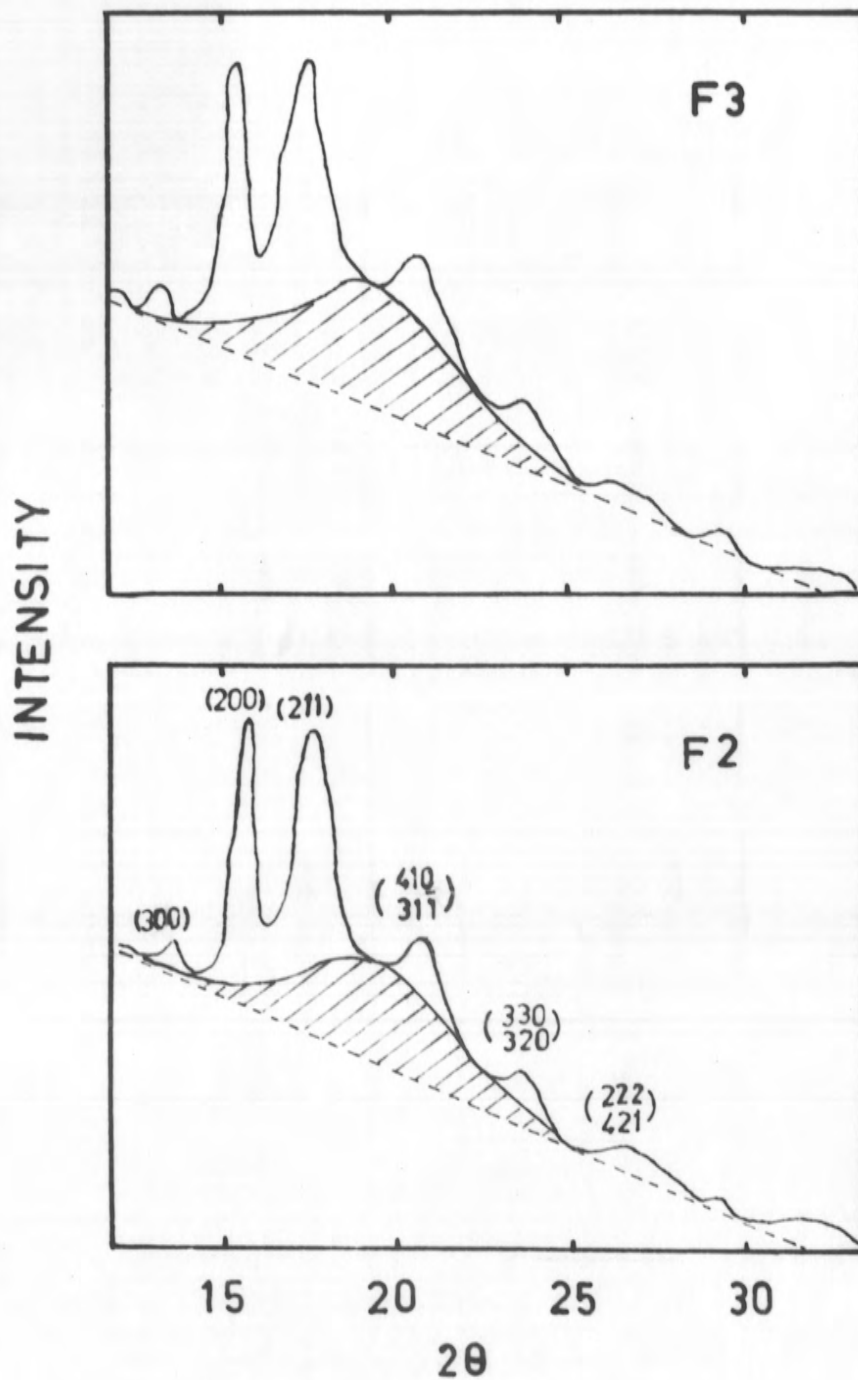


Figure 2-2.2. X-Ray diffractograms for isotactic polystyrene fractions, F2 and F3. The base-line and diffraction curve for the amorphous content are also shown in the figure.

range which gives well-ordered stereoregular polymers this characteristic property. In the case of isotactic polystyrene the presence of bulky phenyl groups at alternate sites permits the chain to take up, with some difficulty however, a preferred conformation of relatively high stability²⁸ during the orientation process. Thus although the more flexible crystalline polyethylene with its less bulky substituents²⁹ melts at a relatively low temperature in the vicinity of 137°C,^{30,31} oriented isotactic polystyrene has been reported to exhibit sharp melting points between 221°C^{18,32,33} and 240°C^{7,9,22} with one value quoted³⁴ as high as 250°C. Variations in the degree of crystallinity due to the nature of the heat treatment as much as the inherent degree of tacticity probably explains the wide range of melting points recorded in literature for isotactic polystyrene samples.

(b) Experimental results

All fractions of isotactic polystyrene used in this project showed evidence of uniformly high crystallinity not only because of their sharp, high melting points of 230-231 ± 1°C but also because all exhibited some degree of birefringence when being viewed with the polarizing microscope before the phase change took place. The independence of the melting point on the molecular weight of the fractions was not unexpected as Natta et al.³⁵ have shown that highly crystalline polypropylenes with the same stereoregularity have melting points which reach a limiting value for molecular weights above 100,000.

2-4 Specific Volume Measurements

(a) Relation between crystallinity and specific volume

The crystallinity of a polymer can be derived from the density of a sample under the assumption that the crystalline and amorphous regions are two separate thermodynamic phases³⁶ with specific volumes corresponding to V_c and V_a respectively. Because of the closer packing of chains the density of crystalline regions is higher than that of amorphous regions. For any sample of specific volume, V , the degree of crystallinity, X_{SV} , (i.e. the fraction of monomeric units in the crystalline lattice) will be given by

$$X_{SV} = \frac{V_a - V}{V_a - V_c} \quad (2-4.1)$$

provided that the density of the polymer sample is directly proportional to its crystalline content. It follows that any improvement of crystalline order by orientation during thermal treatment will lead to a higher value of the crystallinity index.

In the case of isotactic polystyrene Takeda et al.¹⁶ have shown that the degree of crystallinity based on equation (2-4.1) is given by

$$X_{SV} = 16.13 (0.950 - V) \quad (2-4.2)$$

where the density of the perfectly crystalline isotactic form³⁷ was calculated to be $1.126 \text{ gm. cm.}^{-3}$ from unit cell dimensions⁶ while for amorphous polystyrene, obtained by quenching molten polystyrene,

the value^{16,18} was 1.052 gm. cm⁻³.

Natta and co-workers³⁸ calculated the theoretical dilatometric curve of a completely crystalline polystyrene sample based on comparative volumetric data of atactic and isotactic polystyrene. From this they were able to derive the following relation for the degree of crystallinity of polystyrene at 25°C,

$$X_{SV} = 18.87 (0.950 - V). \quad (2-4.3)$$

(b) Crystallinity of isotactic polystyrene fractions

In this work the density of fragments of films of isotactic polystyrene fractions, annealed at 175°C for 16 hours, were determined by a flotation technique (see section 4-3c) giving the degree of crystallinity shown in Table (2-4.1).

Table (2-4.1)

Density and crystallinities of isotactic polystyrene fractions

	F2	F3	F4	F5
Density (gm. cm. ⁻³)	1.080	1.082	1.079	1.081
X_{SV} (equation 2-4.2)	0.40	0.43	0.38	0.42
X_{SV} (equation 2-4.3)	0.45	0.49	0.43	0.47

The results compare favourably with those reported by Takeda¹⁶ and Yamada²² for similarly treated samples. It is noteworthy that the

crystallinities determined by this method are lower than the values obtained by X-ray and infra-red techniques. Lindenmeyer^{40a} and others^{40b} have pointed out that measurements of the density of single crystals of polyethylene are significantly less than the calculated density of a perfect crystal but that the apparent amorphous content could be accounted for both by the incorporation of a small percentage of voids into the crystal as defects and by the mispacking of folds in adjacent lamella. It follows therefore that the calculation of crystallinities based on the crystallographic density of isotactic polystyrene will always lead to low values because no allowance can be made for the presence of voids in an otherwise completely oriented crystal.

It is interesting to note that Hay³⁹ has reported considerable variations in the density of isotactic polystyrene for small changes of annealing conditions. While a sample annealed at 175°C for 20 hours had a density of 1.070 gm. cm.⁻³, a sample held at 166°C for 3 hours showed a density of 1.081 gm. cm.⁻³. Additional unpublished work by Hay on the kinetics of crystallization which has recently been discussed by Meares,⁴¹ indicates the difficulty in assessing with certainty the isotacticity of polystyrene by this method.

2-5 Infra-red Spectra

(a) Relation of infra-red spectra to structure of macromolecules

In recent years a study of the infra-red spectra of polymers both in the solid state and in solution has led to evidence for

structure in these states.^{42,43} Some absorption bands can be assigned to the crystallized solid because they are absent in a solution of the polymer, while in other cases bands, which do not appear with the atactic polymer, are found both in the solid state and in solutions of the tactic polymers. They must therefore result from short-range intra- and intermolecular interactions in the ordered conformation of the stereoregular polymer chains.

(b) Infra-red spectra of polystyrene and relation to structure

With the observation that atactic polystyrene shows a single peak at 1070 cm.^{-1} compared with two peaks by the isotactic form at 1058 cm.^{-1} and 1080 cm.^{-1} , Morton and Taylor⁴⁴ were able to use the existence and relative heights of the latter peaks as a qualitative index for the isotacticity of polystyrene. Following the work by Tadokoro et al.^{45,46} which suggested that certain bands in the $1000\text{--}1500\text{ cm.}^{-1}$ range were related to alternate sequences of trans and gauche conformation along the carbon-carbon chain, a thorough analysis of atactic and isotactic polystyrene was carried out by the Takeda^{16,47} group. From studies in the molten state and in solution as well as with quenched and crystallized solids they were able to identify bands which were specific for isotactic polystyrene.¹⁶ They confirmed that the 1054 cm.^{-1} and 1085 cm.^{-1} peaks were correctly assigned by Tadokoro et al. and that the 567 cm.^{-1} peak originated in the same way. They also concluded that the 543 cm.^{-1} band of atactic polystyrene, which Liang and Krimm⁴⁸ had

assigned to short range interactions between a vibrational mode related to the phenyl group and the -C-C- chain, was due to the trans-trans conformational sequence in syndiotactic parts. In addition they found that the 984 cm.^{-1} and 587 cm.^{-1} bands were characteristic of the crystallized solid and therefore must be related to the isotactic content because only polystyrene with isotactic configuration could possibly form micro-crystalline regions. With the further observation that the optical density of the 1030 cm.^{-1} band showed the same linear relationship with film thickness for both atactic and isotactic polystyrene, Takeda's group were able to obtain a relationship between the degree of crystallinity, X_{IR} , and the ratio, R_{984} , of the optical density of the 984 cm.^{-1} band, characteristic of the crystallized solid, to the optical density of the 1030 cm.^{-1} band measured on the same film specimen,

$$X_{\text{IR}} = 1.96 (R_{984} - 0.058) \quad (2-5.1)$$

In a similar manner Utiyama⁴⁹ obtained an indication of the isotacticity of polystyrene fractions by evaluating the degree of crystallinity from the ratio of the optical densities of the 984 cm.^{-1} and 1945 cm.^{-1} bands,

$$X_{\text{IR}} = 0.50 (D_{984}/D_{1945}) - 0.170 \quad (2-5.2)$$

(c) Crystallinity of isotactic fractions from infra-red analysis

The infra-red spectra of annealed samples of each isotactic fraction were obtained as described in section (4-3d). Typical

examples of spectra for isotactic films may be compared with those from a solution in carbon disulphide and from atactic films as shown in figures (2-5.1) and (2-5.2). Direct qualitative evidence for high isotacticity of all fractions is provided by the existence of well-defined 1054 cm.^{-1} and 1085 cm.^{-1} peaks of approximately the same intensity²⁶ (the Morton and Taylor⁴⁴ index) and by the presence in the spectra of all crystallized solids (as in the work of Takeda¹⁶) of a tendency of the 543 cm.^{-1} band to show only as an ill-defined shoulder on the band appearing in the vicinity of 560 cm.^{-1} .

An approximate quantitative indication of the isotacticity of each fraction was obtained from calculated values of the crystallinity index by utilizing equations (2-5.1) and (2-5.2). The results are summarized in the following table.

Table 2-5.1

Crystallinity of isotactic polystyrene fractions from
infra-red analysis

	F1	F2	F3	F4	F5
Equation (2-5.1)	0.54	0.47	0.57	0.50	0.50
Equation (2-5.2)	-	0.54	0.52	0.49	0.53

Because of some criticism of Takeda's work by Yamada²² it is of interest to compare the primary data upon which the characterization of samples depends, with the corresponding results of the Japanese group.¹⁶ Figure (2-5.3) shows satisfactory agreement between the

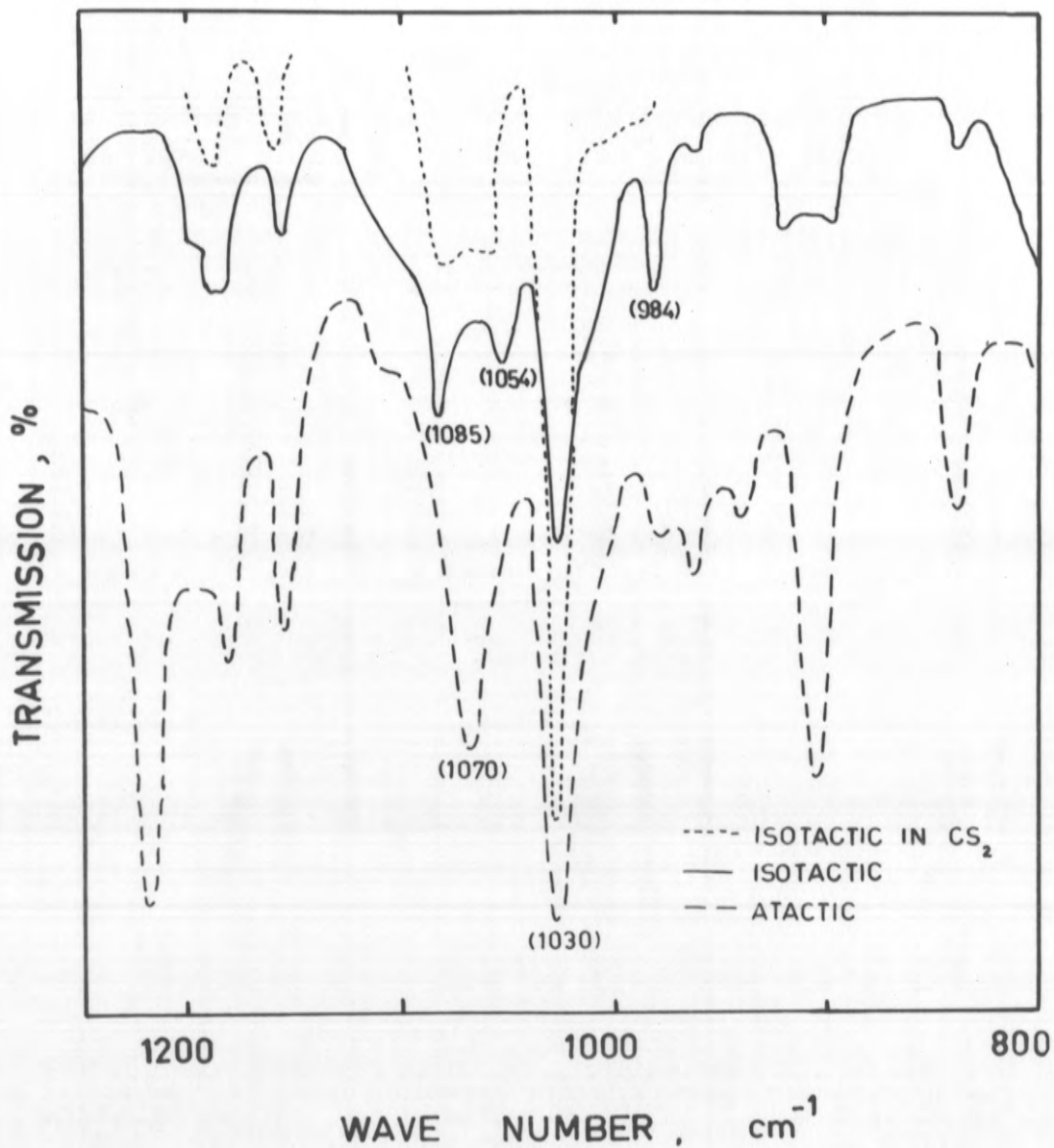


Figure 2-5.1. Infra-red spectra of isotactic and atactic polystyrene showing characteristic absorption bands. Range, 800-1200 cm⁻¹.

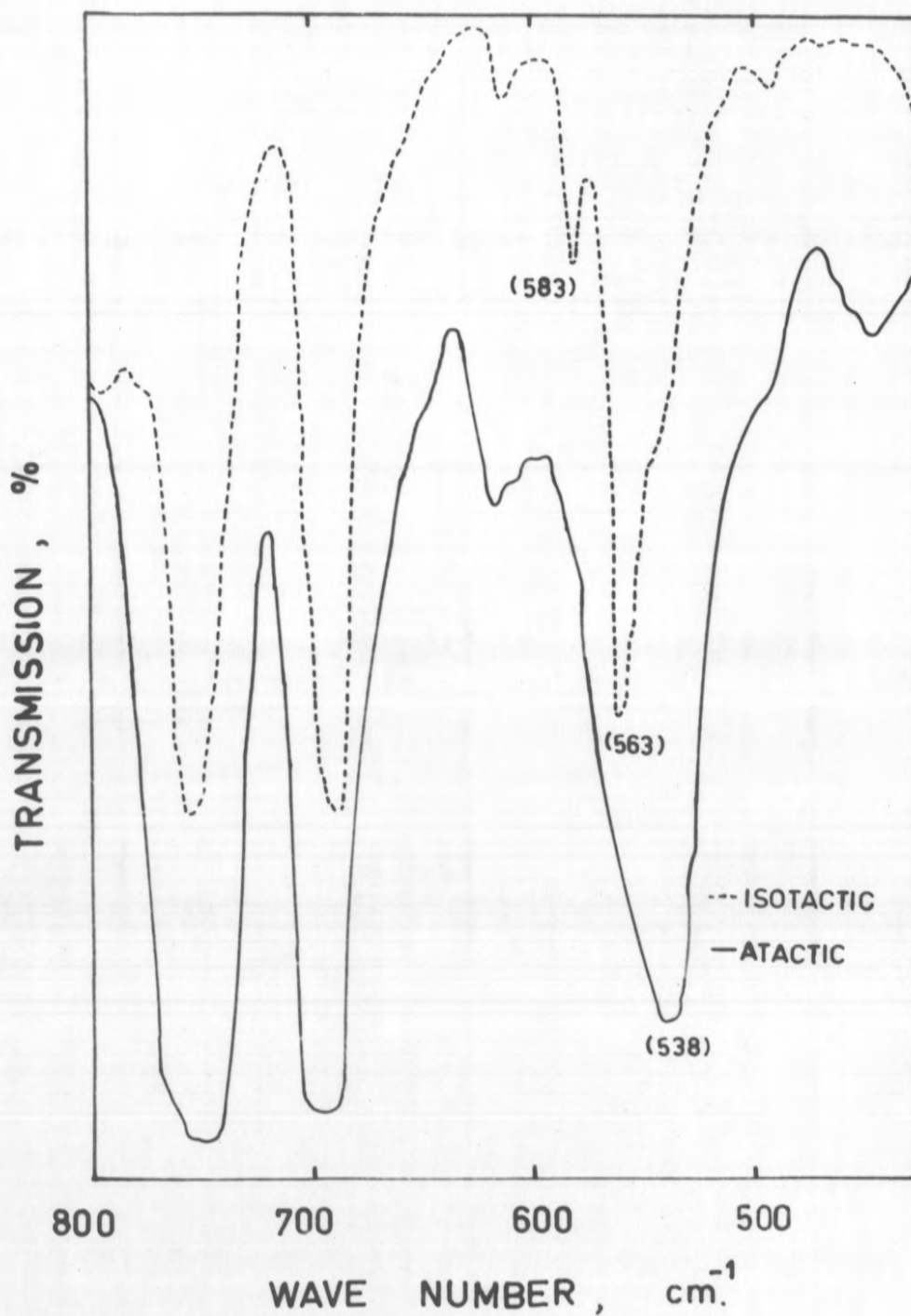
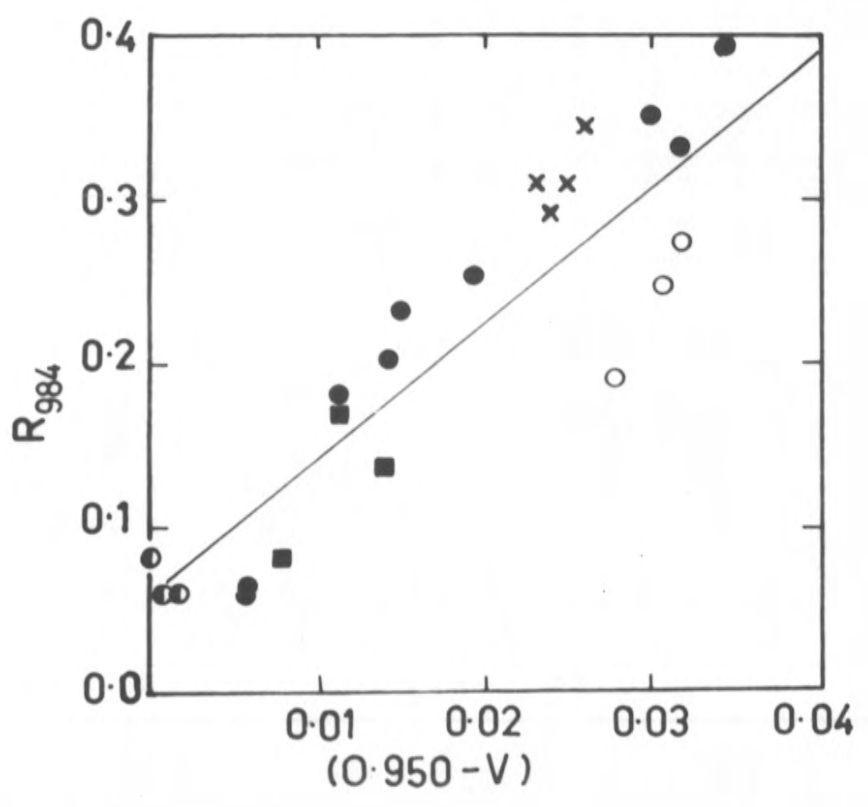
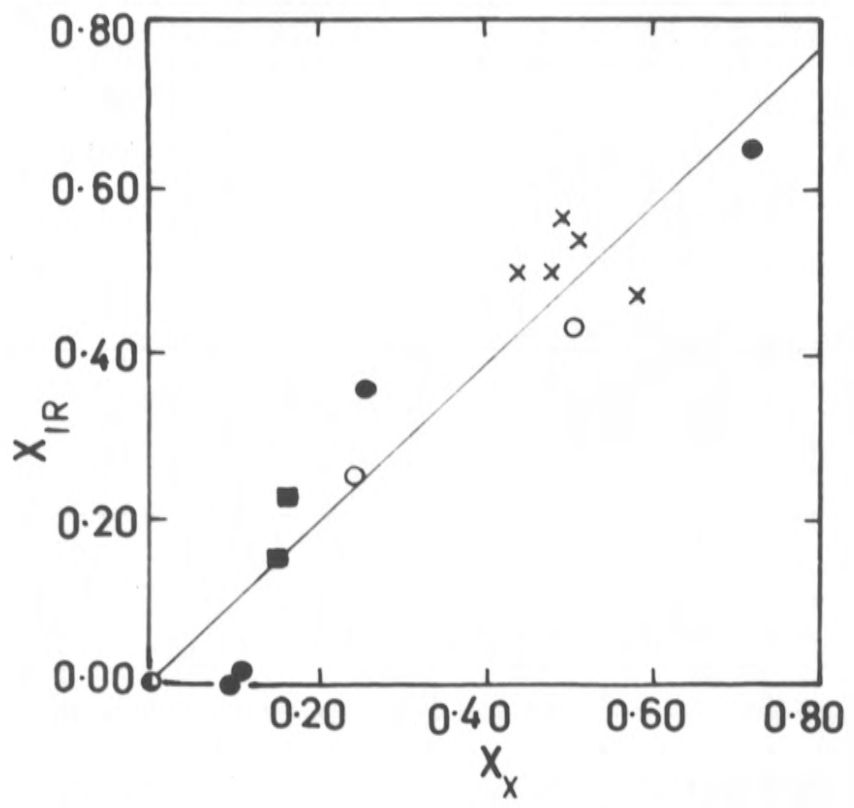


Figure 2-5.2. Infra-red spectra of isotactic and atactic polystyrene films. Range, 475-800 cm⁻¹.

Figure 2-5.3. Comparison of the relationship between X-ray diffraction, specific volume and infra-red results obtained in this work with those by Takeda et al.¹⁶

- CPS I
- ◐ APS
- CPS II
- × oriented films of F1-F5 in this work
- CPS III



R_{984} value and the difference in specific volumes of purely atactic polystyrene and the samples under test. This remark also applies to a plot of the infra-red crystallinity indices against the corresponding values obtained by X-ray diffraction.

2-6 General Conclusions on the Isotacticity of the Polystyrene Fractions

In view of the fact that the intrinsic nature of high polymers makes it impossible for even fully isotactic polystyrene to be crystallized completely it is obvious that any experimental determination of the degree of crystallinity will always be lower than the inherent isotacticity of the sample. For this reason the results obtained by X-ray diffraction, specific volume measurements and infra-red spectra (Tables 2-2.1, 2-4.1 and 2-5.1), clearly indicate that all fractions, F1 - F5, were highly isotactic in nature. This conclusion was supported by other properties such as sharp high melting points, the birefringence of samples and the insolubility in methyl ethyl ketone.

For a more complete characterization however, it was desirable to determine the average size of the macromolecules in the various fractions and this was achieved most conveniently by measurement of molecular weights by viscometry and sedimentation as reported in the following two sections.

Part 2 - Solution State Characterization

2-7 Molecular Weight by Viscometry

(a) Intrinsic viscosity of polymer solutions - relation to molecular weight

The reduced viscosity, ^{50,51,52} η_{sp}/c , of polymer solutions becomes increasingly dependent on concentration as the latter increases and it is the limiting value at infinite dilution $[\eta]$, called the intrinsic viscosity, which is normally related to the molecular weight of the polymer sample,

$$[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c = \lim_{c \rightarrow 0} (\eta - \eta_0)/\eta_0 c \quad (2-7.1)$$

A number of equations⁵⁰ have been proposed to enable the intrinsic viscosity to be determined as accurately as possible, the most commonly used equations being those due to Huggins,⁵³ Kraemer⁵⁴ and Schulz⁵⁵ respectively,

$$\eta_{sp}/c = [\eta] + k_1[\eta]c \quad (2-7.2)$$

$$\frac{1}{c} \ln \eta_r = [\eta] - k_2[\eta]^2 c \quad (2-7.3)$$

$$\eta_{sp}/c = [\eta] + k_1[\eta]\eta_{sp} \quad (2-7.4)$$

where k_1 and k_2 are constants for a given polymer-solvent system.

Besides deriving equation (2-7.4) by an extension of Kuhn's hydrodynamical treatment and showing that the Huggins' equation is an

approximation of it, Ibrahim^{56,57} and Kobayashi⁵⁸ have pointed out

the possible dangers of using equations (2-7.2) and (2-7.3) to deter-

mine the intrinsic viscosity especially when the relative viscosity is in excess of 1.2. Other authors⁵⁹⁻⁶² have referred to the anomalous behaviour of even uncharged polymers at very low concentrations where a maximum is observed. A convenient procedure has been to plot a pair of functions such as η_{sp}/c and $1/c \ln \eta_r$ against c and to extrapolate to the same point, $[\eta]$ at zero concentration.⁵⁰ The parameter, k_1 , usually called the Huggins' constant, is a complex function⁵⁰ of polymer-polymer and polymer-solvent interactions and although its theoretical significance may not have been established its empirical significance - high values in poor solvents and low values in good solvents - is well accepted.

Although an absolute value for the molecular weight of a polymer cannot be derived from solution viscosity measurements^{50,51,63} the dependence of the intrinsic viscosity on molecular weight for a given polymer-solvent system at a stated temperature can be determined by prior calibration against a primary standard molecular weight method such as osmometry or light-scattering. For flexible chain molecules the relationship can usually be expressed empirically by the Mark-Houwink equation,

$$[\eta] = KM^a, \quad (2-7.5)$$

in which the constants K and a can be determined from the linear log-log plot of the intrinsic viscosity against the number (or weight) average molecular weight for well fractionated samples in the appropriate solvent at the specified temperature.

(b) The Mark-Houwink equation for the polystyrene-benzene system

For the case of the polystyrene-benzene system at 30°C many reports of the constants of the Mark-Houwink equation are available in the literature^{33,64-69} for both atactic and isotactic polymers. Although fractionation procedures differed slightly there was generally excellent agreement between the various groups⁶⁷ which suggested that there was little difference between the intrinsic viscosity-molecular weight relationship for the two forms of polystyrene. However, in spite of the fact that the equation obtained by most workers,

$$[\eta] = 1.06 \times 10^{-4} \bar{M}_n^{0.735}, \quad (2-7.6)$$

and that found by Ang,⁶⁸

$$[\eta] = 0.95 \times 10^{-4} \bar{M}_n^{0.77}, \quad (2-7.7)$$

for isotactic polystyrene appear to be in reasonable agreement, the molecular weight, \bar{M}_v , calculated from these equations must vary considerably for any given value of the intrinsic viscosity. For this reason a determination of the number-average molecular weight of fraction F3 by osmometry was made in order to decide which equation suited the experimental results more satisfactorily.

(c) Number average molecular weight of fraction F3

The concentration dependence of the reduced osmotic pressure of a polymer solution can be represented⁷⁰ as a power series by

$$\pi/c = RT \left(\frac{1}{\bar{M}_n} + A_2c + \dots \right) \quad (2-7.8)$$

compared with the theoretical relationship,

$$\pi/c = \frac{RT}{\bar{M}_n} (1 + \Gamma_2 c + \Gamma_3 c^2 + \dots). \quad (2-7.9)$$

It follows that the relationship between the second virial coefficients is given by

$$\Gamma_2 = A_2 \bar{M}_n. \quad (2-7.10)$$

From theoretical considerations⁷¹⁻⁷⁴ concerned with the virial coefficients of polymers in good solvents equation (2-7.9) can be reduced to

$$(\pi/cRT)^{1/2} = (1/\bar{M}_n) [1 + 0.5\Gamma_2 c] \quad (2-7.11)$$

when dilute solutions are used. Plots of $(\pi/cRT)^{1/2}$ against c should therefore be linear⁷⁵ with the intercept and the slope of the line yielding the values of \bar{M}_n and Γ_2 respectively. This has been found to apply in a number of solvents for polystyrene and its derivatives.^{67,73,76,77}

Figure (2-7.1) shows the results of osmotic pressure determinations for the isotactic polystyrene fraction, F3, in benzene at 30°C. From the intercept it was found that the number average molecular weight was $2.72 (\pm 0.05) \times 10^5$ compared with the viscosity number molecular weights of $3.2_3 \times 10^5$ and $2.1_0 \times 10^5$ calculated from equations (2-7.6) and (2-7.7) respectively. Ang's equation, therefore, was not used to calculate the results of other fractions that are shown in Table (2-7.1).

It is of interest to note that the slope of the graph in figure (2-7.1) yielded the following values for the second virial coefficients of F3 in benzene at 30°C,

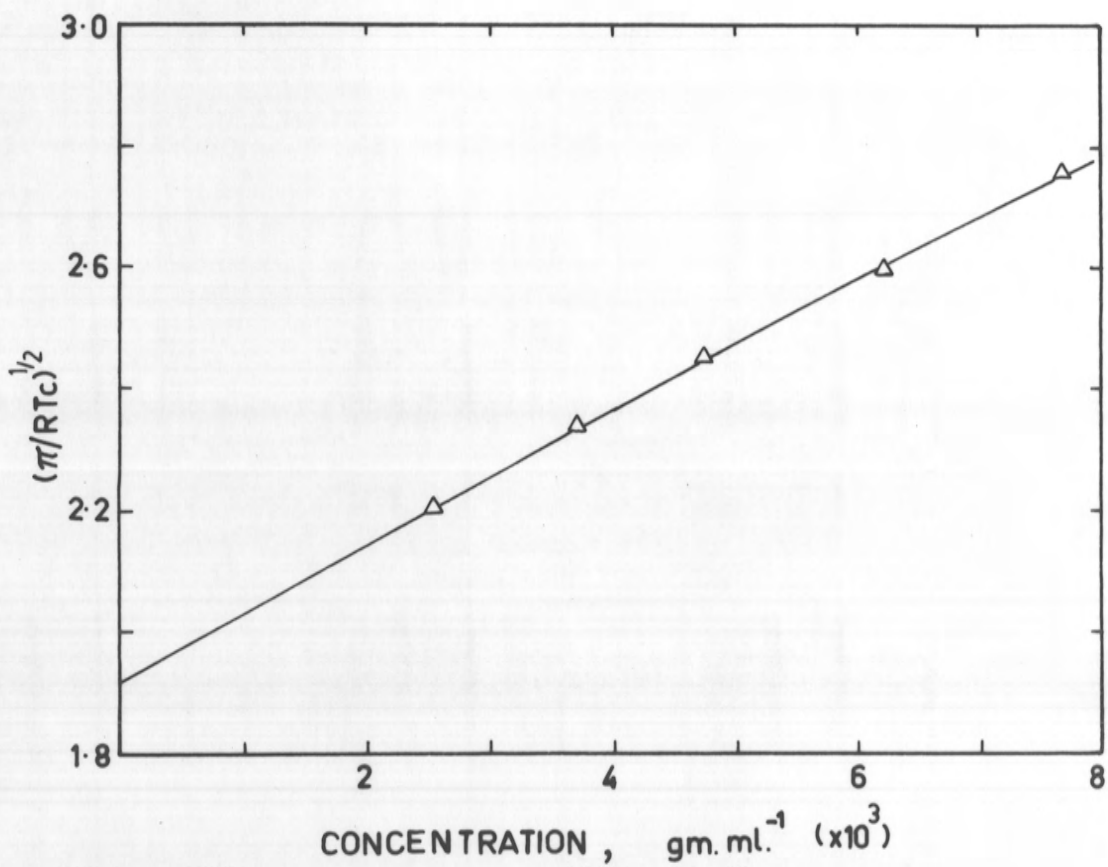


Figure 2-7.1. Osmotic pressure data for isotactic polystyrene fraction, F3, in benzene at 30°C. Osmotic pressure in atmospheres.

$$\Gamma_2 = 116 \pm 7 \text{ cm.}^3 \text{ gm.}^{-1} \text{ and } A_2 = 4.3(\pm 0.4) \times 10^{-4} \text{ cm.}^3 \text{ mole gm.}^{-2}.$$

This value of A_2 compares favourably with the 3.7×10^{-4} found by Hookway and Townsend⁷⁸ for an unfractionated atactic polystyrene (\bar{M}_n , 2.21×10^5), in benzene at 31.5°C. It is also in the range expected from a comparison⁷⁰ of values of A_2 for polystyrene in toluene at 30°C found by Krigbaum and Flory^{79,80} and Natta and his co-workers.⁷⁷

(c) Viscosity number molecular weights of the isotactic polystyrene fractions

Figure (2-7.2) shows values of η_{sp}/c and $\ln \eta_r/c$ plotted against concentration for the five fractions of isotactic polystyrene. No advantage was to be gained by using equation (2-7.4) because, with the exception of high concentrations of fraction F5, the relative viscosity was always less than 1.2. Furthermore the concentrations of solutions were too high to expect the upward curvature that has been reported at very low concentrations. The resultant intrinsic viscosity, viscosity number molecular weights and Huggins' constants are listed in the table below.

Table (2-7.1)

Viscosity data for isotactic polystyrene fractions in benzene at 30°C

	F1	F2	F3	F4	F5
$[\eta]$, ml.gm. ⁻¹	35.7±0.5	73.0±0.6	118.5±0.6	155.2±0.9	175.9±1.5
k_1	0.36	0.37	0.40	0.39	0.39
\bar{M}_v	6.3×10^4	1.67×10^5	3.23×10^5	4.64×10^5	5.52×10^5

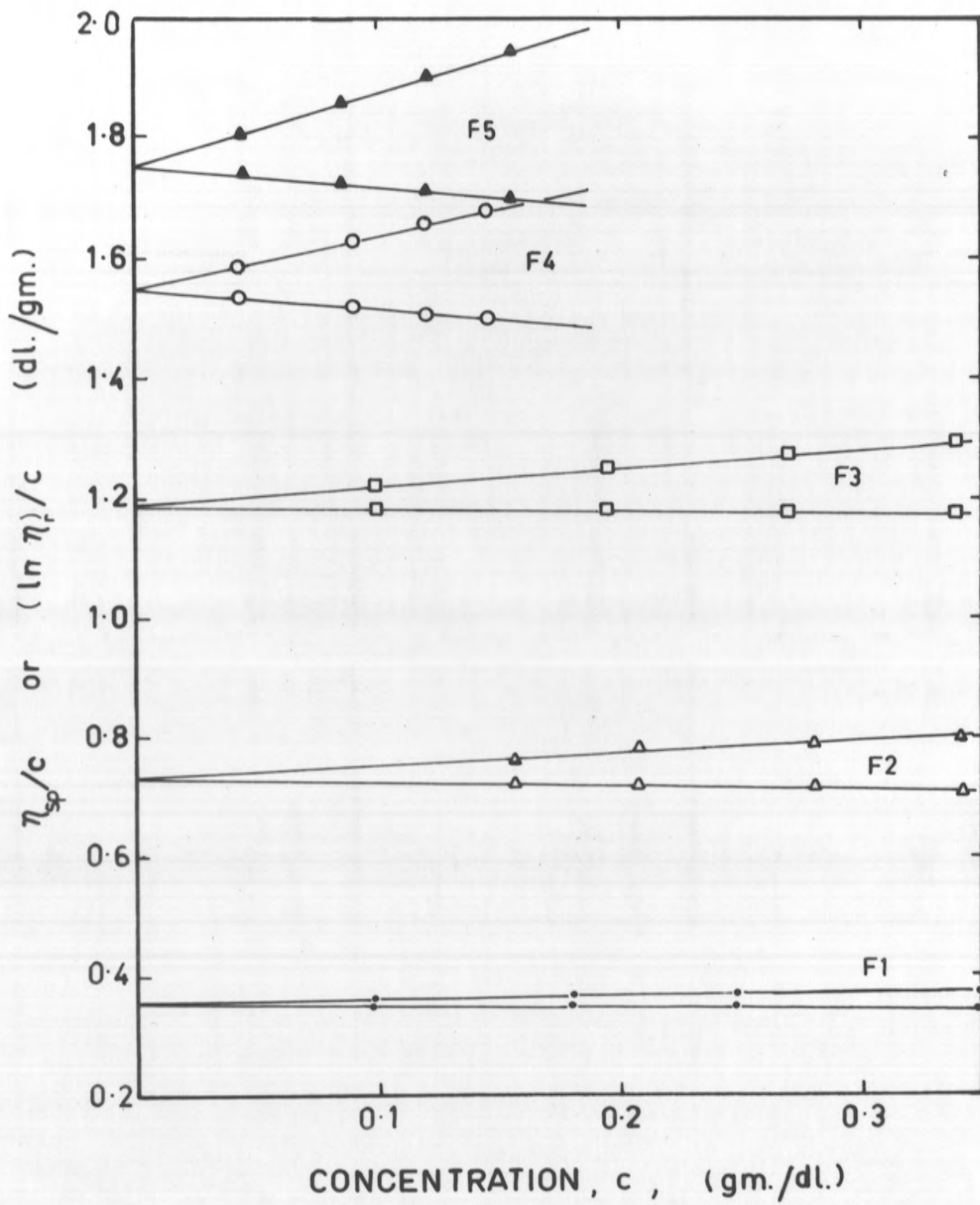


Figure 2-7.2. Viscosity plots for isotactic polystyrene fractions, F1-F5, in benzene at 30°C.

Upper curves: η_{sp}/c Lower curves: $1/c \ln \eta_r$

2-8 Characterization by Sedimentation Velocity Measurements

The molecular weight of a polymer cannot be calculated from sedimentation coefficients alone but only by combination^{81-87,97} with the intrinsic viscosity or the diffusion coefficient of the polymer in the same solvent at the same temperature. In systems containing organic solvents the necessary extrapolation to infinite dilution is complicated by the fact that the sedimentation coefficient is both concentration and pressure dependent. As two methods^{88,89} have recently been suggested for the extrapolation of sedimentation coefficients to infinite dilution and zero hydrostatic pressure a comparison of the alternative procedures for the calculation of the pressure dependence coefficient will be made in an appendix in addition to the characterization of the various polystyrene fractions.

(a) Effect of concentration on the sedimentation coefficient

Although the concentration dependence of the sedimentation coefficient⁸¹⁻⁸³ varies considerably with different polymer-solvent systems the data generally fit the equation,

$$s = s_0 / (1 + kc) = s_0 / (1 + \alpha), \quad (2-8.1)$$

where s_0 and s are the sedimentation coefficients at infinite dilution and concentration c respectively and k is a constant for a given polymer-solvent system under specified conditions. The sedimentation coefficient at infinite dilution is obtained by extrapolation of the plot of $1/s$ against c to zero concentration.

(b) Effect of pressure on the sedimentation coefficient

At the speeds of rotation during ultracentrifugation the pressure on the solution varies from one atmosphere at the meniscus to as high as 200 atmospheres^{89,90} at the bottom of the cell at 59,780 r.p.m. This pressure gradient produces an effect on the sedimentation coefficient as a function of distance from the meniscus as it affects the viscosity⁸⁹⁻⁹¹ and density^{89,90,92} of the solvent as well as the partial specific volume of the solute.⁹³ Figure (2-8.1) shows the typical non-linearity of a $\log_{10} x$ versus t plot exhibited by solutions of polystyrene in benzene where x is the distance of the boundary from the axis of rotation.

The quantitative relation for the pressure dependence of the sedimentation coefficient is given by⁹⁴⁻⁹⁶

$$s^p = s^0(1 - \mu p + \theta p^2) \quad (2-8.2)$$

where s^0 and s^p are the sedimentation coefficients at hydrostatic pressures of zero and p , while μ and θ are the pressure coefficients. To a close approximation^{89,95} the pressure at any position below the meniscus can be calculated by

$$p = \frac{1}{2} \omega^2 x_0^2 \rho_0 \left(\frac{x^2}{x_0^2} - 1 \right) \quad (2-8.3)$$

where x_0 and x are the distances of the meniscus and the solution from the centre of rotation. It follows that

$$s = s^0[1 - m(y - 1)] \quad (2-8.4)$$

in which $y = (x/x_0)^2$ and the pressure dependence parameter, m , is

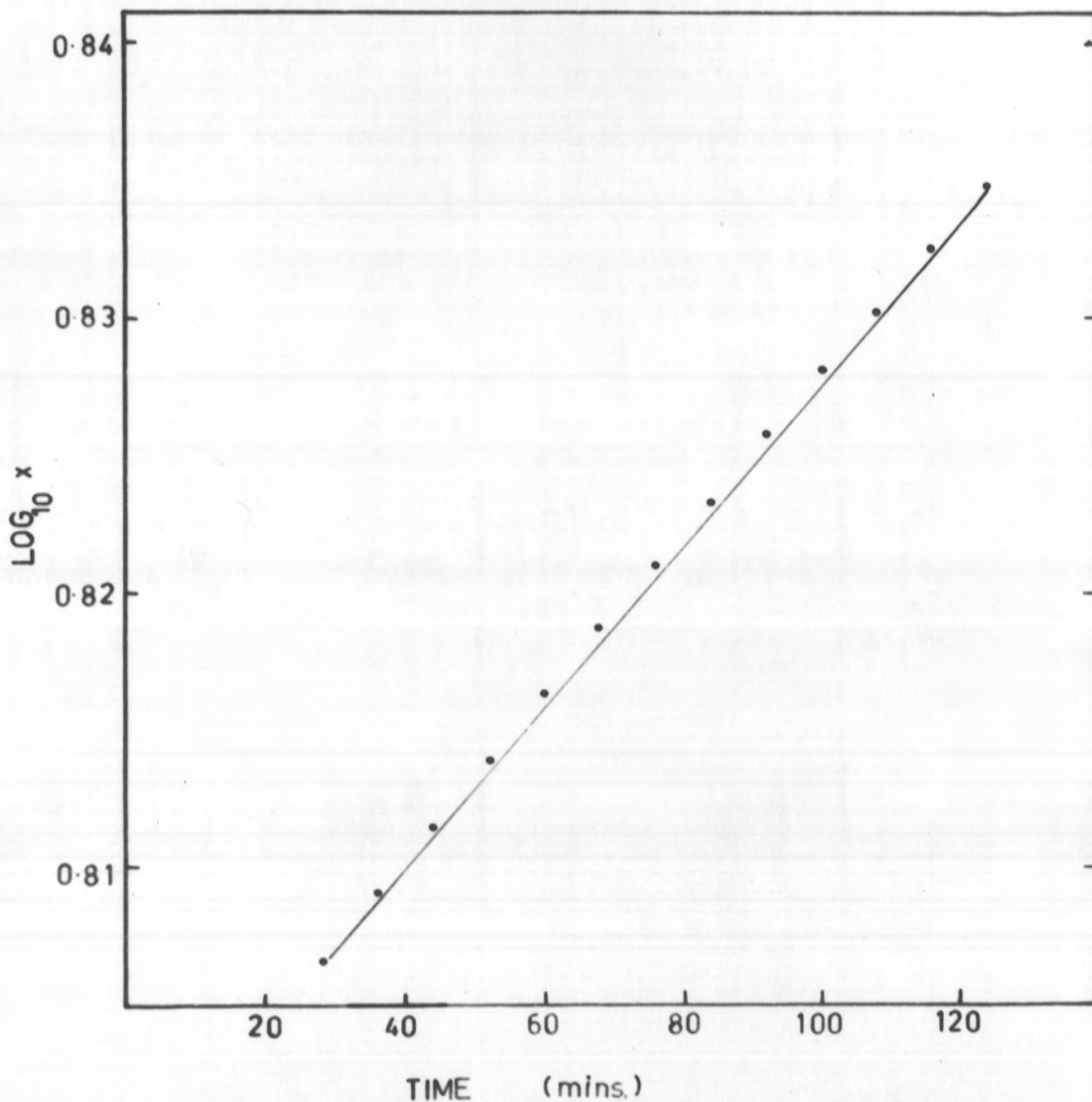


Figure 2-8.1. Change in $\log x$ with time. Fraction F3 in benzene at 30°C. Concentration, 0.625₂ gm. dl.⁻¹. Rotor speed, 59,650 r.p.m. The straight line between the first and last points illustrates the non-linearity of the plot.

given by

$$m = \frac{1}{2} \mu \omega^2 x_o^2 \rho_o \quad (2-8.5)$$

(c) Sedimentation coefficient of isotactic polystyrene in benzene at zero hydrostatic pressure and infinite dilution

After the sedimentation of each polystyrene fraction in benzene at 30°C had been carried out as described in section (4-6) the sedimentation coefficients, s_o^o , at zero hydrostatic pressure and various concentrations, were calculated by the method described by Billick⁸⁸ (see appendix to this section). Figure (2-8.2) shows the values of $(1/s_o^o)$ plotted against concentration for the five isotactic polystyrene fractions. The resultant sedimentation coefficients, s_o^o , at zero concentration and zero hydrostatic pressure with standard errors are listed in table (2-8.1) together with the constant, k , of equation (2-8.1). The bracketted values for fractions F3 and F5 are those obtained by using the alternative method suggested by Cantow and co-workers⁸⁹ (see appendix to this section).

Table (2-8.1)

Sedimentation coefficients at zero hydrostatic pressure and infinite dilution for isotactic polystyrene fractions in benzene at 30°C.
Speed 59,650 r.p.m.

	F1	F2	F3	F4	F5
s_o^o (sveds.)	4.47±0.21	5.39±0.32	6.97±0.08 (6.84±0.08)	7.86±0.40	9.89±0.20 (9.96±0.20)
k (dl.gm. ⁻¹)	0.97 ₆	1.27 ₄	1.96 ₅	2.03 ₀	2.83 ₅

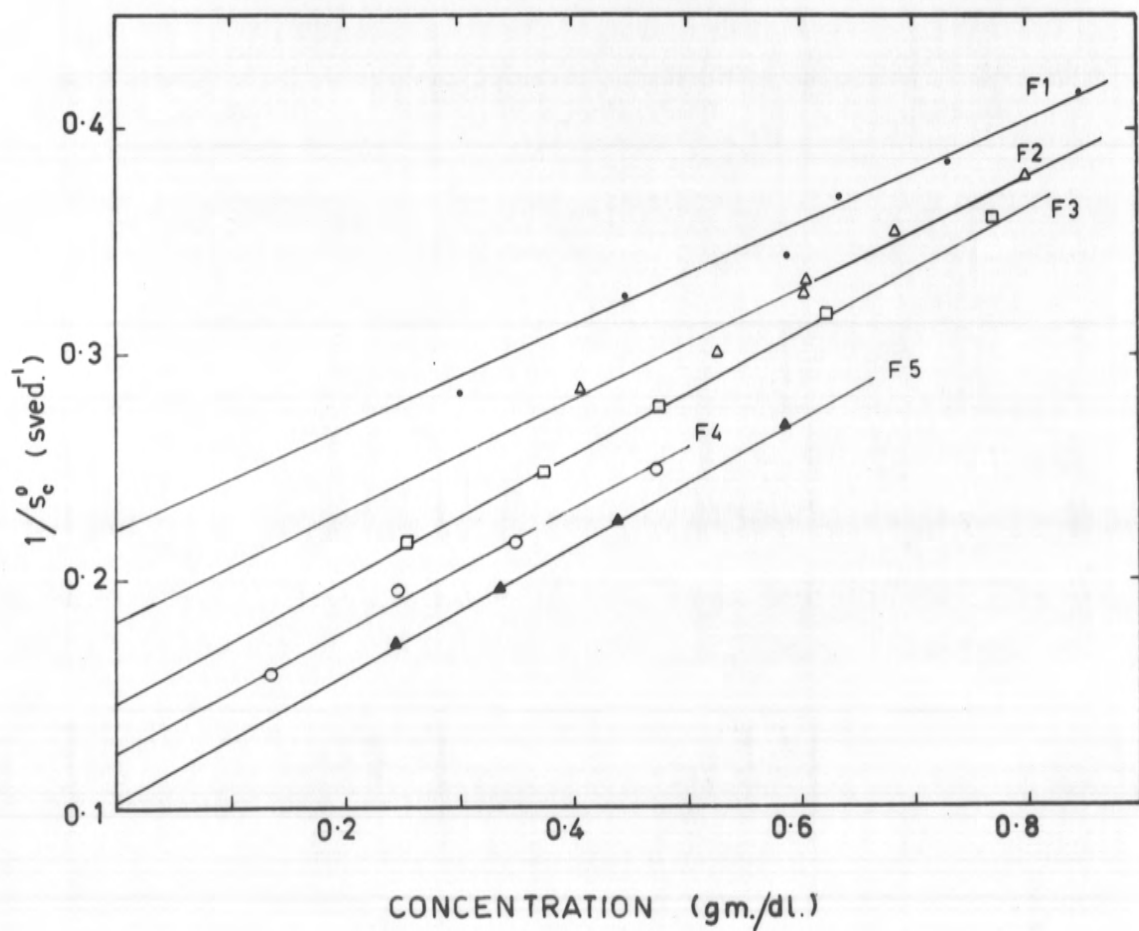


Figure 2-8.2. Concentration dependence of the pressure-corrected sedimentation coefficient. Isotactic polystyrene fractions in benzene at 30°C. Speed, 59,650 r.p.m.

(d) Molecular weights using the Mandelkern-Scheraga equation

The molecular weight, $M_{s\eta}$, of a polymer can be calculated from the intrinsic viscosity and the sedimentation coefficient at zero concentration and atmospheric pressure in the same solvent by means of the Mandelkern-Scheraga equation,⁸⁵⁻⁸⁷

$$\frac{s_0 [\eta]^{1/3} N \eta_0}{M^{2/3} (1 - \bar{v}\rho)} = \phi^{1/3} p^{-1}, \quad (2-8.6)$$

where \bar{v} is the partial specific volume of the polymer in the solvent, ρ is the density of the solution, N is Avogadro's number and η_0 is the viscosity of the solvent. To a close approximation there has been experimental verification^{85,87} of the constancy of the left-handed side of equation (2-8.6) for randomly coiled polymers in any solvent at any temperature. Later investigations,¹⁰⁰ however, indicated that $s_0 [\eta]^{1/3} N \eta_0 / M^{2/3} (1 - \bar{v}\rho)$ should be equated to a quantity β which for theta solvents is equal to $\phi^{1/3} p^{-1}$ but for very good solvents is 0.97 of this value.

With the assumption that β has the value of 2.60×10^6 - benzene is taken to be a very good solvent for isotactic polystyrene - and using the data set out in section (2-6c) and tables (2-7.1) and (2-8.1) the molecular weights of the polystyrene fractions, shown in table (2-8.2), were calculated by using the Mandelkern-Scheraga equation.

Table (2-8.2)

Molecular weights of isotactic polystyrene fractions from viscosity and sedimentation data. Benzene at 30°C as solvent.

	F1	F2	F3	F4	F5
$M_{sn} \times 10^{-4}$	$9.2_3 \pm 0.5_4$	17.5 ± 1.5	32.7 ± 0.6	44.9 ± 3.4	67.5 ± 2.1

The considerable discrepancy between M_v and M_{sn} for fraction F1 is probably due to higher polydispersity which is evident from the sedimentation velocity photographs shown in figure (4-6.1). The molecular weight dependence of the sedimentation coefficient at zero pressure and infinite dilution is shown in figure (2-8.3) together with the result obtained by Billick for an atactic polystyrene sample ($M_w = 2.51 \times 10^5$) in toluene at 25°C.

Appendix to section (2-8)

Treatment of sedimentation data for the effects of pressure on the sedimentation coefficient

(a) Billick method⁸⁸

(i) Calculation of s_0^0

Following the solution by Wales⁹⁸ of Fujita's⁹⁵ original equation which related the boundary position to time for a polymer of low dispersity when the sedimentation coefficient depends on both pressure and concentration, Billick⁹⁹ obtained the following solution,

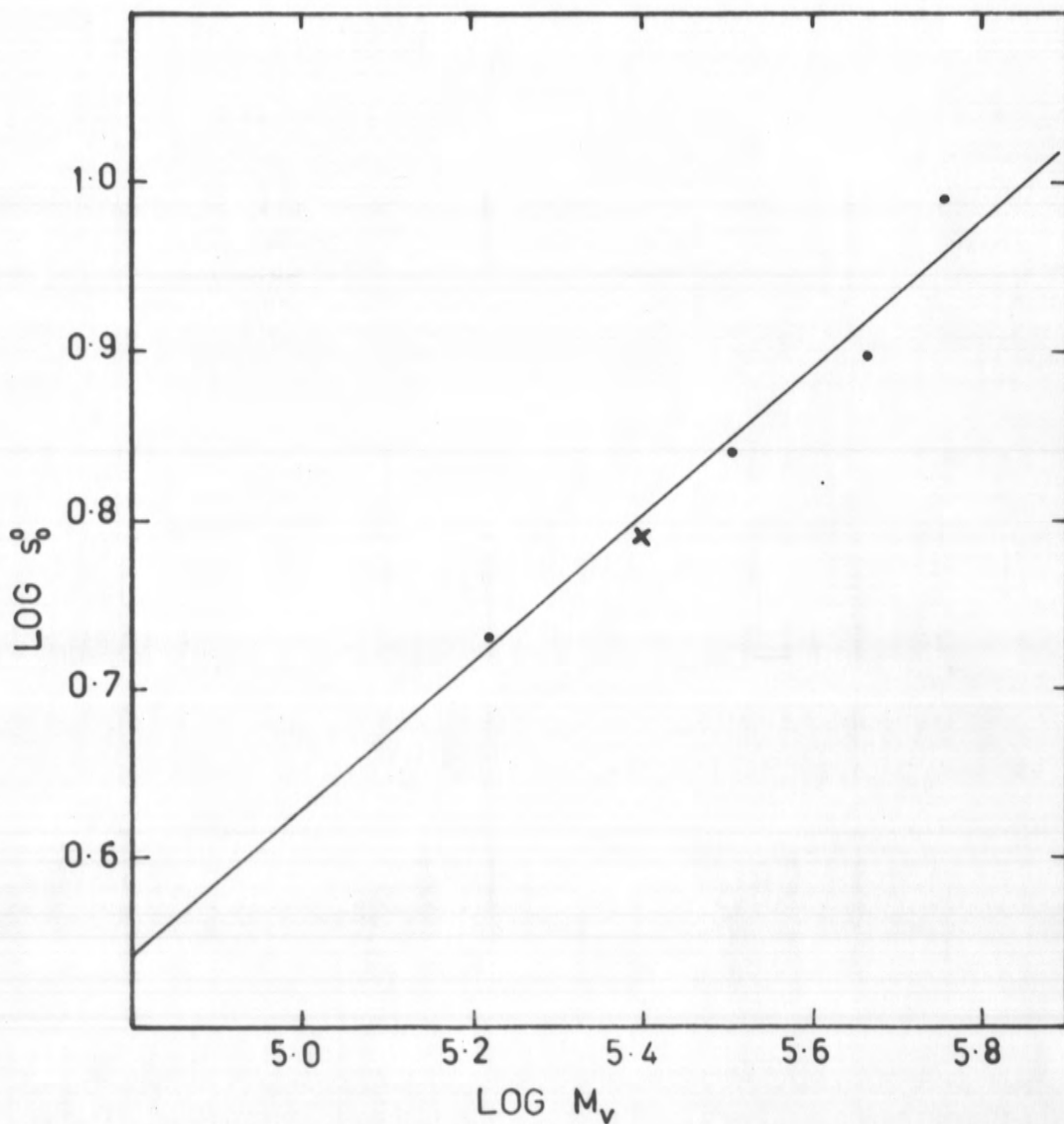


Figure 2-8.3.

Molecular weight dependence of the sedimentation coefficient at infinite dilution and zero hydrostatic pressure for isotactic polystyrene fractions in benzene at 30°C. A result obtained by Billick for atactic polystyrene in toluene at 25°C is also shown.

$$s = \frac{\ln x/x_0}{\omega^2 t} = \frac{s_0^0}{(1 + \alpha)} \left[1 - \frac{m(2\alpha + 1) - \alpha}{(1 + \alpha)} \times \frac{s_0^0 \omega^2}{(1 + \alpha)} t \right] \quad (2-8.7)$$

where s_0^0 is the sedimentation coefficient at zero hydrostatic pressure and infinite dilution and α and m , the concentration and pressure dependence parameters, have the significance as above in equations (2-8.1) and (2-8.5). Billick then expressed equation (2-8.7) in the form,

$$\ln x = \ln x_0 + s_0^0 \omega^2 t - B(\omega^2 t)^2 \quad (2-8.8)$$

from which s_0^0 and B may be obtained by computing experimental values of $\ln x$ and $\omega^2 t$ by a least squares program. A linear plot of $1/s_0^0$ versus concentration then gives s_0^0 and α from the intercept and slope respectively.

(ii) Calculation of the pressure dependence parameter of the sedimentation coefficient

In expressing equation (2-8.7) in the form of equation (2-8.8) Billick⁸⁸ showed that

$$B/(s_0^0)^2 = \frac{m(2\alpha + 1) - \alpha}{(1 + \alpha)} \quad (2-8.9)$$

- From computed values of B and s_0^0 together with those of the concentration dependence parameter, α , the pressure dependence parameters, m and μ , were calculated from equations (2-8.9) and (2-8.5). Table (2-8.3) lists the experimental results for fractions, F3 and F5.

Table (2-8.3)

Sedimentation data used in the calculation of the pressure dependence parameters. Isotactic polystyrene, F3 and F5, in benzene at 30°C. Speed, 59,650 r.p.m.

	c (gm.dl. ⁻¹)	s ⁰ (sved.)	B (sved. ⁻²)	m	μ × 10 ⁹ (cm. ² dyn. ⁻¹)
F3	0.2443	5.835	20.73	0.72 ₂	1.2 ₀
	0.3386	5.104	17.02	0.76 ₈	1.1 ₈
	0.4398	4.439	12.44	0.76 ₂	1.2 ₅
	0.5866	3.732	9.48	0.80 ₄	1.2 ₂
F5	0.2540	4.64 ₇	13.7 ₅	0.72 ₇	1.2 ₁
	0.3735	4.00 ₅	12.5 ₁	0.84 ₅	1.2 ₂
	0.4768	3.61 ₉	8.2 ₂	0.74 ₉	1.2 ₃
	0.6252	3.13 ₄	6.7 ₇	0.80 ₀	1.2 ₀
	0.7700	2.76 ₈	4.4 ₀	0.73 ₄	1.0 ₈

The standard errors were in the range 0.01-0.02 for s⁰ and 0.55-1.0 for B while the corresponding average error for μ was 0.05 × 10⁻⁹ (see section 4-6f for details of calculation).

The values of μ compare very favourably in magnitude and precision with those obtained by Billick⁸⁸ for atactic polystyrene in toluene at 25°C. An approximate theoretical value of 1.1 × 10⁻⁹ cm. dyn.⁻¹ was calculated from the interpolated pressure coefficients of the viscosity and the density of benzene as outlined by Cantow⁸⁹

and discussed in the experimental section (4-6e).

(b) Cantow et al.⁸⁹ method

(1) Calculation of s_c^0

From equation (2-8.3) the hydrostatic pressure in the solution at a distance x from the axis of rotation is proportional not only to $(x^2/x_0^2 - 1)$ but also to the distance below the meniscus, $(x - x_0)$, to a good approximation provided that this distance is not too great,⁸⁹

$$x_0 < x < x_0 + 0.7.$$

From the position of the schlieren peaks at known times during an ultracentrifuge run the sedimentation coefficients, s_c^P , at the different positions in the solution were calculated. These values of s_c^P were then plotted against the distance below the meniscus and a least squares extrapolation yielded the sedimentation coefficient, s_c^0 , at zero hydrostatic pressure for each concentration of polymer solution. Figure (2-8.4) shows the data obtained for fraction, F5. The sedimentation coefficient, s_c^0 , at infinite dilution was then obtained in the usual manner with the results agreeing almost completely with those obtained by the Billick method (see Table 2-8.4).

Table (2-8.4)

Sedimentation coefficient, s_c^0 , calculated by the Billick and Cantow methods. Fraction F5 in benzene at 30°C. Speed, 59,650 r.p.m.

Concentration (gm.dl. ⁻¹)	0.2443	0.3386	0.4398	0.5866
1/ s_c^0 (Billick)	0.171 ₄	0.195 ₉	0.225 ₃	0.268 ₀
1/ s_c^0 (Cantow)	0.171 ₀	0.195 ₈	0.225 ₂	0.268 ₂

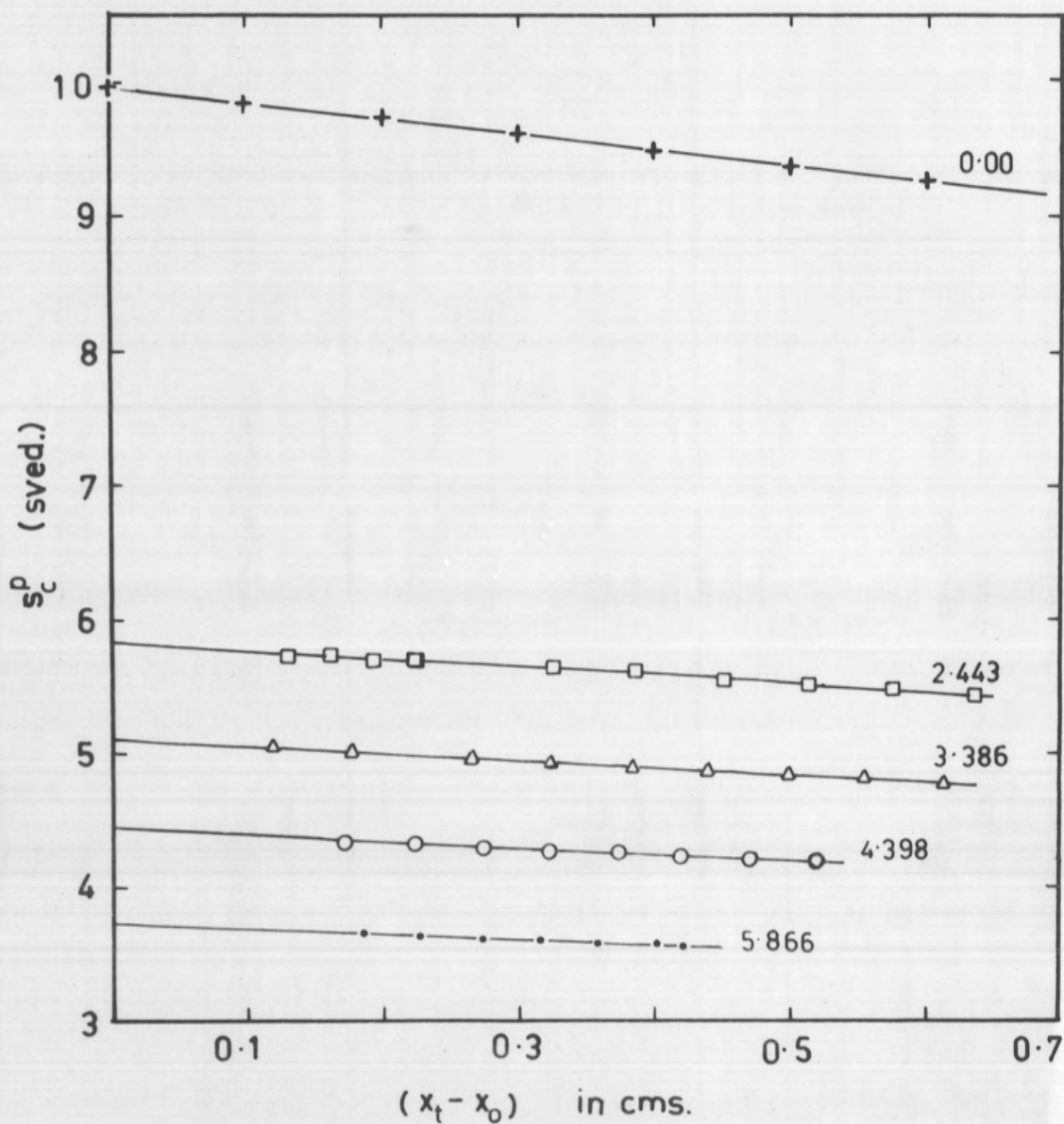


Figure 2-8.4. Extrapolation of sedimentation coefficients to zero hydrostatic pressure at the concentrations (in gm. litre⁻¹) indicated. Isotactic polystyrene, F3, in benzene at 30°C. Speed 59,650 r.p.m.

That this is not unexpected can be seen by rearranging equation (2-8.8) in the form,

$$s_c^p = \ln(x/x_0) = s_c^0 - B\omega^2 t \quad (2-8.10)$$

and combining equations (2-8.2) and (2-8.3) to give

$$s_c^p = s_c^0 [1 - \text{const.} (x - x_0)] \quad (2-8.11)$$

for cases in which the distances below the meniscus are small.

(11) Calculation of the pressure dependence parameter of the sedimentation coefficient⁸⁹

From the least squares equation for the lines in figure (2-8.4) the sedimentation coefficients, s_c^p , at positions "0, 0.1, 0.2 0.7 cm. below the meniscus" (see section 4-6c) were calculated and plotted against concentration as shown in figure (2-8.5). The least squares intercepts of these lines then gave the sedimentation coefficient of the polystyrene in benzene at infinite dilution and at pressures (calculated from equation 2-8.3) corresponding to positions 0, 0.1 0.7 cm. below the meniscus. These results are represented graphically for fraction 5 in figure (2-8.6). From equation (2-8.2), with neglect of higher terms in pressure, the slope of the line was equated to $s_c^0 \mu$. The value of μ , $6 \times 10^{-10} \text{ cm.}^2 \text{ dyn.}^{-1}$ which was obtained, is low compared with the calculated value of approximately $11 \times 10^{-10} \text{ cm.}^2 \text{ dyn.}^{-1}$ but as the calculation of μ by the Billick and Cantow methods can be shown to be equivalent⁹⁰ the discrepancy and errors involved in the two methods must arise from a

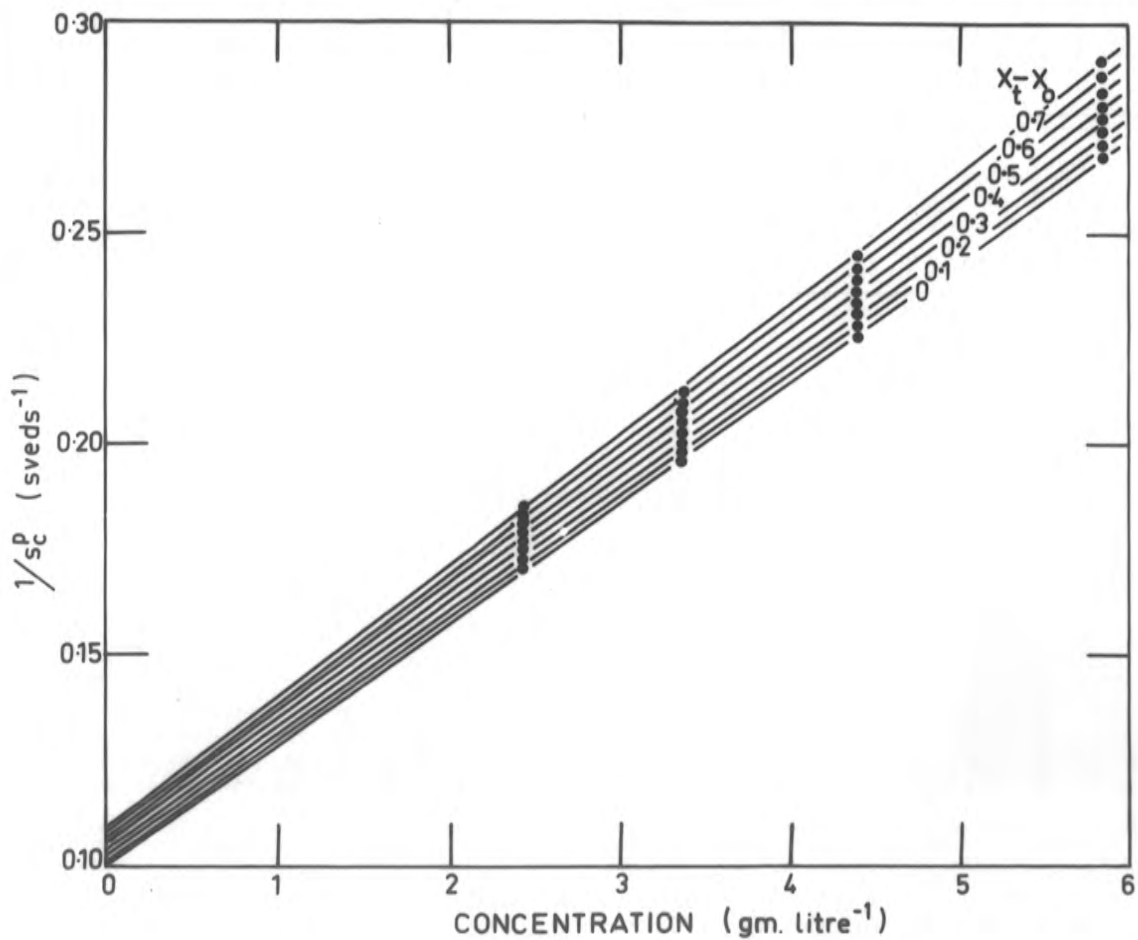


Figure 2-8.5. Extrapolation to zero concentration of sedimentation coefficients at constant hydrostatic pressure (Cantow method). Isotactic polystyrene, F5, in benzene at 30°C.

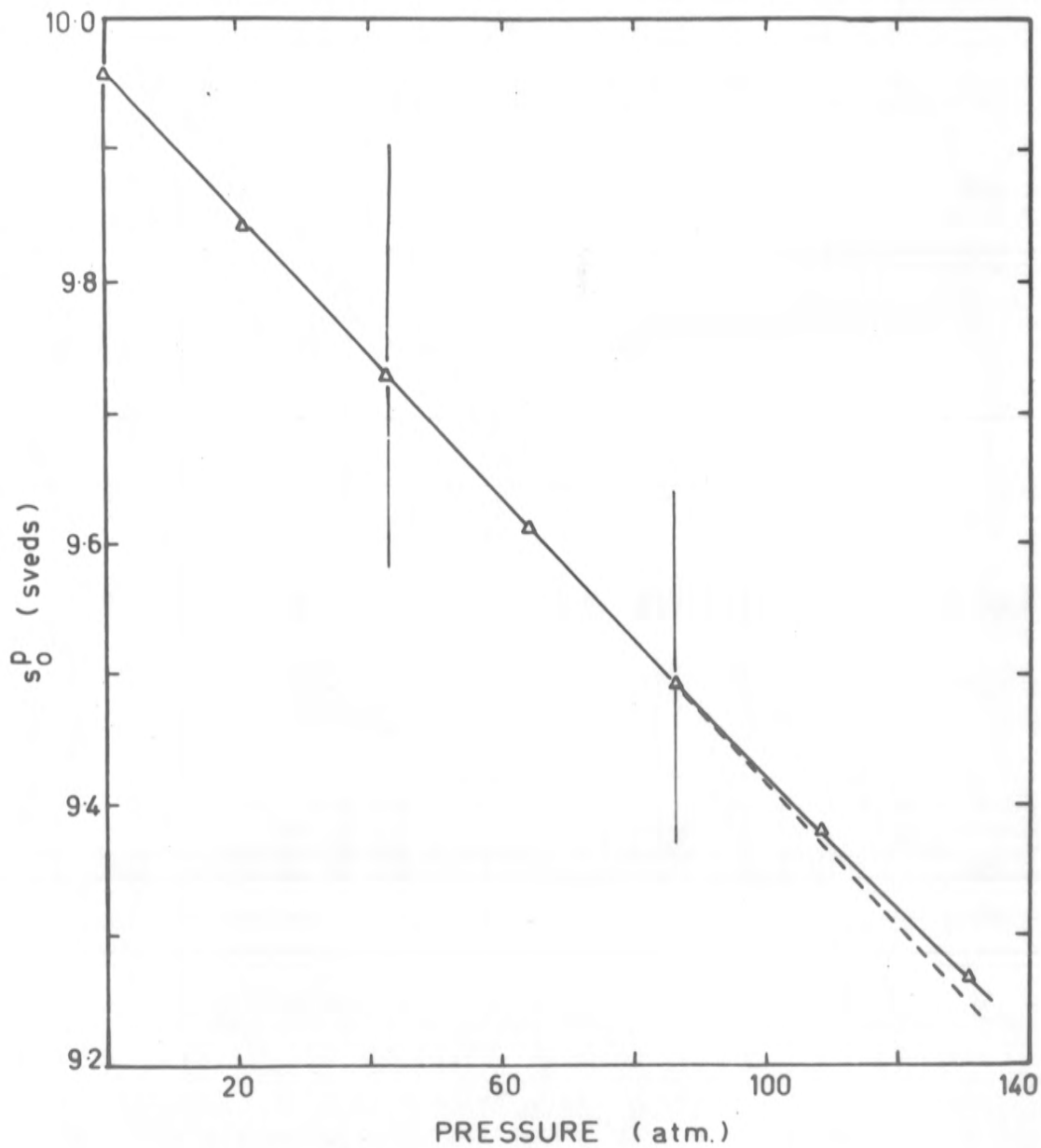


Figure 2-8.6. Pressure dependence of the sedimentation coefficient at infinite dilution. Isotactic polystyrene fraction, F5, in benzene at 30°C.

difference in the weighting of the experimental results. The Billick method works closer to this data in that s_c^0 and B are determined in one step and the final calculation of μ is not very sensitive to errors in k. On the other hand the Cantow method relies on data obtained from a series of interpolations (figure 2-8.4) and extrapolations (figure 2-8.5) so leading to possible errors of the magnitude shown in figure (2-8.6).

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CHAPTER IIICOMPARISON OF ISOTACTIC AND ATACTIC POLYSTYRENE SULPHONIC ACIDS

The characterised isotactic polystyrene fractions and atactic polystyrene samples, S103 and S108, were sulphonated by using a liquid sulphur trioxide-triethyl phosphate complex in chloroform as solvent. (See section 4-7c). Attempts were made to detect differences between the purified isotactic and atactic polystyrene sulphonic acids by two of the usual methods for solid state characterisation and then by various solution state studies.

3-1 Solid State Comparison of Isotactic and Atactic PolystyreneSulphonic Acids(a) Infra-red spectra

In a study of the infra-red spectra of polystyrene sulphonic acids Hart and Janssen¹ showed that the polyacid prepared by sulphonation of atactic polystyrene gave a spectrum identical to that obtained from the polyacid prepared by polymerization of para-styrene sulphonic acid. Figure (3-1.1) shows that the infrared spectra of isotactic and atactic polystyrene sulphonic acids are not only identical to each other but also correspond to those reported by the above authors. The absence of bands characteristic of those for crystalline isotactic polystyrene is not unexpected due to the fact that

- (1) the sulphonic acid group gives rise to strong absorption bands²⁻⁵ at wavelengths in the same range as those for the expected crystalline isotactic polystyrene bands,
- and (2) para-substitution in the benzene ring prevents crystallization

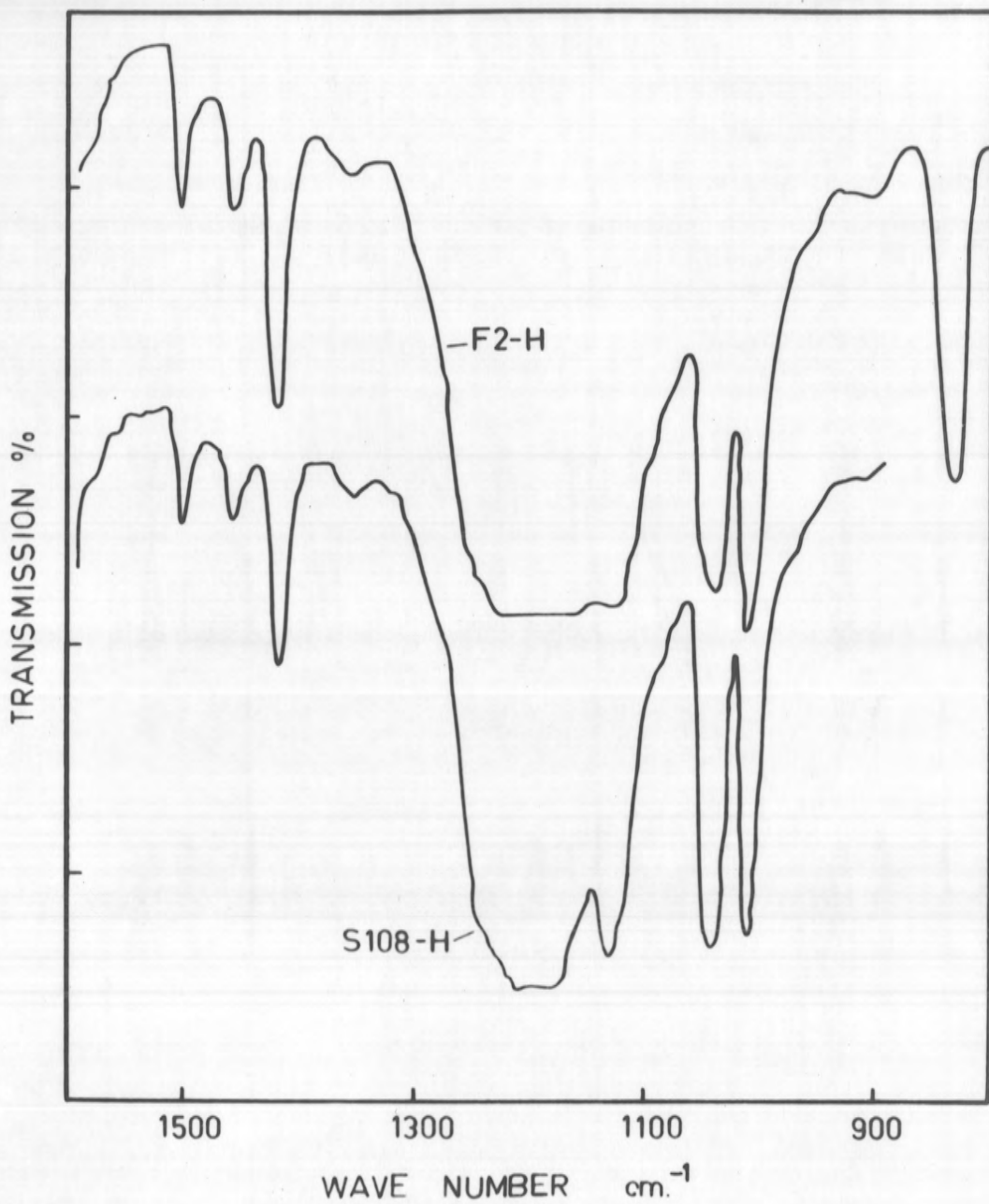


Figure 3-1.1a. Infra-red spectra of isotactic and atactic poly-styrene sulphonic acids using the potassium bromide disc technique. Range, 800-1600 cm.⁻¹.

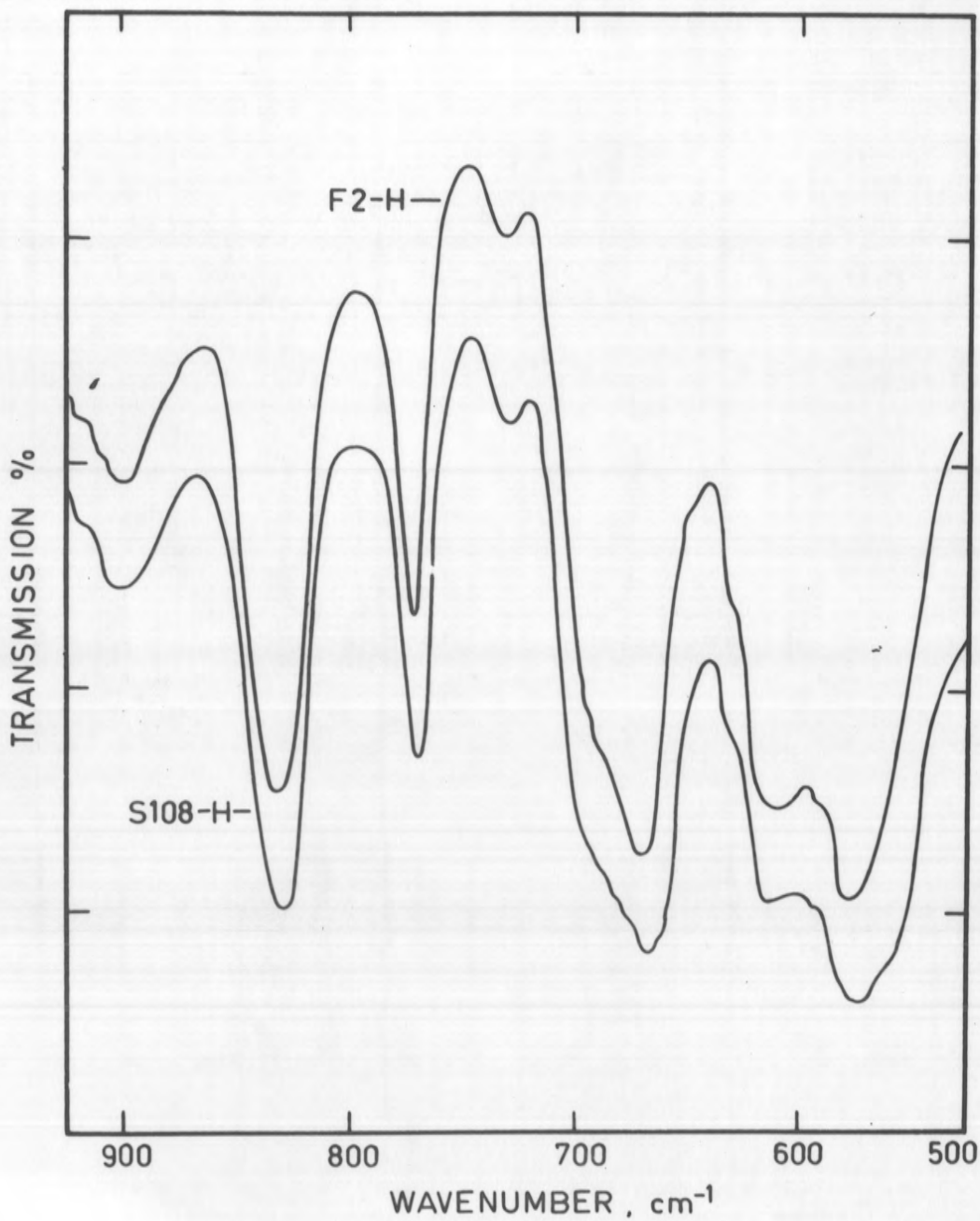


Figure 3-1.1b. Infra-red spectra of isotactic and atactic polystyrene sulphonic acids using the potassium bromide disc technique. Range 500-900 cm⁻¹.

of substituted stereoregular polystyrene^{6,7} except in the case of poly-fluorostyrene. Furthermore because of the tendency to form sulphone linkages⁸ at temperatures much in excess of 100°C, annealing of the films was restricted to prolonged heating at 80-90°C and it is possible that these conditions may not have induced orientation to any great extent even if the polyacids had been crystallizable.

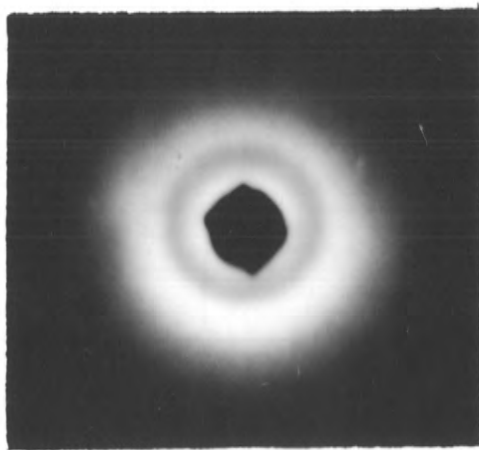
(b) X-ray diffraction

For the same reasons referred to above X-ray diffraction powder patterns of both types of polystyrene sulphonic acids and their sodium salts were expected, and found, to correspond to those of amorphous polymers⁹ as is evident in figure (3-1.2). There was a slight suggestion of order apparent in one sample of the isotactic polystyrene sulphonic acid, F3-H, which had been held over phosphorus pentoxide at 90°C for several days.

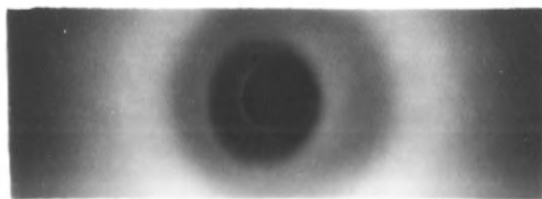
(c) Retention of stereoregularity in sulphonated isotactic polystyrene

Although there is no justification to suppose the non-retention of the isotactic sequence in the sulphonated polystyrene due to the high energy barrier to rotation about the carbon-carbon bond of the main chain,¹⁵ an attempt was made, nevertheless, to verify the accuracy of this assumption. If isotactic polystyrene sulphonic acid could be hydrolysed back to the parent polystyrene and, after orientation, shown to be crystalline by infrared spectroscopy and X-ray diffraction, the existence of the isotactic sequence in the polysulphonic acid will have been proved.

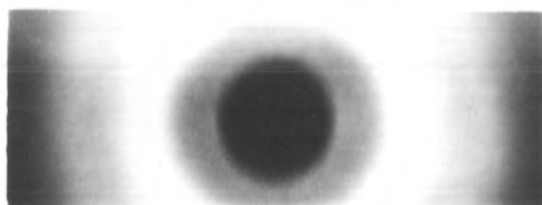
Figure 3-1.2. X-ray diffraction patterns of isotactic and atactic polystyrene sulphonic acids.



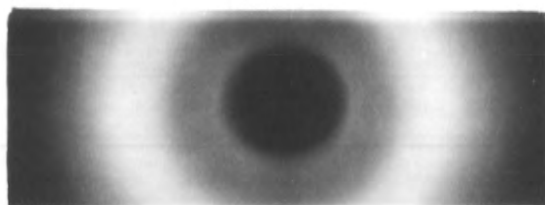
F3-H



S108-H



F3-H



F3-Na

Aromatic sulphonic acids have been desulphonated by heating aqueous solutions for prolonged periods at elevated temperatures in the presence of moderately high concentrations of mineral acids such as sulphuric or phosphoric acids.¹⁰⁻¹² As ortho- or para-substitution has been reported to facilitate the hydrolysis¹⁰ an attempt was made to recover polystyrene from polystyrene sulphonic acid (see section 4-7e) by the above method. In all cases, especially at high temperatures, degradation took place and no yield of polystyrene was obtained.

Other possible methods^{13,14} involving the use of metals with mineral acids and Raney-nickel catalyst, with and without prior reduction to the thiol by lithium aluminium hydride, were not attempted as these techniques with simple aromatic sulphonic acids give relatively low yields of desulphonated product rather than the complete hydrolysis which would be necessary to characterise polystyrene.

3-2 Solution Studies Involving Optical Activity

Solutions, containing randomly oriented molecules, are capable of being optically active only if the solute molecules lack planes or centres of symmetry¹⁸ such that they are not superposable on their mirror images. The activity will be exhibited only if the solution contains an excess of one of the (usually) two forms of the molecule and this can arise from the presence of asymmetric atoms or from the structure as a whole being asymmetric. In the latter case right- and left-handed helical arrangements are examples of asymmetric conformations as they are non-superposable mirror images

of each other. Thus a system containing macromolecules all coiled in the same helical sense should be optically active even in the absence of asymmetric atoms.

(a) Possibility of optical activity in vinyl-type polymers

(1) Effect of asymmetric carbon atoms in the main chain

Most of the carbon atoms at alternate positions¹⁸⁻²¹ along the backbone of vinyl-type polymers (Figure 1.1) are only pseudo-asymmetric because two of the tetrahedral linkages are to sections of the main chain which, although differing in length, are identical in the immediate vicinity of the carbon atom being considered. Only those carbon atoms near the end of the chain have a different environment in each direction of the main chain and are therefore truly asymmetric. With sufficiently long macromolecules, however, the proportional contribution to optical activity by these chain ends will be negligible whether the polymer is atactic or isotactic. Even for low molecular weight polymers optical activity arising from these end effects will not be exhibited because of intermolecular¹⁹ compensation in the same way as in racemic mixtures of simpler asymmetric compounds.

(2) Structural asymmetry

For stereoregular polymers the possibility of optical activity due to other kinds of uncompensated asymmetry has to be considered.

Although isotactic chains have been shown to retain to some extent their helical conformation when the solid polymer is dissolved,¹⁶ these helical sections are as likely to be right-handed

as left-handed¹⁹⁻²² so that structural contributions to optical activity should also cancel.

In view of the above factors it was not surprising that aqueous solutions of both atactic and isotactic polystyrene sulphonic acids showed no measurable optical activity.

(3) Effect of optically active groups in the side-chain

An asymmetric side group may affect the optical activity in two ways:-

Firstly, the asymmetry of the group itself will induce optically active transitions within that group, or in adjacent chromophores, and the magnitude of the optical rotatory power will be a function of the four groups about the asymmetric carbon atom. When bonded to the polymer chain the optical rotatory power should be a function of the nature of the chain but the source of the optical activity will still be essentially the asymmetry of the side chain.

Secondly, the side groups carrying the centre of asymmetry may restrict the number of conformations possible for the chain by a purely steric effect,^{18,22} and if the resulting conformations are asymmetric, optical activity should be produced in the chain. In some instances the optical activity is markedly dependent on the stereoregularity of the polymer but attempts^{25,26} to interpret these findings in terms of a helical conformation in solution have been questioned.^{18, 23,27,28} It seems likely, however, that there must be some overall helicity in one preferred sense for activity to arise from this secondary source, since only a helix will induce electronic transitions

having linear and rotatory charge displacements which are the necessary requirements for optical activity.

It would be expected therefore that if the asymmetric side-group induces a preferred helicity in the chain, optical activity should be associated with electronic transitions arising in the asymmetric side group itself together with transitions arising in the helical chain. The latter would be expected to arise in the far ultra-violet regions of the spectrum since essentially a saturated carbon chain is involved.

In the case of dissolved polyelectrolytes the additional effect of charge groups on the optical activity has to be considered. Kulkarni²³ and Morawetz^{18,23} studied the effect of ionization on the optical activity of weak vinyl-type polymeric acids and compared these values with those of their simple molecular analogues. They concluded that although optical activity studies were suitable for revealing qualitatively the existence of conformational transitions in polymers, the multiplicity of effects possibly involved makes a detailed interpretation very difficult.¹⁸ It was felt, however, that the optical activity of the polymers could not be correlated with the existence of helical regions within the chains.

(b) Limitations of previous studies

Although optical activities of polymers have been found to be greatly different from those of their monomeric analogues, many of the discussions referred to above have been based on very limited experimental data such as measurements of optical rotation at the Na_D

line only. Such data can only indicate structural differences in solution without offering evidence of the source of the optical activity and it is the source of the activity which might be correlated with structure. For this purpose measurements of activity should be extended over a wide wave-length range to the regions in which Cotton effects are involved. Circular dichroism spectra would give more direct information on the magnitude of the activity arising from the various separate sources.

The main aim in the present work was to detect any structural differences of isotactic and atactic polystyrene sulphonate ions in solution. The available instrumentation, however, did not allow measurements to be extended to the Cotton effect regions so that the results obtained cannot be more than tentatively interpreted.

(c) Optical rotatory dispersion of quinine salts of atactic and isotactic polystyrene sulphonic acid

(1) Related previous work

Schulz and co-workers^{24,29-31} recently studied polyelectrolytes which were obtained by reaction of the functional groups of optically inactive polymers with low molecular weight optically active compounds. Salts of the active base, quinine, with inactive strong and weak polyacids were prepared^{24,29} as well as the salts of the inactive polybases, poly-2-vinyl pyridine and poly-4-vinyl pyridine, with various low molecular weight d- and l- acids.³⁰ In one instance measurements over a wave-length range (rather than at the Na_D line only) were reported. In this series of experiments inactive atactic and isotactic poly-2-

vinyl pyridine were neutralized with d-tartaric acid in aqueous solutions. Both polysalts enhanced the molar rotation of d-tartaric acid over the wave-length range 593-365 m μ but at the same time the corresponding salt of the monomer, 2-vinyl pyridine, showed an even greater enhancement. It appears difficult, therefore, to interpret the role that the two types of polymer chain play in enhancing the rotation.

(2) Optical rotatory dispersion of the quinine salts of polystyrene sulphonic acid

In the present work the quinine salts of atactic and isotactic polystyrene sulphonic acids were prepared in both methanol and dimethyl formamide solutions. Figure (3-2.1) shows that the specific rotations, $[\alpha]_{\lambda}$ of both salts form plain rotatory dispersion curves over the visible region. The activities are considerably higher than that of the parent base and the stereoregular salt produces the greater enhancement. It is possible, therefore, that the difference in the optical activity of the salts (and probably the magnitude of the optical rotatory power) is associated with conformational differences between the atactic and isotactic polyanions in solution. The molar rotations at 589 m μ are listed in table (3-2.1) and, where possible, are compared with other results.^{24,31}

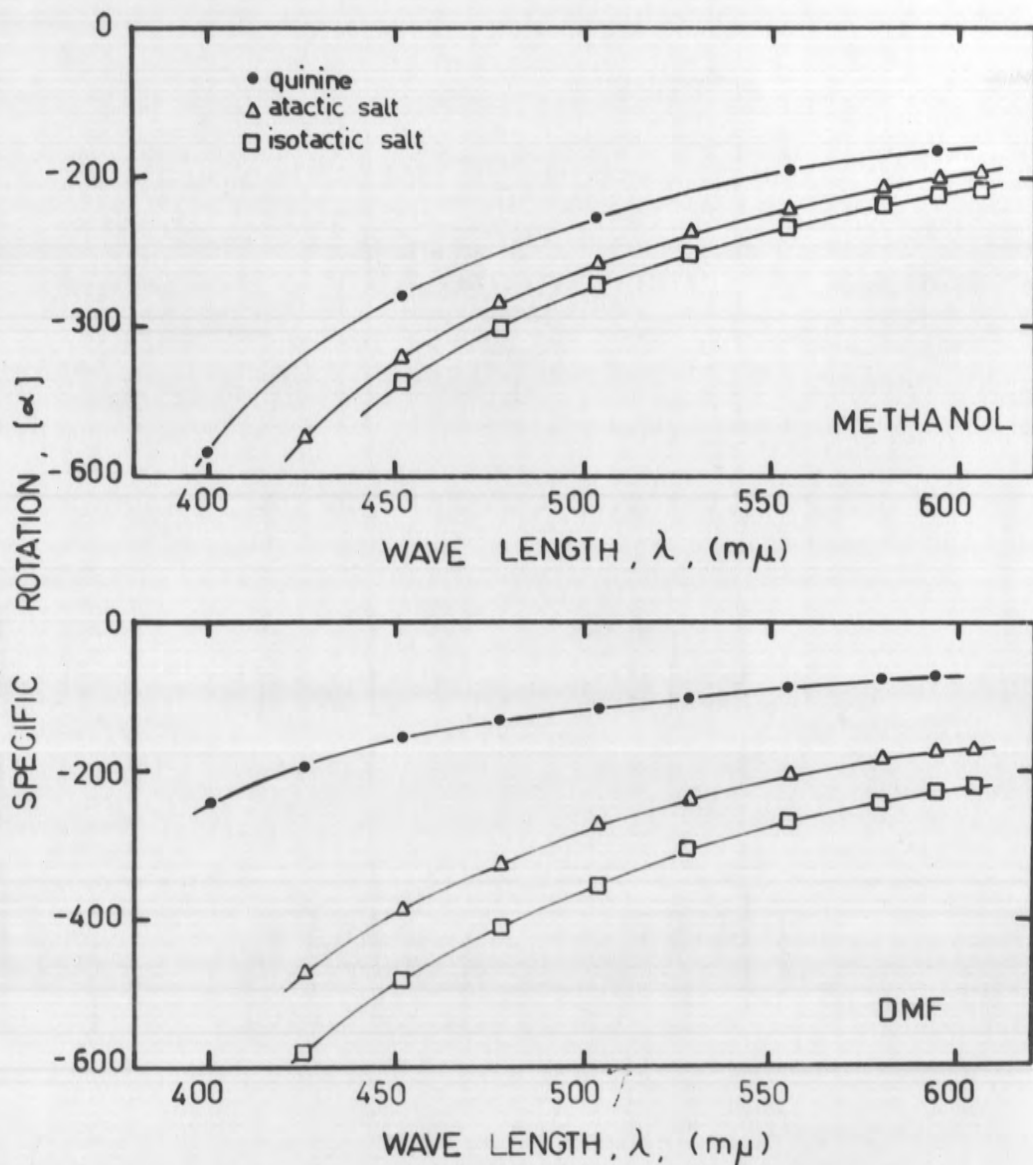


Figure 3-2.1. Optical rotatory dispersion curves for quinine salts of atactic (S103-H) and isotactic (F3-H) polystyrene sulphonic acid.

Upper curve: methanol as solvent; $c = 0.0455$ moles quinine litre $^{-1}$.

Lower curve: N-N dimethyl formamide as solvent; $c = 0.433$ moles quinine litre $^{-1}$.

Temperature, 30°C.

Table (3-2.1)

Comparative values of molar rotations for quinine salts of poly-
styrene sulphonic acid

Solvent	Substance	This work $[M]_D^{30}$	Schulz ¹¹ $[M]_D^{25}$
D.M.F.	quinine	-254	-255.5
	atactic salt	-575	-562.8
	isotactic salt	-758	-
		(0.0433 molar in quinine, Q)	(0.05 molar Q)
methanol	quinine	-540	-538.8
	atactic salt	-662	-666
	isotactic salt	-743	-
		(0.0455 molar Q)	(0.05 molar Q)

(3) Drude plots of the quinine salts

The portions of an isolated rotatory dispersion curve well removed from the region corresponding to the absorption responsible for the activity are closely approximated by the one-term Drude equation,

$$[\alpha]_{\lambda} = A_0 / (\lambda^2 - \lambda_0^2) \quad (3-2.1)$$

This gives the specific rotation, $[\alpha]_{\lambda}$, as a function of the wavelength and approximates the rotatory dispersion curve to a hyperbola

with the asymptote at a wavelength, λ_0 , which corresponds to the anomaly in the rotatory dispersion curve. λ_0 is then the wavelength of the electronic transition responsible for the activity. In general the measured activity is the sum of all such contributions so that experimentally the appropriate Drude equation is³³

$$[\alpha]_{\lambda} = \sum_1 A_1 / [\lambda^2 - (\lambda_0)_1^2], \quad (3-2.2)$$

and this will apply only outside all active absorption regions.

However if experimental data can be fitted to a one-term Drude equation this would suggest that one contribution to the activity is dominant. The wave-length of the electronic transition concerned, λ_0 , will be given from the slope of $[\alpha]_{\lambda} \lambda^2$ plotted against $[\alpha]_{\lambda}$ since rearrangement of equation (3-2.1) gives

$$[\alpha]_{\lambda} \lambda^2 = A_0 + \lambda_0^2 [\alpha] \quad (3-2.3)$$

One-term Drude plots of the rotatory dispersions of quinine and the quinine salts of isotactic and atactic polystyrene sulphonic acids were found to be strictly linear over the spectral range of measurement (figure 3-2.2). This suggests that one transition is dominant for the observed activity in each instance.

This contrasts with the previously mentioned results³⁰ for d-tartrates of poly-2-vinyl pyridines whose single term Drude plots were not linear although in this case the data covered the region approaching the rotatory dispersion anomaly¹⁷ where the Drude equation might not be expected to apply (figure 3-2.3).

The λ_0 values obtained from the linear Drude plots in the

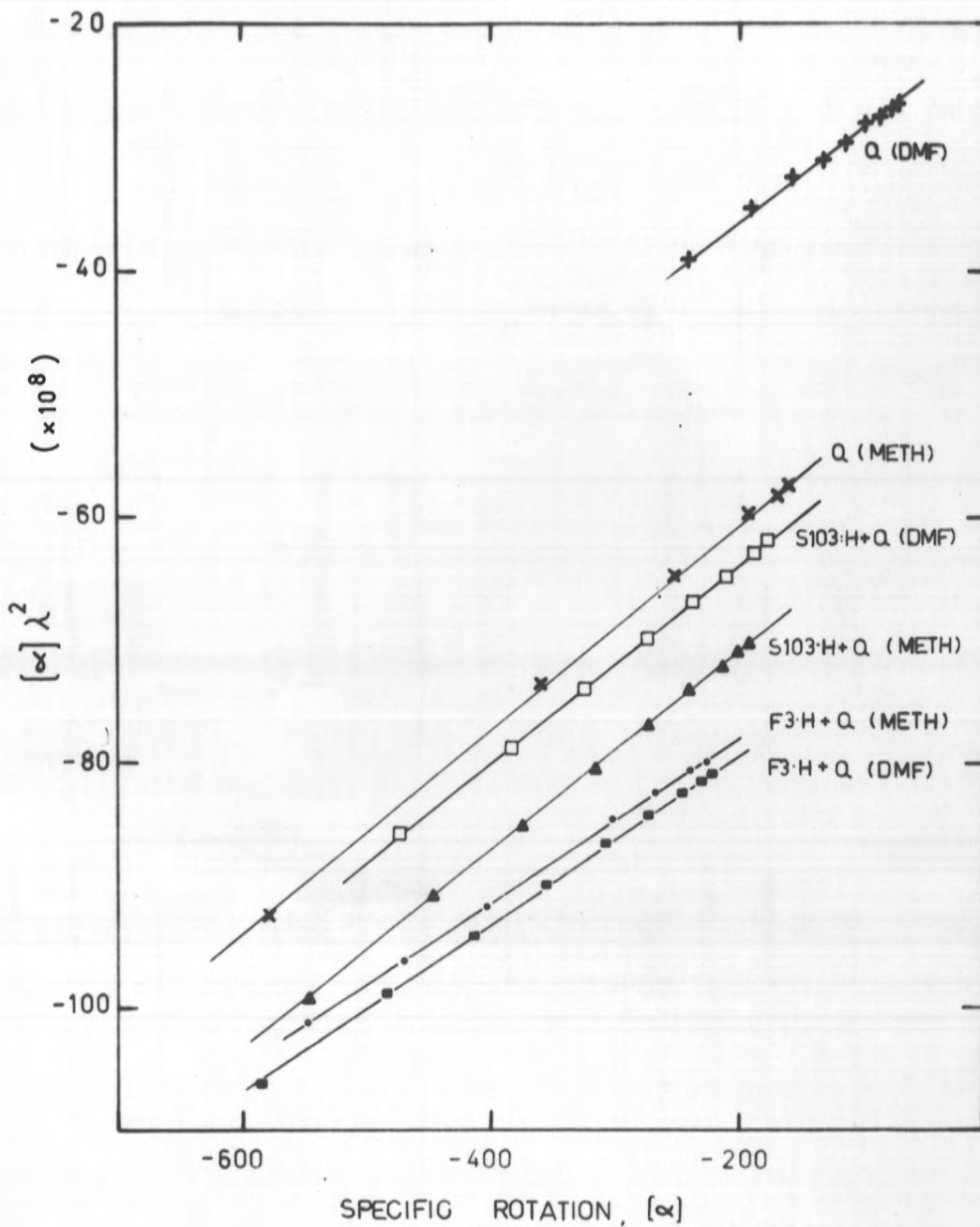


Figure 3-2.2. One-term Drude plots of the rotatory dispersions of quinine, Q, and the quinine salts of isotactic and atactic polystyrene sulphonic acids, F3-H and S103-H, in methanol and dimethyl formamide. Temperature 30°C.

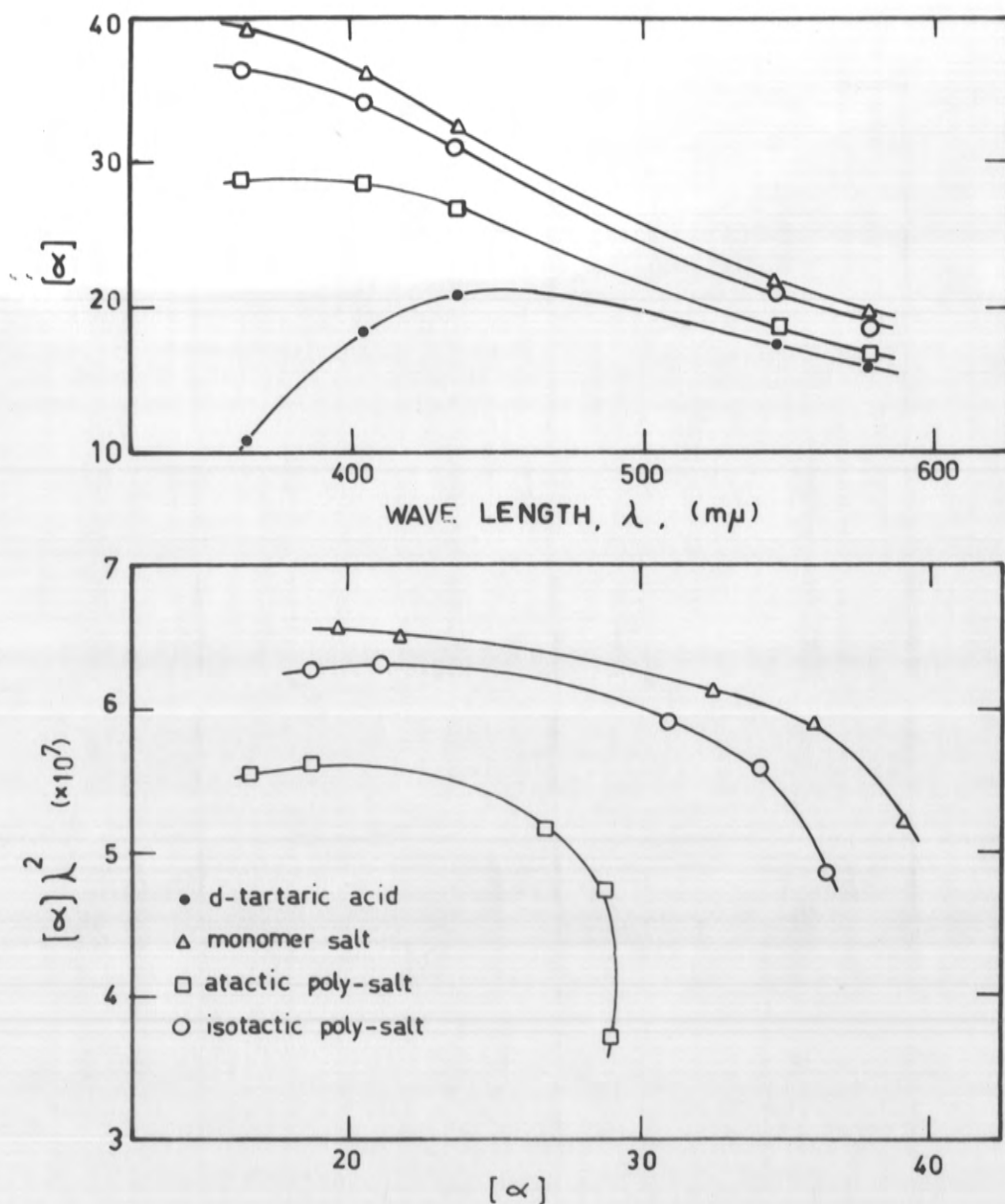


Figure 3-2.3. Optical rotation data from the results of Schulz and Schwaab.³⁰ Water as solvent.

Upper figure: optical rotatory dispersion curves,
 Lower figure: simple Drude plots.

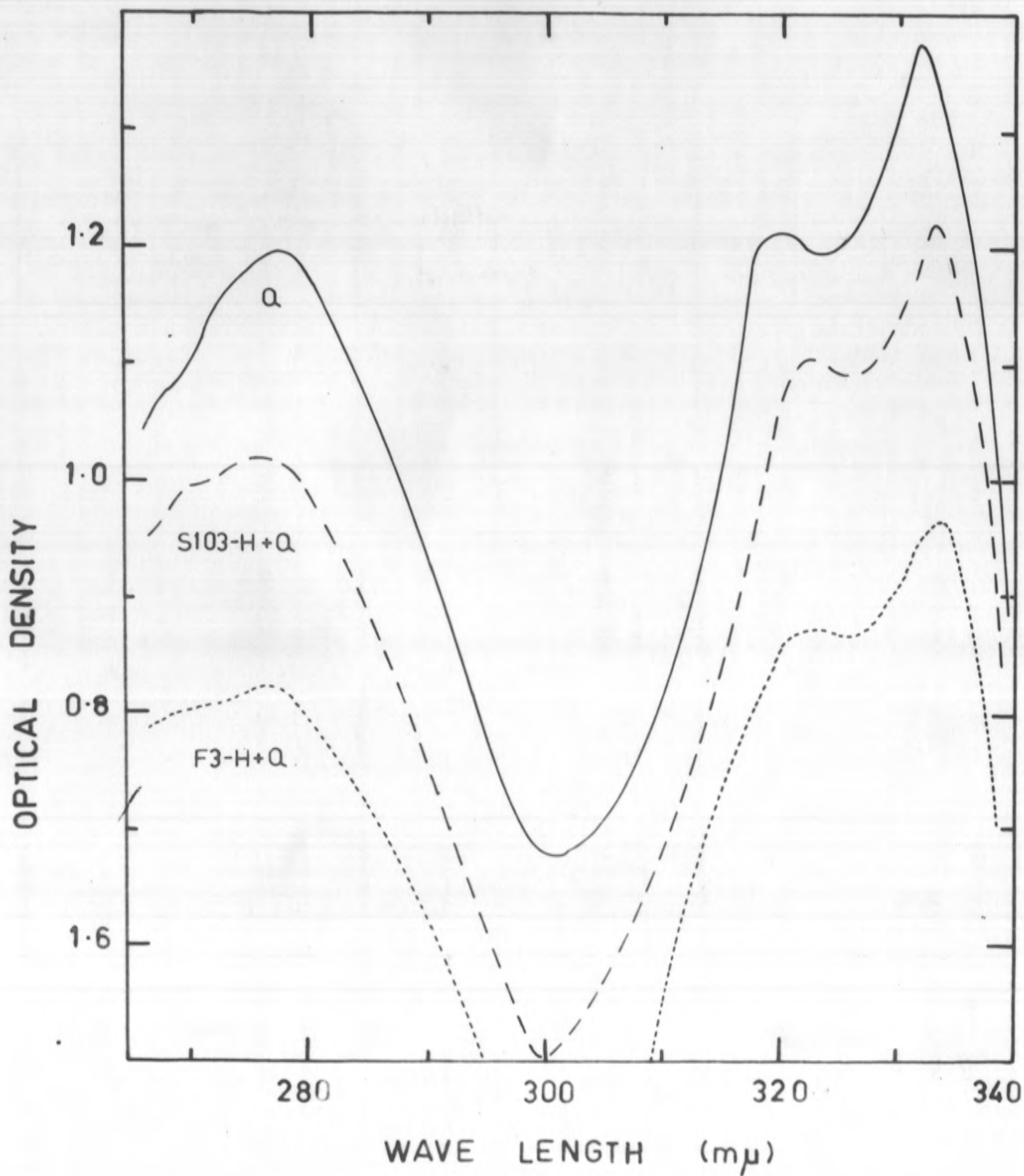


Figure 3-2.4. Ultra-violet spectra of solutions of quinine and the quinine salts of isotactic (F3-H) and atactic (S103-H) polystyrene sulphonate acids. Solvent, dimethyl formamide.

present work are shown in table (3-2.2) together with absorption maxima (figure 3-2.4).

Table (3-2.2)

Substance	Solvent	λ_0 (m μ) (Drude plot)	λ (m μ) (absorption max.)
quinine	methanol	280 (± 4)	279, 322, 333
	DMF	276	277, 320.5, 332
quinine + isotactic acid	methanol	261	270(sh) 280, 325, 334
	DMF	262	270(sh) 276.5, 323, 334
quinine + atactic acid	methanol	284	270(sh) 279.5, 324.5, 333.5
	DMF	284	270(sh) 276, 323, 334
S103-H	methanol	-	256, 262, 268

(sh, shoulder)

(4) Conclusions

The quinine salts of the two types of polysulphonic acids have distinctly different λ_0 values which suggest that the dominant activity might arise from different sources. In the atactic quinine salt $\lambda_0 = 284$ m μ might correspond to the quinine absorption bands at about 279 m μ and the λ_0 value, 276-280 m μ , for quinines. On the other hand the λ_0 value at about 261 m μ for the isotactic quinine salt is

somewhat lower than the absorption bands of quinine both in the free state and in the form of the salts. It is difficult to decide on the assignment of the $\lambda_0 = 261 \text{ m}\mu$ transition to a quinine absorption or to the $262 \text{ m}\mu$ unpolarised absorption observed in the free polymer. If it were associated with the polymer as an additional source of activity over that of the atactic salt, it is difficult to appreciate that the $284 \text{ m}\mu$ activity (as in the atactic case) would not contribute to such an extent as to show evidence of non-linearity in the Drude plot.

Enhancement of the quinine activity by the atactic polyacid is not unexpected since when ions associate in some preferred mutual orientation there can be mixing between transitions of the same symmetry so that some bands can be enhanced in activity with a compensating decrease in others.^{34a} In the region studied it seems that the quinine bands are enhanced at least in the atactic polysalt. The ion association is likely to be qualitatively of the same type in the two types of polysalts and the greater enhancement in the isotactic case could be due to the combined effects of the quinine enhancement as well as a contribution from overall helicity.

It is interesting to note that the reverse effect to that speculated above for the isotactic polysalt has been shown from measurements of optical activity on the complex formed when the cationic dye, acridine orange, was adsorbed on optically active l-glutamic acid.^{34b,c} When the polypeptide had the α -helix conformation Cotton effects were included at the visible absorption bands of the inactive dye and this was ascribed to the dye molecules being oriented in helical arrays due to preferred steric interactions. When the polypeptide had the

random coil form no Cotton effects were evident in the dye absorptions.

3-3 Dye Binding Studies

(a) Introduction

In recent years considerable research has been conducted on the binding of basic dyes to polyanions particularly in the case of nucleic acids, polynucleotides and to a lesser extent to other polyelectrolytes. It has been found that this dye binding process is often accompanied by characteristic shifts of the dye absorption maximum which appear to be closely related to those which occur when dye molecules aggregate in a concentrated solution. These shifts which are generally considered to be dependent on the fraction of dye cations on neighbouring sites,^{35,36} vary not only with the dye to polymer ratio but also with the nature of the macromolecular binding sites. As research has progressed it has become increasingly obvious that any explanation of these spectral shifts was unlikely to be found in a simple mechanism involving the reaction of a dye cation with a single anionic binding site but rather in a complex process³⁷ involving many simultaneous interactions and conformational relations. Any mechanism must take into account interactions between the dye and binding site, interactions between neighbouring dye molecules bound on the polymeric matrix and changing interactions between neighbouring binding sites brought about by the presence of the bound dye.

(b) Interactions of cationic dyes with polyanions

As the primary aim of this present work was to detect structural differences in solution between atactic and isotactic

polystyrene sulphonate ions the main features of the binding of dyes to related flexible polyelectrolytes will be discussed without detailed reference to the complexity of effects that can arise. For this reason the following remarks chiefly apply to the binding of dyes such as acridine orange and proflavine to polyelectrolytes of high charge density such as heparin, polyphosphates and polyvinylsulphonates.

The study of cationic dye binding to this type of polyanion^{36,37,39,45,46} has mainly involved observations of changes of the visible dye spectrum which occurred when the polyelectrolyte was gradually added to dye solution of a concentration at which only monomers exist in solution. In general it has been found that an increase in the concentration of flexible polyelectrolytes of high charge density has resulted in a continuous hypsochromic shift of the dye maximum. As a β -band (due to dye dimers) and possibly a γ -band (due to higher stacks of dye cations on the polyanion) developed a simultaneous hypochromic effect was observed. This spectral shift continued until a polymer to dye ratio of approximately 1:1 had been reached. Further addition of polymer resulted in spectral changes in the opposite direction with the gradual development of an α -band, the maximum peak shift of which was produced with a widely varying ratio of excess polymer sites to dye molecules. Bradley and Wolf³⁶ explained this bathochromic shift in terms of the aggregation theory by assuming that polyanions with a high charge density (e.g. heparin and polyphosphates) required a very high excess of binding sites to unstack the closely packed sequences of dye molecules on the

polyion and so develop the α -band which is characteristic of dye cations bound at widely separated distances on the polyion. Weill and Calvin⁴⁶ have reported that the large hypochromicity and large hypsochromic shift with both acridine orange and proflavine in the presence of polyphosphates still persisted at high polymer to dye ratios presumably because of strong coupling between the dye molecules.

More recently Bean et al.³⁷ have investigated the stoichiometry of the reaction of a complex thiocarbocyanine dye with a wide variety of polyanions. They have suggested that although dye-dye interactions occurred, an important influence on the development of the α - and β - bands may in fact have been the conformation of the dye to the site and the polymeric matrix. They pointed out that previous hypotheses have all assumed that the function of the polyanion was the provision of a passive matrix for the anionic sites, the spacing of which controlled the distance and therefore interaction, between bound cationic dyes.

It is of interest to note that during a study of the nature and stability of the metachromatic compound formed when the equivalence ratio of polymer to dye was close to unity, Pal and Schubert^{47,48} found that the equivalence ratio of the heparin-dye complex was always in excess of unity.⁴⁵ They pointed out that as heparin had a very high charge density (one carboxylate ion, one ester sulphate ion and one amido-sulphate ion per repeating unit³⁸) the average charge separation was only 2.9Å. As the calculated distance between dye molecules in dimers was 3-4Å they suggested that the use of all charge sites as binding sites would lead to gross overcrowding of dye

molecules. As a result the number of sites potentially available for binding was concluded to be greater than the number that could be effectively used. Calculations⁴⁸ on the basis of the average distance between binding sites of 4 Å gave a higher effective equivalent weight for heparin which then led to an equivalence ratio of 1.0 for the formation of the metachromatic complex.

(c) Binding of proflavine to poly-styrene sulphonic acids

(1) Proflavine (3,6 diamino-acridine)

In the low concentration range (less than 4×10^{-5} molar) in which Beer's Law is obeyed,⁴⁵ proflavine shows a single absorption peak at 443 mμ with a molar extinction coefficient of 4.1×10^4 for aqueous solutions. As the concentration is increased the extinction coefficient becomes smaller presumably due to the formation of dye aggregates.⁴¹ Contrary to the findings with many other dyes the increased hypochromicity of the solution at low pH is not accompanied⁴⁵ by the gradual appearance of a shoulder on the low wavelength side which finally develops into a peak at high concentrations leaving a shoulder in place of the original peak. Morthland, de Bruyn and Smith⁴² have shown however that at a pH of 10 proflavine does exhibit two peaks. In the dye-binding studies described below the proflavine concentration was always kept within the range in which Beer's Law holds. By working in the visible region observations of changes in the proflavine spectrum were not complicated by the necessity to allow for contributions from polystyrene sulphonic acid which absorbs to a negligible extent in this wave-length range.

(2) Effect of the addition of poly-styrene sulphonic acids to proflavine in aqueous solution

On the addition of aqueous poly-sulphonic acid solutions to proflavine there was a large hypochromic effect in the visible region together with a hypsochromic shift up to the stage at which the polymer to dye ratio was slightly in excess of unity. At this stage the single absorption peak of the dye remained but had shifted from 443 m μ to 434 m μ which, compared with the previously described dye-binding studies, corresponded to the development of a γ -band presumably due to dye-dye interaction between the closely packed dye cations on the anionic sites of the polyanion. (See Fig. 3-3.1a). A similar blue shift of the proflavine maximum was observed with both atactic and isotactic poly-acids. The occurrence of the maximum hypsochromic shift at a polymer to dye equivalence ratio of approximately 1.1:1 is probably due to the same reason that an abnormally high equivalence ratio was necessary for the formation of the corresponding heparin-proflavine complex.¹⁴ The degree of sulphonation of all polystyrene samples (see Table 4-8.1) was in the range of 1.10 to 1.14 so that proflavine binding to two sulphonate groups in one benzene ring may lead to overcrowding especially as one sulphonate group is always in the para-position.¹

As the ratio of polyanion sites to dye cations became increasingly larger there was a gradual red shift of the dye maximum with a simultaneous slowly decreasing hypochromic effect until with a very high excess of polyelectrolyte a maximum bathochromic shift to 452 m μ

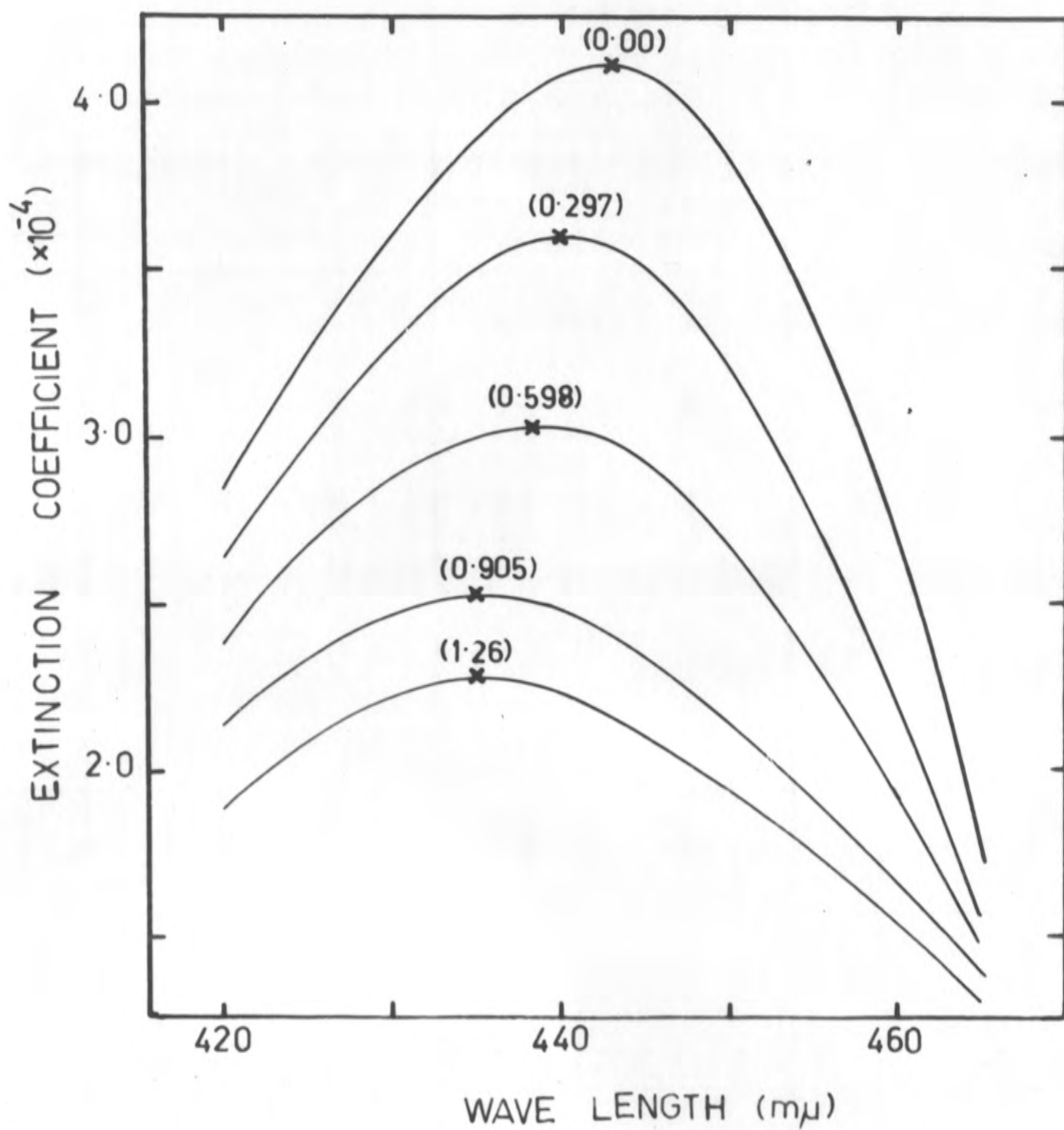


Figure 3-31a. Effect of an increasing polystyrene sulphonic acid, S108-H, to proflavine ratio on the spectrum of the dye. Salt-free aqueous solvents at 30°C. Low polymer to dye ratio as indicated on the spectrum.

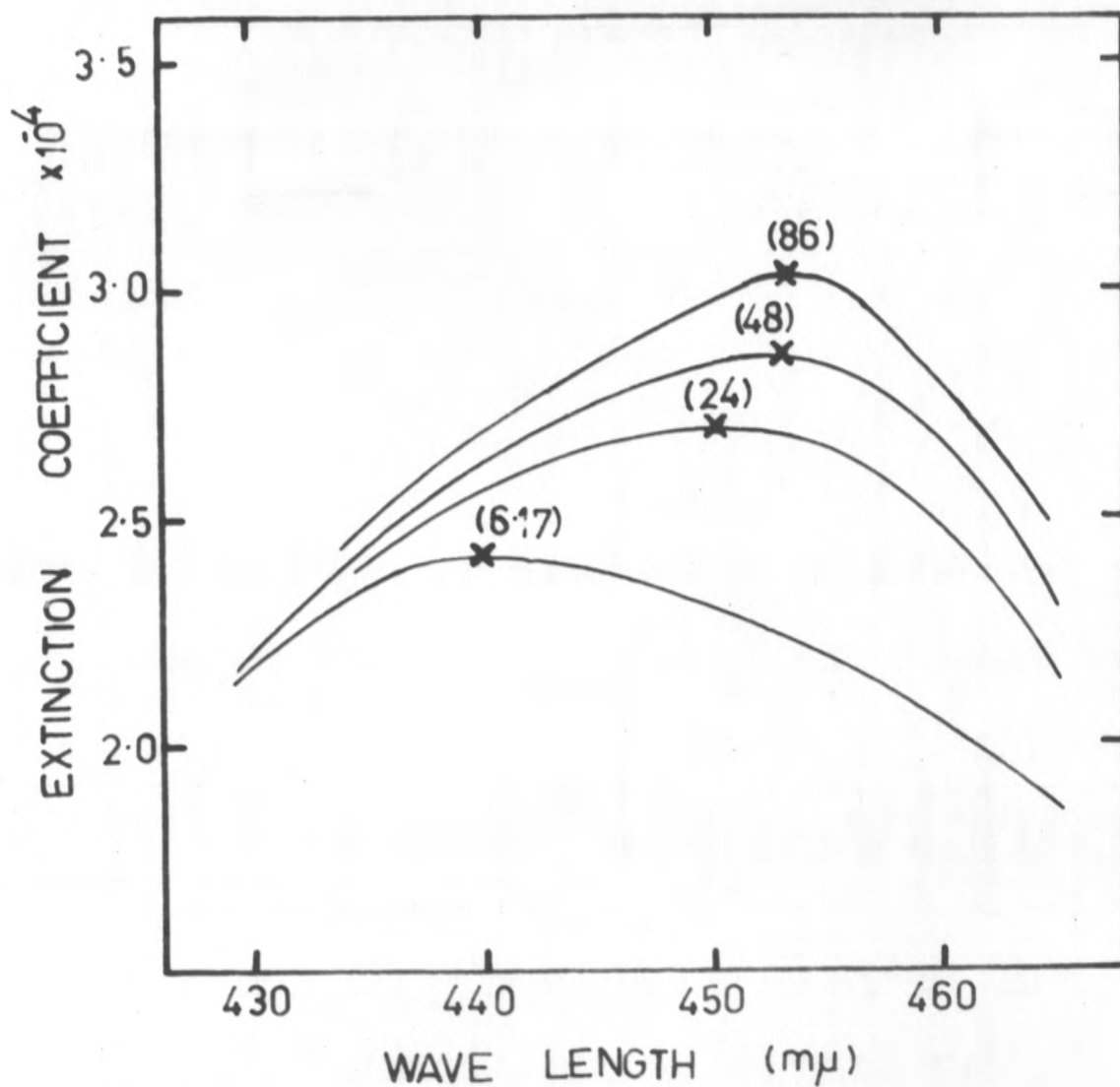


Figure 3-3.1b. Effect on the spectrum of proflavine of a high polystyrene sulphonic acid, S108-H, to dye ratio. Salt-free aqueous solutions at 30°C. The polymer to dye ratio is indicated on the spectrum.

had occurred as shown in figure (3-3.1b). This change corresponded to the tendency of the dye absorption spectrum to return to the α -band corresponding to the monomeric dye as the dye molecules, randomly spaced on binding sites, became so widely separated that dye-dye interactions tended to disappear.

Although the extent of the bathochromic shift of the proflavine maximum was identical on the addition of both types of polyacids, the extinction coefficient measured at 452 m μ was significantly lower for the two samples of isotactic polystyrene sulphonic acids ($\epsilon_{452} = 2.85 - 2.9 \times 10^4$) than for the corresponding atactic compounds ($\epsilon_{452} = 3.1 - 3.15 \times 10^4$). The variation of the extinction coefficient of proflavine at 452 m μ with polymer to dye ratio is shown in figures (3-3.2) and (3-3.3).

The greater interaction in the proflavine-polystyrene sulphonic acid system must therefore have arisen from conformational differences between the isotactic and atactic polyelectrolytes in solution. Owing to the complexity of the interaction between cationic dyes and polyanions the reason for different effect in the two cases cannot be deduced with any certainty. It is noticeable that the minimum extinction coefficient which corresponded to the stage at which the maximum hypsochromic shift to 434 m μ occurred, did not appear to differ significantly between the two different types of polysulphonic acids.

(3) Effect of a low salt concentration on the binding of proflavine to polystyrene sulphonic acids

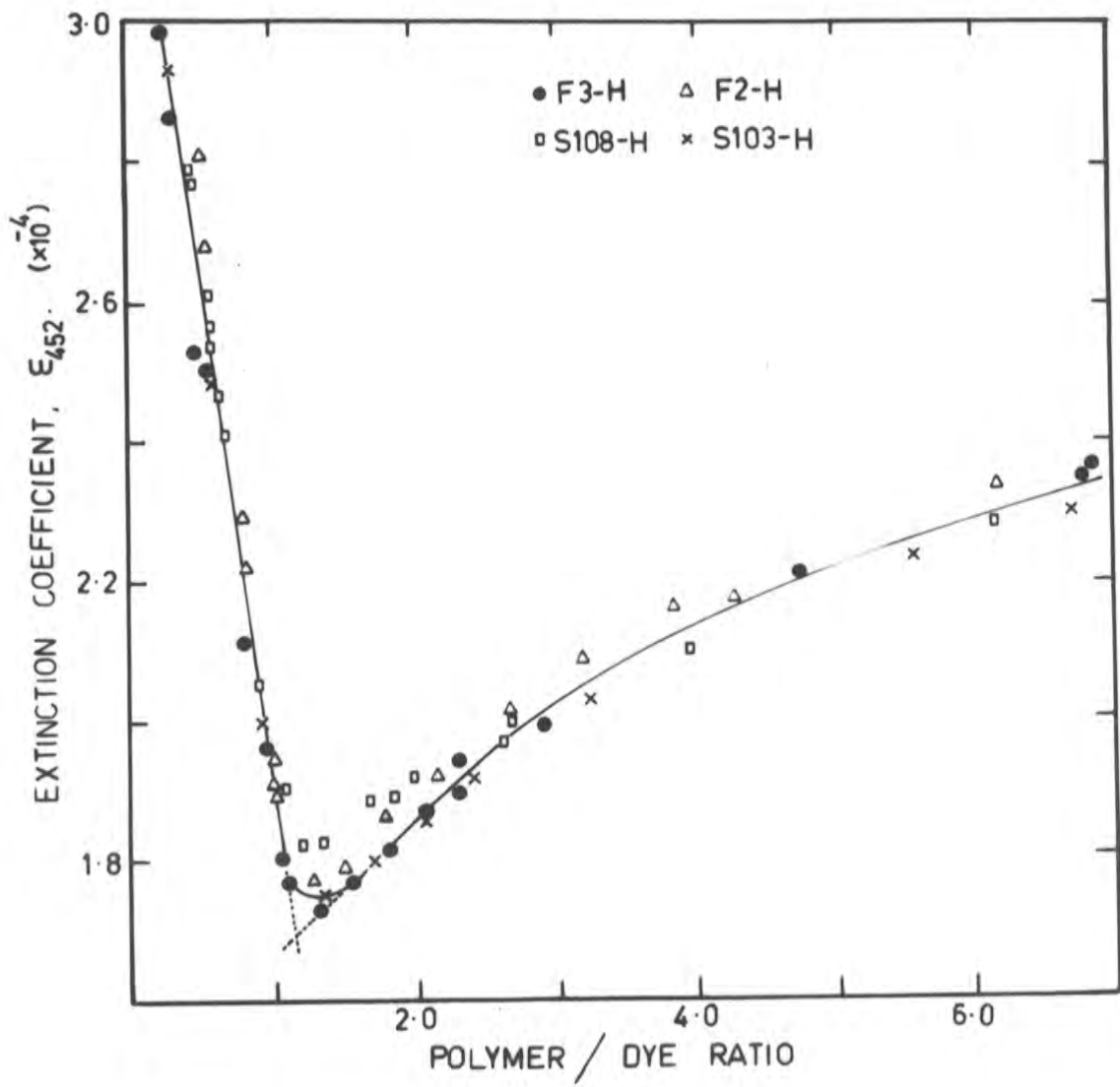


Figure 3-3.2. Variation of the extinction coefficient of proflavine at 452 mμ on the addition of polystyrene sulphonic acid. Low polymer to dye ration. Salt-free solutions.

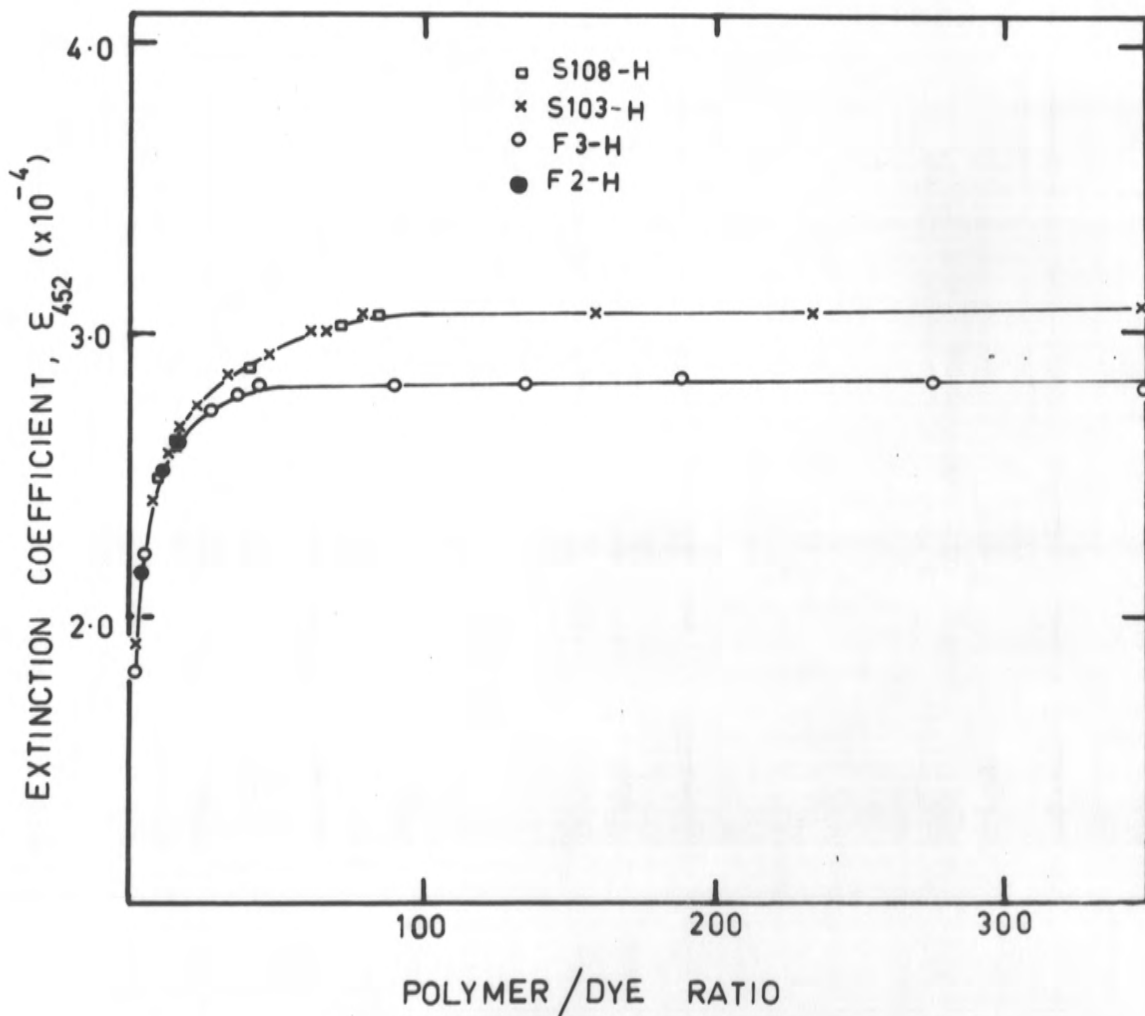


Figure 3-3.3. Variation of the extinction coefficient of proflavine at 452 m μ on the addition of a considerable excess of polystyrene sulphonic acid. Salt-free solutions.

Similar experiments to those described above were carried out in 0.0034M sodium chloride solution and produced the same initial hypsochromic and final bathochromic shifts as well as similar changes in the extinction coefficient of proflavine as illustrated in figure (3-3.4). The limiting values of the extinction coefficient of proflavine however, were raised above the corresponding values in the absence of salt by roughly the same extent to 3.2×10^4 and 3.45×10^4 in the presence of isotactic and atactic polystyrene sulphonic acids respectively. Presumably the competition of sodium ions and proflavine ions for the binding sites on the polyanion produced these changes by releasing more free dye into solution leaving almost unchanged the effects due to conformational differences of the two types of polysulphonic acids.

(4) Effect of temperature on the dye-polyanion complex at a high polyacid to dye ratio

As an increase in temperature has been found to bring about conformational changes in solutions of some ordered polyelectrolytes, the temperature-absorbancy profiles of the dye-polymer complex were examined. Figure (3-3.5) shows that the optical density (corrected for volume change on heating) of these dye-complexes with atactic polystyrene sulphonic acids changed very little over the temperature range investigated. In the presence of isotactic acids, however, no initial change was evident but at temperatures between 45°C and 55°C there was a sudden decrease in hypochromicity corresponding to an 8-10% increase in the initial optical density. This raised the

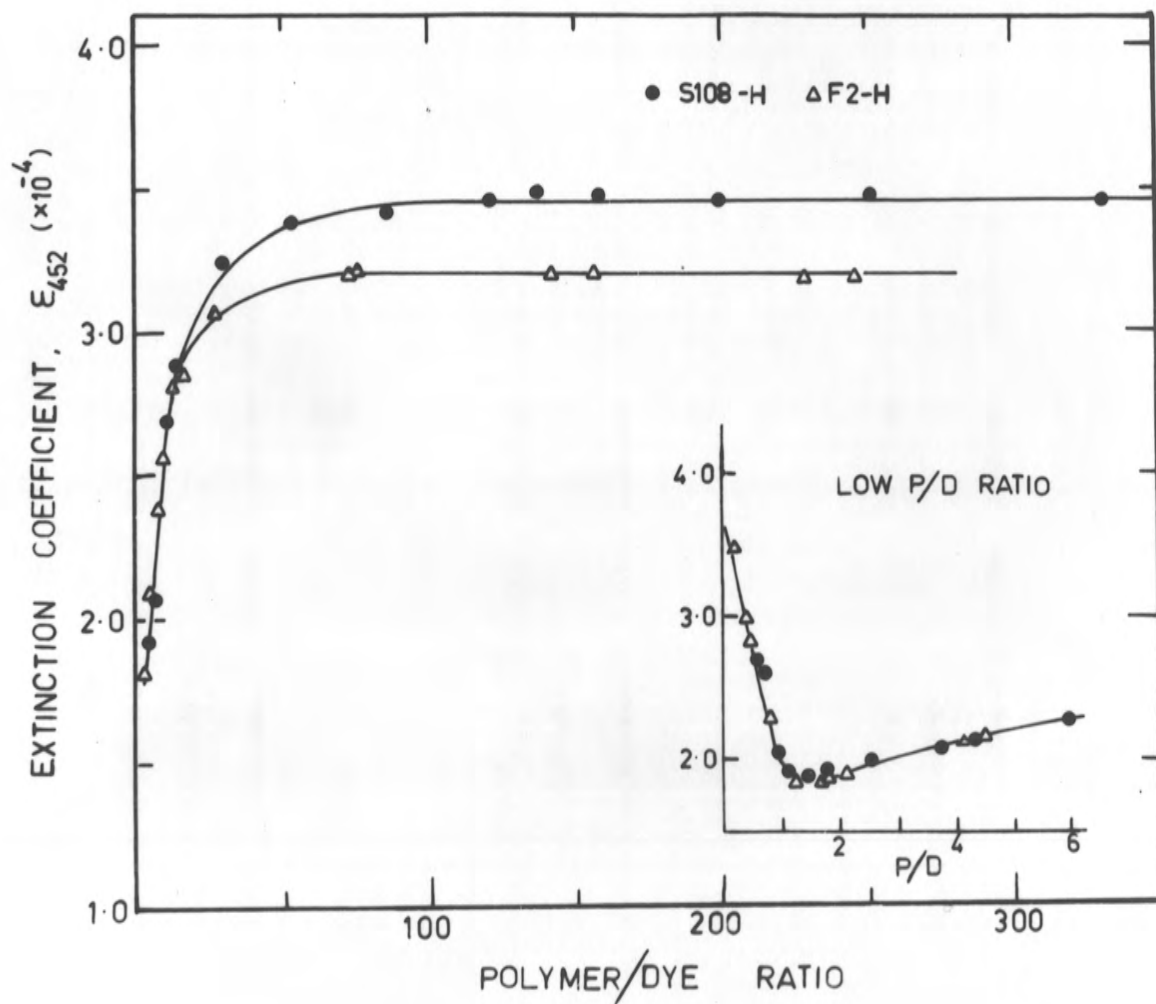


Figure 3-3.4. Variation of the extinction coefficient of proflavine at 452 m μ on the addition of an increasing concentration of polystyrene sulphonic acid. 0.0034M sodium chloride solutions.

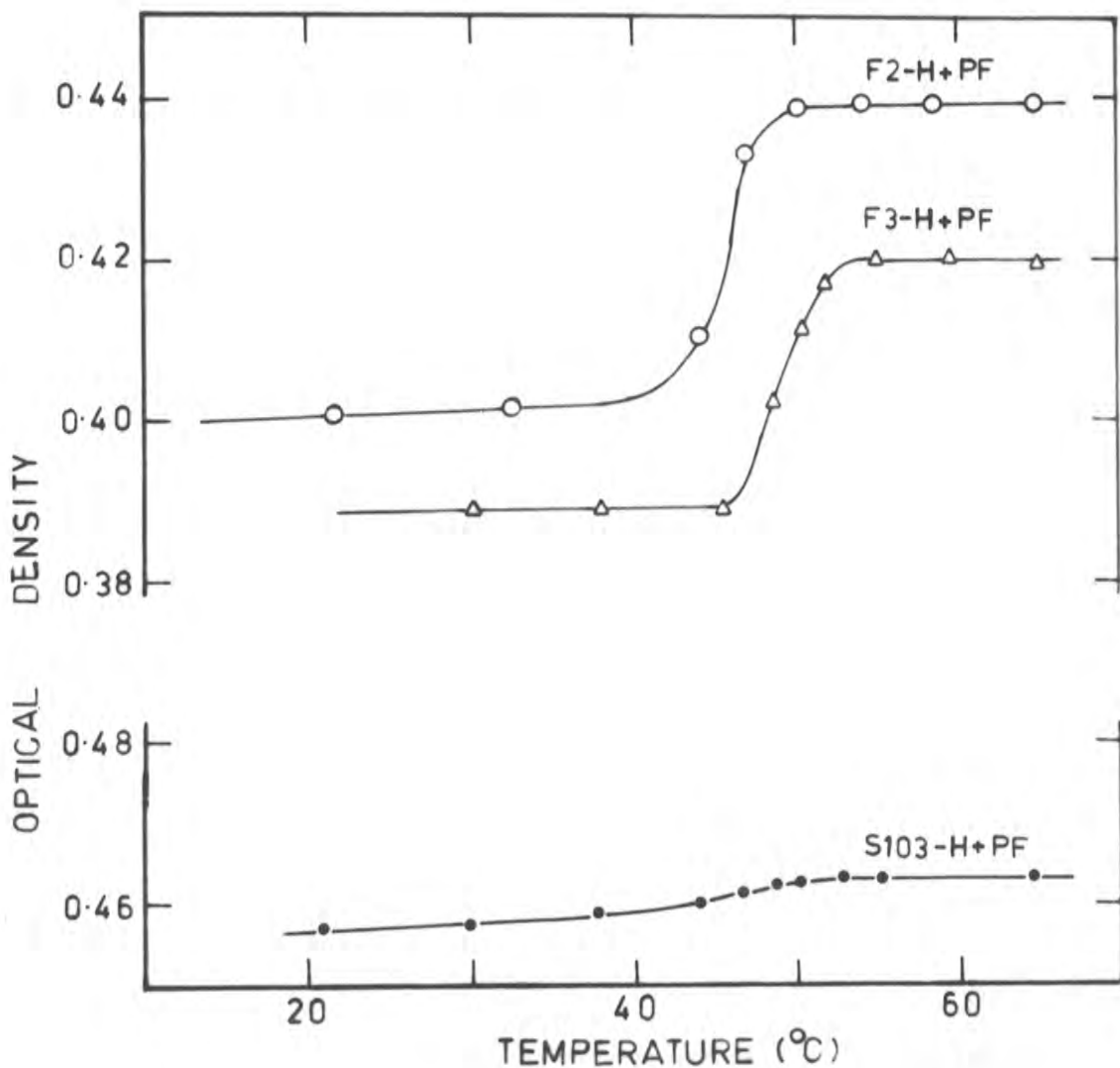


Figure 3-3.5. Temperature dependence of the extinction coefficient of proflavine at 452 m μ in the presence of a high excess of polystyrene sulphonic acid. Salt-free aqueous solutions.

extinction coefficient approximately to that expected for proflavine in the presence of the atactic acid under similar conditions. No change in the nature of the absorption spectrum was observed with the maximum remaining at 452 m μ . This indicates the likelihood that the conformation of the isotactic polystyrene sulphonic acid-proflavine complex changes to that corresponding to the atactic complex when the temperature is in the vicinity of 50°C.

3-4 Temperature Dependence of Optical Density and Reduced Viscosity

Structural changes of macromolecules such as native deoxyribonucleic acid in solution with temperature have been demonstrated by observations of the variation of the extinction coefficient and the reduced viscosity of solutions with an increase in temperature. Although changes of a similar magnitude were not anticipated, the temperature dependence of these properties was investigated for solutions of atactic and isotactic polystyrene sulphonic acid with the aim of detecting any possible conformational differences between the two types of polyelectrolytes.

(a) Temperature dependence of the optical density

No significant changes in the extinction coefficient of the two types of polystyrene sulphonic acid were observed as the aqueous solutions were heated from room temperature to above 80°C.

(b) Temperature dependence of reduced viscosity

In one of the few reports⁴⁹ in literature of this study Mock and Marshall⁵⁰ have shown that the reduced viscosity of aqueous solutions (including those containing small amounts of simple

electrolyte) of a sulphonated 1:1 vinyl toluene-styrene copolymer was a gradually decreasing function with temperature. Similar results were obtained by Ise⁵¹ with aqueous solutions of a weak polyelectrolyte prepared by partially acetalizing poly-vinyl alcohol with glyoxylic acid. On the other hand Eisenberg and Woodside⁵² found some indication that the reduced viscosity of potassium poly-vinyl sulphonate in a suitable concentration of simple electrolyte as theta-solvent appeared to show a slight increase in unperturbed dimensions with a rise in temperature.

Attempts have been made to explain these apparently contradictory results. As a rise in temperature decreases the dielectric constant of water, the forces of repulsion between charge sites on the macroion become greater and the polyion expands. An increase in reduced viscosity with temperature would therefore be expected if intra-polyion interaction alone determined the extension of the polyion. Ise⁵¹ pointed out, however, that the effect of simultaneous increases of inter-polyion repulsion on the configuration of the polyion tends to lead to a decrease in extension and therefore to a lower reduced viscosity as the temperature rises.

In this work the effect of minute quantities of ionic impurity in water on the reduced viscosity⁵³ (see attached paper) was minimized by using aqueous polystyrene sulphonic acid solutions at concentrations which were considerably higher than those in the range expected to produce maxima in reduced viscosity-concentration plots. As shown in figure (3-4.1) the reduced viscosity of aqueous solutions of both isotactic and atactic polyacids at first showed a similar

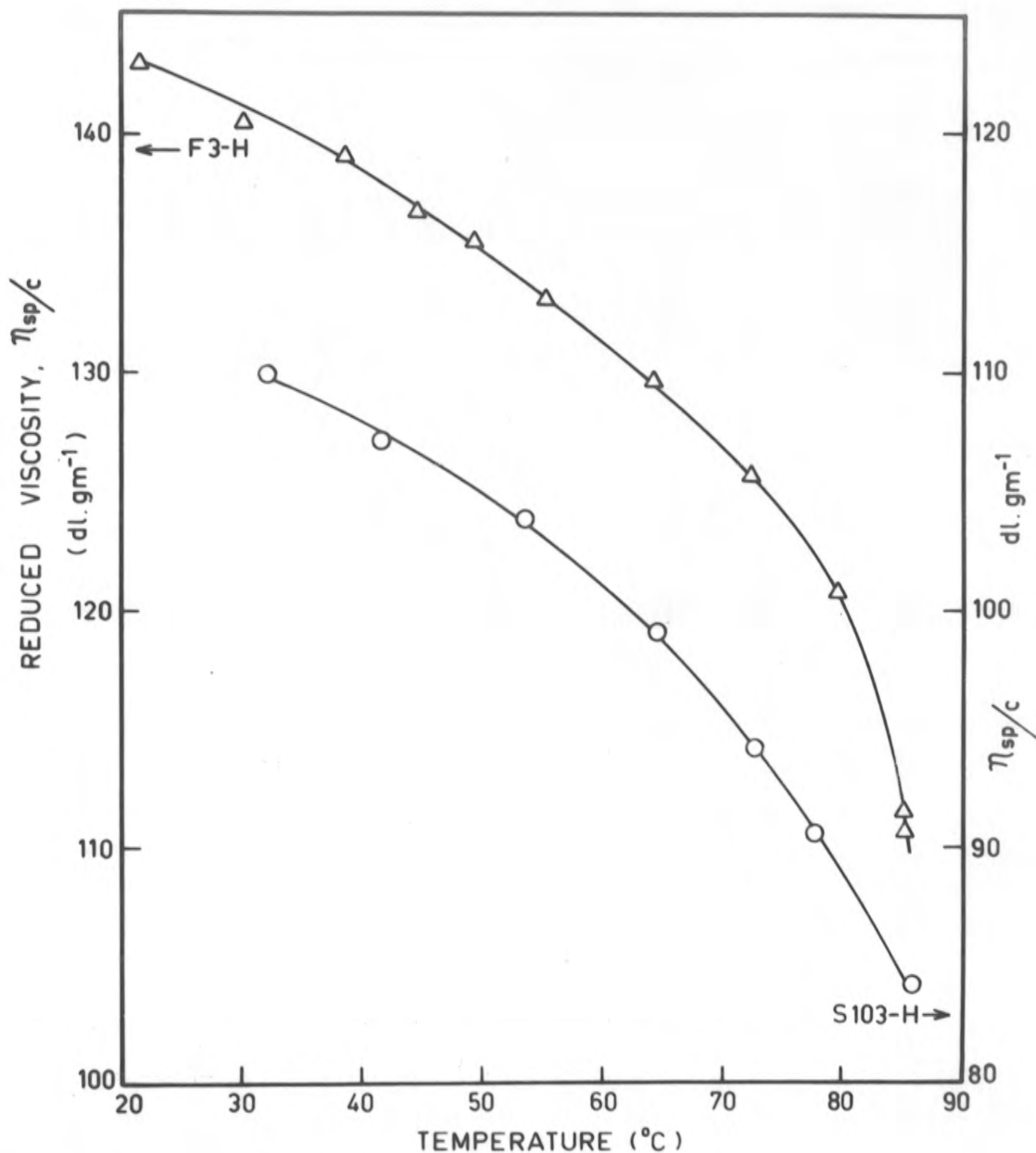


Figure 3-4.1. Temperature dependence of the reduced viscosity of salt-free aqueous polystyrene sulphonate solution.

$$c_{F3-H} = 6.29 \times 10^{-2} \text{ gm.dl.}^{-1}$$

$$c_{S103-H} = 5.18 \times 10^{-2} \text{ gm.dl.}^{-1}$$

gradual decrease with temperature at constant concentration to that reported above.^{50,51} At temperatures approaching 80°C, however, the greater rate of change in the case of isotactic polystyrene sulphonic acid solutions indicated the possibility that some structural differences originally existed between the two types of poly-acid in solution. In the presence of a very small amount of simple electrolyte the reduced viscosity of the isotactic polyacid, which was lower in magnitude as expected, changed less rapidly with temperature but once again the solution showed a similar rapid change in the same high temperature range.

3-5 Electrical Conductance and Transference Studies of Ion Binding

(a) Introduction

Many of the properties of linear polyelectrolyte solutions which are anomalous when compared with those of simple electrolytes can be explained in terms⁵⁴ of non-specific binding of counterions to the polyion although in other cases they may arise from specific complex formation.^{54,55,57,58} It was proposed⁵⁶ that the counterions were localised near the polyions due to the high electrostatic potential which originated in the fixed charges of the polyion. Thus although the potentiometric and conductimetric titration curves of poly-sulphonic acids⁵⁸ with bases were typical of those of completely ionized acids,⁵⁹ a fact which has been confirmed by Raman spectra⁶⁰ and proton magnetic resonance,⁶¹ the apparent degree of ionization was very low in aqueous solutions as shown, for example, by conductance^{8,50,62,63} and pH measurements.^{50,58,63}

The experiments of Wall,⁶⁴ Fuoss,⁶⁵⁻⁶⁷ Strauss⁵⁷ and their co-workers left no doubt that counterions were associated under certain conditions with the polyion kinetic units. On the basis of these conductance, transference and self-diffusion studies they concluded that a fraction, f , of the counterions was able to move freely in solution but the remaining fraction, $(1 - f)$, was regarded as being bound to the polyions and moving with them in the opposite direction in the electric field.

In this work the charge fraction of the polystyrene sulphonate ion in the case of both the atactic and isotactic polyacids and their sodium salts was determined from the combined results of conductance and transference

(b) Basic equations for calculation of charge fraction from conductance and transference measurements in salt free solutions

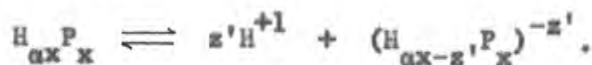
Spiro⁶⁸ has shown that when electrolytes are incompletely dissociated in solution all basic equations used in the determination of transference numbers should be expressed in terms of ion constituents and not in terms of ions. This approach is used in the following derivations.

A polysulphonic acid (or its alkali metal salt) which has a degree of polymerization, x , and degree of sulphonation, α , can be represented by the molecular formula, $H_{\alpha x} P_x$. It follows that the counterion and polyion constituents of the polyelectrolyte are therefore H^+ and P_x^{-z} respectively where $|z| = \alpha x$. If the base molarity of the polyacid (i.e. the number of moles of styrene sulphonic acid

monomeric units in a litre of solution) is m then the electrical molarity, c , of the polyacid is given by

$$c = \alpha m \quad (3.5.1)$$

However due to counterion binding the dissociation of the poly-electrolyte in solution in the absence of simple electrolyte may be considered to give rise to H^+ and $(H_{\alpha x - z'} P_x)^{-z'}$ ions in accordance with the following equation



It follows⁶⁸ that in the above solution

(i) the base molarity and base normality of the polyanion respectively are

$$m_p = m \quad \text{and} \quad c_p = \frac{|z'|}{x} m \quad (3-5.2)$$

and (ii) the base molarity and base normality of the counterions are

$$m_c = c_c = \frac{|z'|}{x} m \quad (3-5.3)$$

Since the specific conductance of the polyelectrolyte in solution, κ_s , will be the sum of the specific conductance of the polyanions and counterions, κ_p and κ_c

$$\text{i.e.} \quad \kappa_s = \kappa_p + \kappa_c$$

it follows that

$$c\Lambda = c_p \lambda_p + c_c \lambda_c \quad (3-5.4)$$

in which Λ is the equivalent conductance of the solution and λ_p and

λ_c are the equivalent ionic conductances of the polysulphonate ion and counterion respectively. Combination of the above equations yields

$$\text{cm}\Lambda = \frac{|z'|}{x} m\lambda_p + \frac{|z'|}{x} m\lambda_c$$

so that

$$\Lambda = \frac{z'}{z} (\lambda_p + \lambda_c)$$

in which

(i) the equivalent conductance of the polyion, λ_p , and the polyion constituent, $\bar{\lambda}_p$, are identical,

(ii) z'/z is usually referred to as the charge fraction, f , of the polyion.

$$\text{i.e.} \quad \Lambda = f (\lambda_p + \lambda_c) \quad (3-5.5)$$

In this derivation it is assumed that the counterions bound to the polyion do not contribute to the conductance. This assumption could be criticised on the grounds that surface conduction⁶⁹ due to the movement of bound ions parallel to the polyion backbone may contribute to the total conductance. The demonstration of the absence of frequency dispersion⁷⁰⁻⁷⁵ during low frequency A.C. and D.C. conductance measurements has shown the above assumption to be correct.

The transference number, T_p , of the polyion in the solution may be defined as the number of equivalents of polyion crossing an imaginary plane in the solution fixed with reference to the solvent when one Faraday of electricity passes through the plane. Since

$$T_p = \frac{\bar{\lambda}_p}{\bar{\lambda}_p + \lambda_c} = \frac{\lambda_p}{\Lambda}$$

it follows that

$$\lambda_p = \Lambda T_p = F u_p \quad (3-5.6)$$

in which u_p is the mobility of the polyanion and F is the faraday.

On combination with equation (3-5.5) it follows that the charge fraction, f , of the polyion can be calculated from

$$f = \frac{\Lambda}{\Lambda T_p + \lambda_c} \quad (3-5.7)$$

using experimental values of Λ and T_p provided that a value can be assigned to the equivalent conductance of the free counterions.

Since no method is known which permits the determination of the mobility of the free counterions in the presence of polyions with their ionic atmospheres the assumption^{64a} has been made that the equivalent conductance of the free counterions, λ_c , is that of the same ion in a solution of a simple 1:1 electrolyte at a concentration corresponding to the value, λ_c^0 , of the free counterions in the poly-electrolyte solution. Thus an expression similar to that derived by other workers^{64,72,76-78} is obtained

$$f = \frac{\Lambda}{\Lambda T_p + \lambda_c^0} \quad (3-5.8)$$

The validity of the above assumption has been questioned but has been justified^{72,77} on the following grounds:-

(1) The mobility of small ions, as shown by measurements of conductance^{79,80} and diffusion coefficients,^{64b} is not changed to any significant extent by considerable increases in macroscopic viscosity brought about by the presence of uncharged polymers in the solution provided that the volume fraction occupied by the polymer segments is small.

(2) Electrophoretic retardation is more likely to affect the polyions^{72,77} with which bound counterions are moving than the more distant free counterions of like charge. The relaxation effect will produce the same fractional decrease in mobility of both polyions and counterions. Evidence for the small effect of electrophoretic retardation of the free counterions is given by the fact that the values of the charge fraction of the polyions in aqueous sodium polyacrylate solutions are in reasonable agreement⁷² when measured by conductance and transport,^{64a} diffusion potential measurements⁸¹ and tracer diffusion techniques.^{64b}

(c) Equivalent conductance of polysulphonic acids and their sodium salts - discussion of published results

Most of the early work with strong polyelectrolytes was carried out using polysalts or poly-quaternary halides which had been prepared by reaction of weak polyacids or weak polybases with strong simple alkalis or alkyl halides respectively. More recently various methods (see section 4-7) have been used to obtain polymeric sulphonic acids and their corresponding poly-salts both of which are believed to dissociate completely into their ions on dissolution in water.^{60,61}

The solution properties of these polysulphonates have been investigated in many ways and have often yielded results which are conflicting even for a given technique as shown by previously reported conductance measurements in table (3-5.1).

For the poly-sulphonic acids of varying degrees of sulphonation the equivalent conductances were generally between 125 and 140 $\text{cm.}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$ in the concentration range 1×10^{-4} to 1×10^{-2} equivalents per litre and showed either no concentration dependence⁶² or a slight increase with concentration.^{8,58} Surprisingly in spite of the hygroscopic nature of these polyacids no reference was made (except by Eisenberg and Ram Mohan⁵⁸) to the extent of hydration of the dried product when the equivalent weight or the degree of sulphonation was stated. The results of Butler and co-workers⁸ are of doubtful significance due to the uncertainty involved in making an allowance, by a method not stated, for the contribution to conductance of the high percentage of sodium polysalt which was present in the polystyrene sulphonic acid sample.

The sodium polysalts showed a concentration dependence which is generally characteristic of strong polyelectrolytes with the equivalent conductance increasing rapidly as the solution became more dilute. The approximate values calculated from a linear plot of $\left(\frac{\sqrt{c}}{\Lambda_0 - \Lambda}\right)$ against \sqrt{c} in one case⁶² were considerably higher than those obtained by other workers. In no paper were transference measurements of polystyrene sulphonic acid or its sodium salt reported. Attempts were made with the polyacid to calculate approximate values of the

Table (3-5.1)

Equivalent conductance of polysulphonic acids - previously reported values

Ref.	Poly-electrolyte	Preparation	Extent of sulphonation	Λ (approx) ($\text{cm}^2 \text{ohm}^{-1} \text{eq}^{-1}$)	c (eq.litre^{-1})
62	HPVT-SS	Roth method (see 4.7)	EW = 210.6	135	$4-8 \times 10^{-4}$
	Na PSS	from aqueous monomer	EW = 206.2	81-76	$2.5-40 \times 10^{-3}$
8	HPSS	from NaPSS by ion exchange or ppn. with HCl	not stated - 33% NaPSS present	151-155	$0.4-4 \times 10^{-4}$
	Na PSS	neutralization of HPSS above	EW taken to be 206	53-48	$0.4-5 \times 10^{-4}$
58	HPVS	from monomeric acid	EW = 120 (2/3 mol- ecule water/ H^+)	136-124-130	$1-9-90 \times 10^{-4}$
	Na PVS	neutralization	-	31-27	$3-60 \times 10^{-4}$
82	Na PSS	PS with conc. sul- phuric acid and silver sulphate - then ion exchange	for acid (a) 5.11 meq.gm^{-1} (b) 4.44 meq.gm^{-1}	39-46-42 37-46-42	0.05-0.45-0.9 0.04-0.3-0.6
63	Na PSS	Dow Chem. Co.	EW 206	38.5	1×10^{-3}
	HPSS	from NaPSS by ion exchange	-	141	1×10^{-3}

83	Na PSS	Monsanto	Degree of sulphonation, 0.91	{ 38	{ 2.96×10^{-4}
				{ 37	{ 7.53×10^{-4}
	HPSS	from NaPSS by ion exchange		{ 128	{ 2.96×10^{-4}
				{ 131	{ 7.53×10^{-4}
73, 75	Na PVAS	esterification of PVA with chloro-sulphonic acid	Degree of sulphonation		
			(a) 0.71	41-29	$2-90 \times 10^{-4}$
			(b) 0.74	39-32	$1-60 \times 10^{-4}$

PVTS polyvinyltoluene sulphonate, PSS polystyrene sulphonate,

PVAS polyvinyl alcohol sulphate, PVS polyvinyl sulphonate

charge fraction by assuming that the polyion made either a negligible contribution⁶² or a small contribution⁶³ to the total conductance. These values were considerably higher than those reported from combined conductance-transference measurements in the next section.

(d) Counterion binding to atactic and isotactic polystyrene sulphonic acids and their sodium salts from conductance and transference measurements

The equivalent conductance and transference numbers of the polyacids and the corresponding sodium salts at 25.00°C are shown in figures (3-5.1) and (3-5.2) respectively, together with the charge fraction calculated by equation (3-5.7).

The equivalent conductance of the polyacids shows a slight increase with concentration as found previously with polyvinyl sulphonic acid⁵⁸ with the magnitude agreeing well with the two values reported by Wiasbrun and Patterson⁸³ for polystyrene sulphonic acid. Transference studies and calculation of the charge fraction of the polyion indicate that the assumption of negligible contribution to conductance by earlier workers^{62,63} is an unjustified approximation.

The equivalent conductance of the sodium salts of the two types of polyacids are in reasonable agreement with some published values^{63,83} but are considerably lower than the values calculated from the graphical results of Mock, Marshall and Slykhouse⁶² and those of Butler and his collaborators.⁸ The increase in conductance with dilution agrees with the general finding for sodium salts of all polysulphonic acids (see Table 3-5.1). The transport number, T_p ,

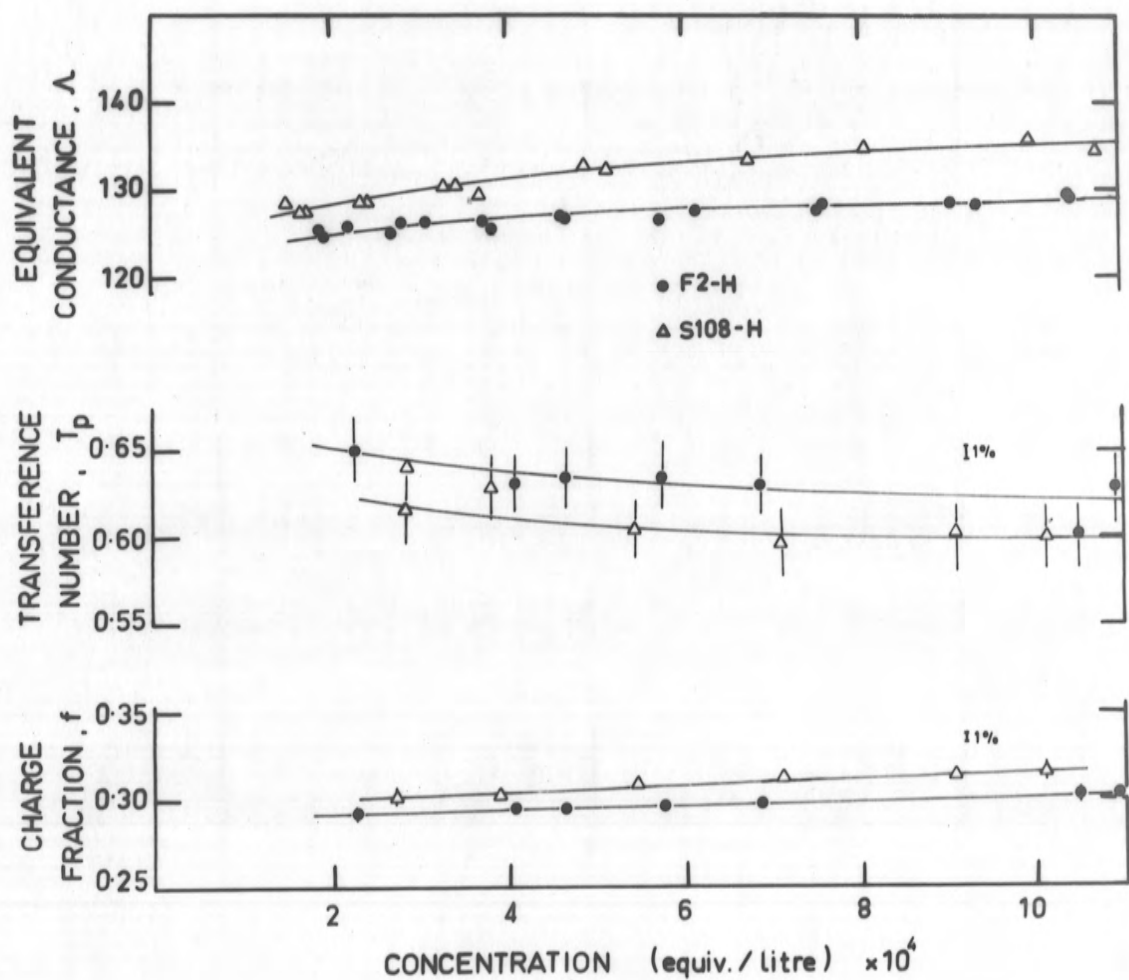


Figure 3-5.1. Charge fraction of the polystyrene sulphonate ion calculated from equivalent conductance and transference number measurements in aqueous polystyrene sulphonic acid solutions at 25.000°C.

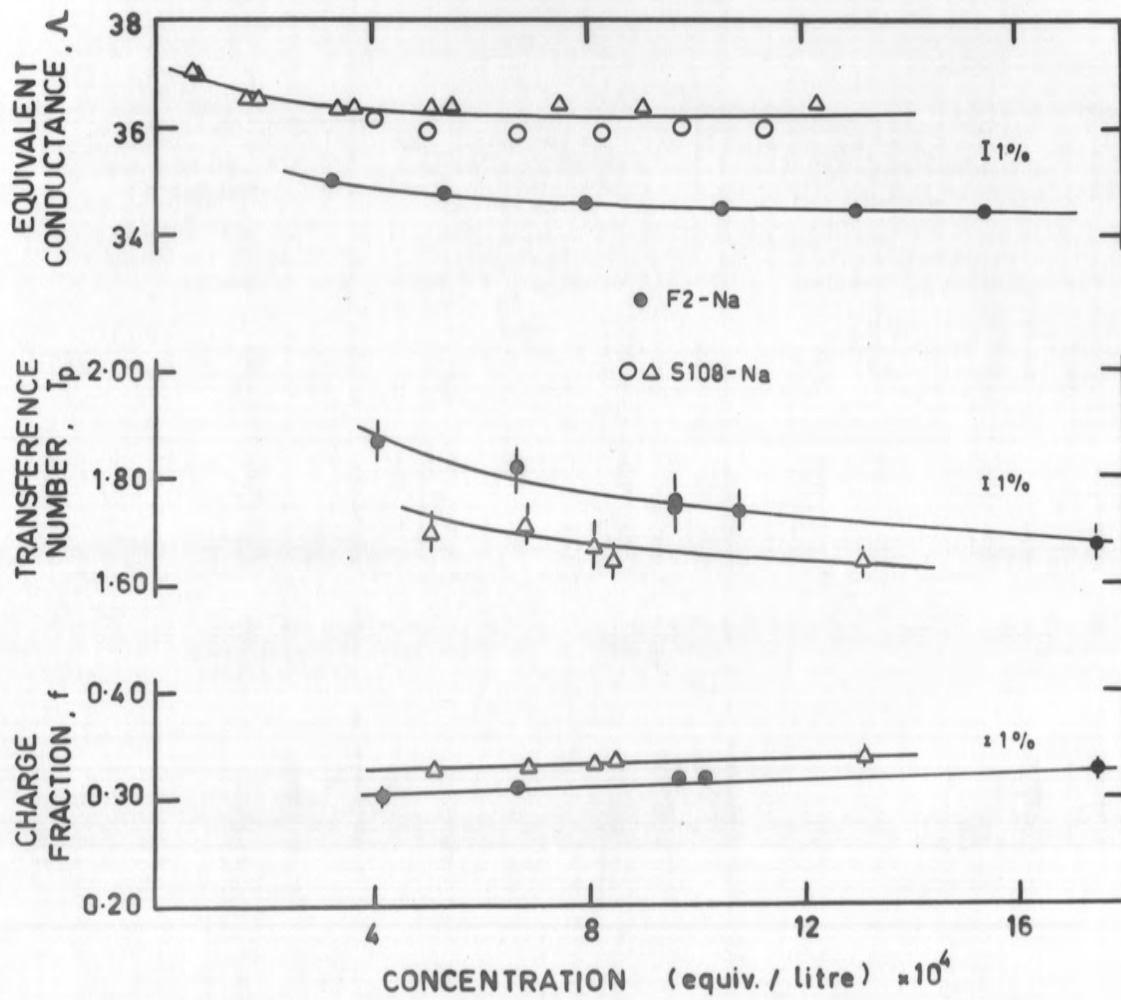


Figure 3-5.2. Charge fraction of the polystyrene sulphonate ion calculated from equivalent conductance and transference number measurements in aqueous sodium polystyrene sulphonate solutions at 25.000°C.

is in excess of unity due to both the low mobility of the free sodium ions and the high fraction of sodium ions moving with the polyanion towards the anode. Similar high values for the transport number, T_p , of the polyacrylate ion in sodium polyacrylate solutions can be calculated from the results listed by Okubo and his co-workers.⁸⁴

As shown in tables (3-5.2 and 3-5.3) the mobilities of the polystyrene sulphonate ions in the case of both the polyacids and the polysalts do not appear to be significantly affected by tacticity although the charge fraction, calculated with the aid of equation (3-5.7), was found to be slightly lower for the isotactic polyelectrolyte. It should be noted, however, that with the polyacids the combined conductance-transference method is not a particularly sensitive way in which to detect differences in the charge fraction of polyions owing to the high contribution, $f\lambda_c^0$, by the counterions to the total conductance, Λ , compared with the contribution, fAT_p , by the polyions.

These results may be compared with those recently reported by Anzuino and co-workers⁸⁵ for the electrophoretic mobility of conventional (probably mainly syndiotactic) and isotactic polymethacrylic acid as a function of pH. At intermediate degrees of neutralization corresponding to the pH range 5-6 the electrophoretic mobility of the isotactic polyelectrolyte was significantly lower. From the potentiometric titration behaviour of these acids,⁸⁶ however, it is obvious that the degree of neutralization at a given pH differed in the two cases and so even if the frictional factor was the same, the electrophoretic mobilities would not be the same. The Italian

Table (3-5.2)

Conductance and transference data for polystyrene sulphonic acids at 25°C

	Conc. $\times 10^4$ (eq. litre $^{-1}$)	T_p	Λ (cm 2 ohm $^{-1}$ eq $^{-1}$)	$u_p \times 10^4$ (cm 2 volt $^{-1}$ sec $^{-1}$)	λ_{H^+} (free)	f
F2.H	2.287	0.65 \pm 0.02	125.8	8.4 \pm 0.3	349.5	0.29 $_2$
	4.080	0.63	126.6	8.3	349.1	0.29 $_5$
	4.644	0.63 $_5$	126.8	8.3	348.9	0.29 $_5$
	5.762	0.63 $_5$	127.4	8.4	348.7	0.29 $_6$
	6.856	0.63	127.9	8.3 $_5$	348.5	0.29 $_8$
	10.487	0.60	129.4	8.0	347.7	0.30 $_4$
	15.28	0.63	130.3	8.5	346.9	0.30 $_3$
S108-H	2.722	0.62	129.2	8.3	349.5	0.30 $_1$
	2.759	0.64	129.3	8.6	349.5	0.29 $_8$
	3.817	0.63	131.0	8.6	349.1	0.30 $_3$
	5.433	0.60	132.5	8.3	348.8	0.30 $_9$
	7.083	0.60	133.6	8.3	348.5	0.31 $_2$
	9.074	0.60	135.0	8.4	348.1	0.31 $_4$
	10.14	0.60	135.2	8.4	347.8	0.31 $_5$

Table (3-5.3)

Conductance and transference data for sodium polystyrene sulphonate at 25°C

	Conc. $\times 10^4$ (eq.litre ⁻¹)	T_P	Λ (cm ² ohm ⁻¹ eq ⁻¹)	$u_p \times 10^4$ (cm ² volt ⁻¹ sec ⁻¹)	λ_{Na^+} (free)	f
F2.Na	4.141	1.87±0.04	34.9	6.7±0.2	49.2	0.30 ₀
	6.663	1.82	34.7	6.5	48.9	0.31 ₀
	9.606	1.73	34.6	6.2	48.7	0.31 ₈
	10.821	1.74	34.5	6.2	48.6	0.31 ₈
	17.56	1.67	34.4	6.0	48.3	0.32 ₅
S108.Na	5.130	1.69	36.4 ₅	6.4	49.0	0.32 ₉
	6.911	1.71	36.4 ₅	6.5	48.9	0.32 ₇
	8.103	1.67	36.4	6.3	48.8	0.33 ₂
	8.410	1.64	36.4	6.2	48.8	0.33 ₆
	13.10	1.64	36.4 ₅	6.2	48.5	0.33 ₈

group⁸⁵ observed that at high pH values the mobilities of the two types of polymethacrylate ions rapidly approached the same limiting value. It follows from the work of Nagasawa et al.⁸⁶ that at complete neutralization the charge fraction of the isotactic polymethacrylate ion must be lower than its atactic or syndiotactic counterpart thus supporting the finding in this work with regard to the two types of polystyrene sulphonate ions.

3-6 Study of Ion Binding Using Electrochemical Cells

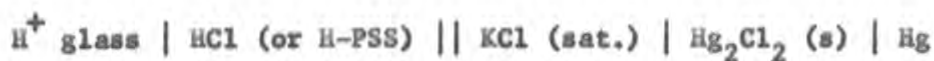
(a) Introduction

Measurements with electrochemical cells have shown that both the activity coefficient of the counterion^{92,96} and the mean ionic activity coefficient⁹³ of the added salt depend on the charge density of the polyion.⁸⁸ As configurational differences may lead to variations in the charge densities of atactic and isotactic polyions^{87a} it was considered worthwhile to attempt measurements with electrochemical cells. Although there are other methods of treatment available,^{14,87b} the results in this work will be interpreted in terms of the parameter, the charge fraction, by employing the simple model of ion binding. Thus those counterions that are bound to the polyion will be considered to be part of the polyion species in solution and to make no contribution to the counterion activity, while those that are free will be assumed to contribute to the activity in the same manner as they would in a 1:1 simple electrolyte solution in the absence of polyelectrolyte.

(b) Measurements using cells with liquid junction(1) Theory of the method

With few exceptions the electrochemical cells employed in this field have consisted basically of half-cells reversible with respect to the counterion coupled through liquid junctions to a reference electrode.⁸⁸ The general method and assumptions involved may be illustrated by reference to the cell used in this work for the estimation of the charge fraction of the polyion in aqueous salt-free polystyrene sulphonic acid solutions:-

The electromotive force of the cell,



is given by

$$E_J^{\text{HCl}} = E_g + E_{\text{cal.}} - \frac{RT}{F} \ln \frac{m_{\text{H}^+}^{\text{HCl}}}{m_{\text{H}^+}^{\text{HP}}} \frac{\gamma_{\text{H}^+}^{\text{HCl}}}{\gamma_{\text{H}^+}^{\text{HP}}} + \epsilon_{1j}^{\text{HCl}} \quad (3-6.1)$$

or

$$E_J^{\text{HP}} = E_g + E_{\text{cal.}} - \frac{RT}{F} \ln \frac{m_{\text{H}^+}^{\text{HP}}}{m_{\text{H}^+}^{\text{HCl}}} \frac{\gamma_{\text{H}^+}^{\text{HP}}}{\gamma_{\text{H}^+}^{\text{HCl}}} + \epsilon_{1j}^{\text{HP}} \quad (3-6.2)$$

when hydrochloric acid and polystyrene sulphonic acid solutions respectively are used. In the equations E_g includes the standard electrode potential and asymmetry potential of the glass electrode, $E_{\text{cal.}}$ is the electrode potential of the saturated calomel electrode, ϵ_{1j} is the liquid junction potential, and m_{H^+} and γ_{H^+} are the molality and activity coefficients respectively of the hydrogen ions in the solution.

If the electromotive force, E_J^{HP} , of the cell is measured in the presence of a known stoichiometric concentration, m_p , of aqueous

polystyrene sulphonic acid solution it is possible to find a concentration of hydrochloric acid, m_{HCl} , which in the cell produces the same electromotive force, E_J^{HCl} , as the concentration of polyacid.

Furthermore if it is assumed that

$$\epsilon_{1j}^{\text{HCl}} = \epsilon_{1j}^{\text{HP}} \quad \text{when} \quad E_J^{\text{HCl}} = E_J^{\text{HP}}$$

then it follows that

$$m_{\text{H}^+}^{\text{HCl}} \gamma_{\text{H}^+}^{\text{HCl}} = m_{\text{H}^+}^{\text{HP}} \gamma_{\text{H}^+}^{\text{HP}} = a_{\text{H}^+}^{\text{HP}} \quad (3-6.3)$$

Further calculations are limited by the absence of a thermodynamic definition for single ion activity coefficients but an arbitrary definition, as has been recently discussed by Frank,⁸⁹ does not necessarily detract from the usefulness of the concept. Single ion activity coefficients are almost invariably defined by the use of the MacInnes convention⁹⁰ in which γ_{K^+} and γ_{Cl^-} in potassium chloride solutions are assumed to be equal. Provided that γ_{Cl^-} is independent of the cation, the single ion activity coefficient of the hydrogen ion in hydrochloric acid, for example, will be given by

$$\gamma_{\text{H}^+} = (\gamma_{\pm}^{\text{HCl}})^2 / (\gamma_{\pm}^{\text{KCl}}) \quad (3-6.4)$$

In general since $a_{\text{H}^+}^{\text{HP}}$ is not known, the term can be factorized to suit the choice of the model. Thus it may be written as

$$m_{\text{H}^+}^{\text{HP}} \gamma_{\text{H}^+}^{\text{HP}} = m_{\text{p}} \gamma_{\text{H}^+}^* \quad (3-6.5)$$

where $\gamma_{\text{H}^+}^*$ is called the stoichiometric counterion activity coefficient, or alternatively, using the model for counterion association, as

$$m_+^{HP} \gamma_+^{HP} = f_{Jp}^m \gamma_+ \quad (3-6.6)$$

where f_J is the fraction of free counterions and γ_+ is the activity coefficient in a solution of a 1:1 electrolyte containing the counterion at a concentration, f_{Jp}^m . It follows that use of the above convention makes it possible to calculate either γ_+^* from equations (3-6.3) and (3-6.5) or f_J from equations (3-6.3), (3-6.4) and (3-6.6).

(2) Interpretation of electrochemical data from cells with liquid junction

The reversible electrodes used in the past⁸⁸ have included ion exchange membranes and glass electrodes as well as the more conventional sodium amalgam and silver-silver halide electrodes. The reference electrode was almost invariably the saturated calomel half-cell. A summary of the previously reported results is given in Table (3-6.1).

In this present work the stoichiometric activity coefficient of the counterions of different polystyrene sulphonic acids and their sodium salts were determined using glass electrodes reversible with respect to hydrogen and sodium ions respectively. The results of these measurements are included in Table (3-6.1) and the charge fractions, f_J , of the polyions are shown graphically in figure (3-6.1).

Inspection of this table shows that at least qualitatively the interpretation of electromotive force data in terms of counterion binding is satisfactory. The observations may be summarised as follows:

Table (3-6.1)

Reported activity coefficients of counterions (underlined) - cells with liquid junction. α = degree of neutralization; c = concentration in equiv. kgm.^{-1} water or litre^{-1} solution.

Ref.	Poly-electrolyte	Technique	α	γ_c^*	c
91	<u>Na</u> -PA	sodium amalgam	0.8	0.17-0.30	$1.56-25 \times 10^{-2}$
92	<u>Na</u> -PVAS	sodium amalgam	0.74	0.12-0.20	$0.1-4 \times 10^{-2}$
	<u>Na</u> -PSS	and	0.824	0.23-0.32	$0.1-4 \times 10^{-2}$
	<u>Na</u> -CS	ion exchange	2.32	0.12-0.14	$1-3 \times 10^{-2}$
	<u>Na</u> -CMC	membrane	0.73 ₆	0.50-0.58	$0.1-2 \times 10^{-2}$
94, 95	<u>PEI-HCl</u>	Ag AgCl	1.00	0.56-0.30	$1 \times 10^{-3}-1.0$
72	<u>PVPBu-Br</u>	Ag AgBr	0.97	0.32-0.28	$0.1-5 \times 10^{-3}$
	<u>PBTA-Cl</u>	Ag AgCl	1.00	0.28-0.26	$0.1-4 \times 10^{-3}$
96	<u>Ag</u> -CMC	Ag AgCl	1.00 0.951	0.29-0.20 0.46-0.33	$1.25-15 \times 10^{-3}$ $1.25-15 \times 10^{-3}$
97	<u>Na</u> -PP		1.00	0.26	
	<u>Na</u> -PVASI	ion exchange	0.47	0.37	
	<u>Na</u> -PVASII	membrane	0.19	0.75-0.65	
	<u>Na</u> -PVS		1.0	0.24	$0.5-6 \times 10^{-2}$
	<u>Na</u> -CS		1.71	0.33	
	<u>Na</u> -CMCI		0.94	0.60-0.47	
	<u>Na</u> -CMCII		0.70	0.80-0.64	
	<u>Na</u> -PA		-	0.23	
98	<u>Na</u> -hepar- inate	"	1.00	0.38	$1-50 \times 10^{-3}$
99	<u>Li</u> -PMA	"	0.89	0.21-0.23	
	<u>Na</u> -PMA		0.83	0.41	$0.8-3.5 \times 10^{-2}$
	<u>Rb</u> -PMA		1.00	0.42-0.4	

100	<u>K</u> -PVS	ion exchange	0.80	0.29	$3.5-5 \times 10^{-2}$
	<u>Na</u> -PVS	membrane	0.80	0.18	
	<u>Li</u> -PVS	"	0.80	0.16	
	<u>Na</u> -PVS	Na ⁺ ion glass	0.80	0.18-0.20	
101	<u>Na</u> -CMC		0.43	0.63-0.44	$1-20 \times 10^{-3}$
	<u>Na</u> -CMC	ion exchange	0.51	0.60-0.42	
	<u>Na</u> -CMC	membrane	0.83	0.52-0.38	
	<u>Na</u> -algin- ate		1.00	0.43-0.30	
102	<u>Na</u> -PP	ion exchange	1.0	0.30-0.26	$0.3-9.8 \times 10^{-3}$
	<u>Na</u> -PSS	membrane	0.82	0.29-0.31	$0.08-2.8 \times 10^{-3}$
	<u>Na</u> -PVS		0.83	0.22-0.27	$0.33-22.7 \times 10^{-3}$
50	<u>H</u> -PVTSS	H ⁺ ion glass	0.845	0.38	2×10^{-4} - 3×10^{-2}
84	<u>Na</u> -PA	Na ⁺ ion glass	1.00	0.28	2×10^{-3} -0.25
This work	<u>H</u> -PSS (atactic)	H ⁺ ion glass	1.15	0.39	$0.1-1.0 \times 10^{-3}$
	<u>H</u> -PSS (iso- tactic)		1.13	0.40	
	<u>Na</u> -PSS (atactic)	Na ⁺ in glass	1.13	0.38-0.40	

PA, polyacrylate

CS, cellulose sulphate

PVS, polyvinyl sulphonate

PP, polyphosphate

PSS, polystyrene sulphonate

PMA, polymethacrylate

PVAS, polyvinyl alcohol sulphate

CMC, carboxymethyl cellulose

PEI, polyethylene imine

PVP-Bu, polyvinyl n-butyl pyridinium

PBTA, polyvinyl benzyl triethyl ammonium

PVTSS, polyvinyl toluene-styrene sulphonate.

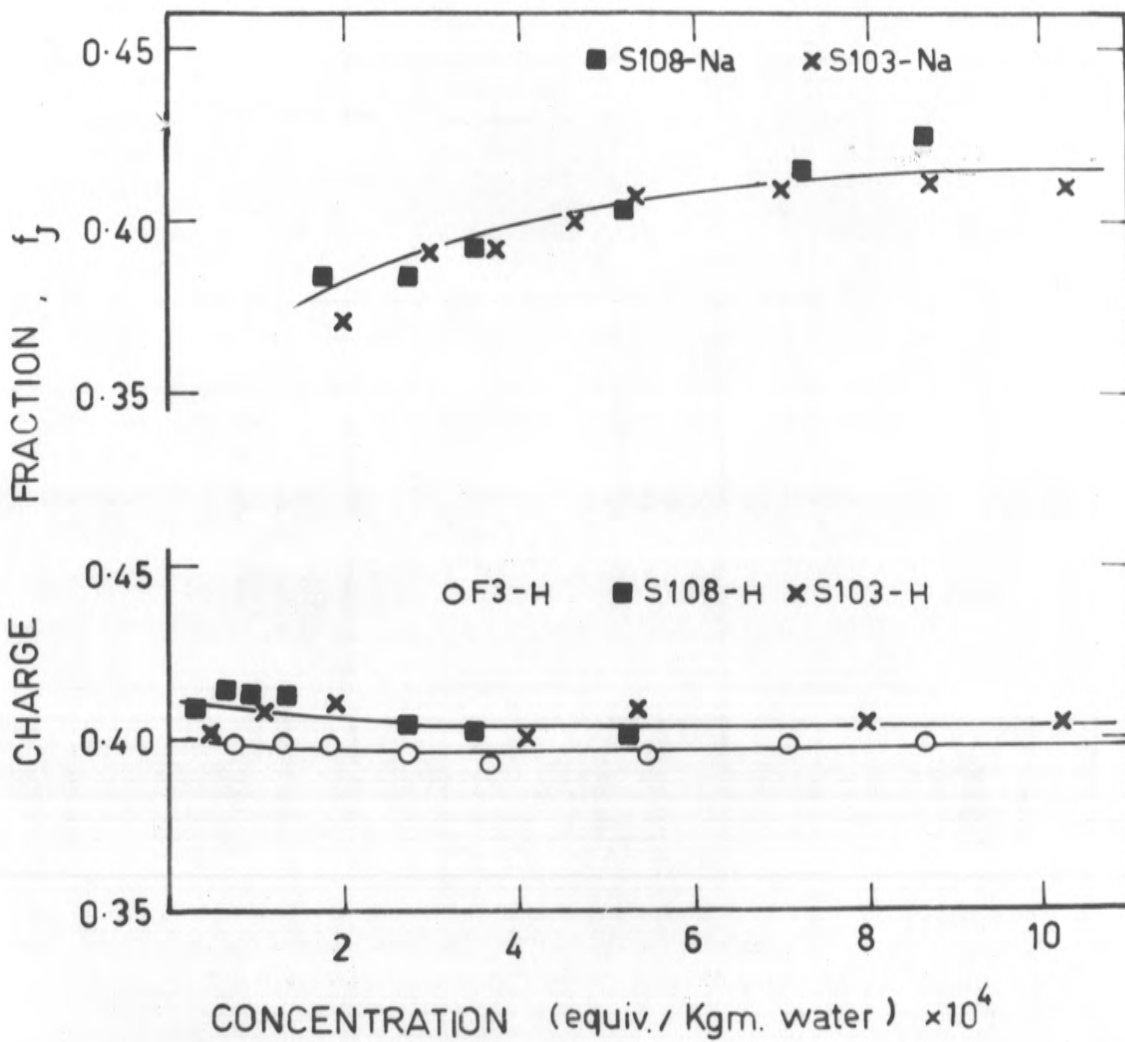


Figure 3-6.1. Charge fraction of the counterion in polystyrene sulphonic acid solutions and their sodium salts. Cells with liquid junction. Temperature, 25.00°C.

(i) The stoichiometric activity coefficient of the counterion, γ_c^* , is generally markedly lower than the activity coefficient of the same ion in a simple electrolyte solution.

(ii) A close relationship^{93,97,102} has been shown to exist between the average repeat distance of charge along a polyion and the activity coefficients of the same counterion measured in salt-free solutions of different polyelectrolytes⁹⁸ at the same molar concentrations. As the charge density is increased the activity coefficient of the counterion approaches a low value^{72,92,93,97} which tends to zero at very high charge density⁹² and is almost insensitive to concentration. On the other hand with polyelectrolytes in which the charge groups are very widely separated the activity coefficients approach values commonly observed with simple electrolytes.⁹⁷

(iii) The activity coefficient of the counterion, γ_c^* , is independent of the molecular weight^{92,97} provided that the degree of polymerization is not too low. It is noteworthy that from a study of the transition from simple electrolytes to polyelectrolytes Lapanje and his co-workers⁹⁴ were able to show that the degree of polymerization must be at least in excess of five before the constancy of the counterion activity coefficient is exhibited.

(iv) The concentration dependence of the activity coefficient of the counterions is controversial and differs considerably between different polyelectrolytes. Thus the counterions of numerous polyelectrolytes have activity coefficients which decrease with concentration,^{94-97,101} some show increases^{92,93,102} and many have values

which are almost independent of concentration.^{50,90,92,93,97-100,102}

This behaviour is in sharp contrast with that for simple electrolytes but does not rule out the possibility that at sufficiently low concentrations⁹² the activity coefficient may rapidly increase and approach unity.

(v) The effect of the size of counterions on their activity coefficient in the presence of the same polyion has been demonstrated, for example by Crescenzi and co-workers.^{99,100} They found that regardless of the chemical nature of the ionizable groups of the poly-anions, the activity coefficients of the alkali metal ions decrease with decreasing ionic radius.

(3) Comments on the results in this work

The activity coefficient of the sodium ion in salt-free sodium polystyrene sulphonate solutions was found in this work to be higher than the values reported by Lyons and Kotin¹⁰² using the ion exchange membrane method for the same polyelectrolyte in the same concentration range. Comparable results obtained by the sodium ion glass electrode technique with the sodium salts of polyacrylic acid⁸⁴ and polyvinyl sulphonic acids^{97,100} were also lower than the values found in the present work. The latter discrepancies can be explained, however, by the lower surface charge density¹⁰² on the polystyrene sulphonate ion due to its greater diameter.

In the case of polystyrene sulphonic acid the activity coefficients of the hydrogen ion compare favourably with the values obtained by Mock and Marshall⁵⁰ for a copolymer vinyltoluene-styrene

sulphonic acid using the same method. It is evident from figure (3-6.1) that the charge fraction of the polystyrene sulphonate ion differs slightly, if at all, for the isotactic and atactic polyacids.

(c) Measurements using cells without liquid junction

(1) Theory of the method

The electromotive force, E , of the following cell,



in the absence or presence of polystyrene sulphonic acid is given by

$$E = E^0 - k \ln (a_{\pm})^2, \quad (3-6.7)$$

where a_{\pm} is the mean activity of hydrochloric acid on the molality scale and k is a constant which is ideally equal to RT/F .

To calibrate the cell the electromotive force is measured at varying molalities of hydrochloric acid and from the resultant linear relationship between E and $\ln(a_{\pm})^2$ the constant k can be determined.

The electromotive force of the same cell containing hydrochloric acid of molality, m , and polystyrene sulphonic acid of molality, m_p , is then measured. The mean ionic activity of hydrochloric acid alone which in the cell produces the same electromotive force as the mixed solution can be calculated and therefore related to the molalities of hydrochloric acid and polystyrene sulphonic acid in the mixture by factorising $(a_{\pm})^2$ according to the ion binding model,

$$(a_{\pm})^2 = (m + fm_p)m(\gamma'_{\pm})^2 \quad (3-6.8)$$

In this equation f is the charge fraction of the polystyrene sulphonate ion and the mean ionic activity coefficient, γ'_{\pm} , is a function of the

ionic strength of the solution. By treating the polyelectrolyte as a 1:1 electrolyte and using an iterative procedure the charge fraction of the polyion can be calculated at the known concentration of simple electrolyte. If the charge fraction is determined at a number of concentrations of hydrochloric acid an extrapolation to zero concentration will give the charge fraction of the polyanion in "salt"-free polyacid. A comparison of the value, f , by this method with the corresponding value, f_J , using cells with liquid junction should give an indication of the uncertainties associated with the neglect of liquid junction potentials in determinations using the latter non-thermodynamic cells.

(2) Experimental results with polystyrene sulphonic acids

(1) Variation of the charge fraction of the polystyrene sulphonate ion with concentration of hydrochloric acid.

When hydrochloric acid solution was progressively added to a solution of atactic polystyrene sulphonic acid in a glass electrode-silver, silver chloride cell, the measured electromotive forces yielded the results shown in figure (3-6.2). It is evident that the charge fraction of the polystyrene sulphonate ion is almost independent of the concentration of hydrochloric acid in the concentration range used. This finding compares favourably with the effect of the concentration of potassium chloride on the charge fraction of the polyvinyl sulphonate ion calculated from the recently published results by Imai and Eisenberg¹⁰⁴ for the cell,



From the limiting values of the membrane distribution coefficient,

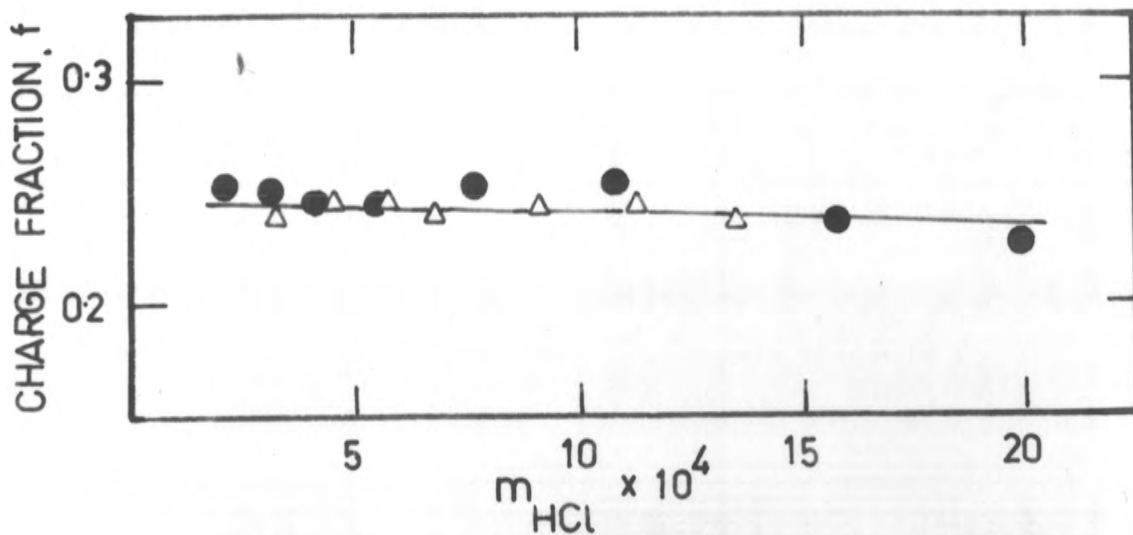


Figure 3-6.2. Variation of the charge fraction of the polystyrene sulfonate ion in the polyacid of approximately constant concentration with the molality of hydrochloric acid. Cell without liquid junction. Temperature, 25.00°C.

$$m_{\text{S103-H}} = 2.38_6 - 2.35_2 \times 10^{-4} \text{ eq./kgm. water}$$

$$m_{\text{S103-H}} = 1.86_4 - 1.84_5 \times 10^{-4} \text{ eq./kgm. water.}$$

r_m^0 , at four molalities of potassium chloride, calculations show that the charge fraction of the polyanion only varies slightly with the concentration of the simple electrolyte provided that this is not too high (figure 3-6.3).

(ii) Variation of charge fraction of the polystyrene sulphonate ion with concentration of polyacid

As the charge fraction of the polyion was independent of the concentration of hydrochloric acid, a second series of experiments was carried out in which the electromotive force of the cell was measured as a function of the concentration of the polyacid in the presence of a slightly changing concentration of hydrochloric acid. The calculated values of the charge fraction of the polystyrene sulphonate ions for both the atactic and isotactic polyacids are shown in figure (3-6.4).

(3) Comparison of the results with atactic and isotactic polyacids

Figure (3-6.4) clearly shows that the charge fraction of the isotactic polystyrene sulphonate ion is lower than that of the atactic form to an extent which is outside the limits of experimental error. This suggests that the surface charge density of the isotactic polyanion is higher than that of the similarly sulphonated atactic polyanion (table 4-8.1). This conclusion agrees with that of Nagasawa and his collaborators⁸⁶ from observations of the potentiometric titration behaviour of isotactic, syndiotactic and atactic polymethacrylic acids. (See section 3-8 for further discussion).

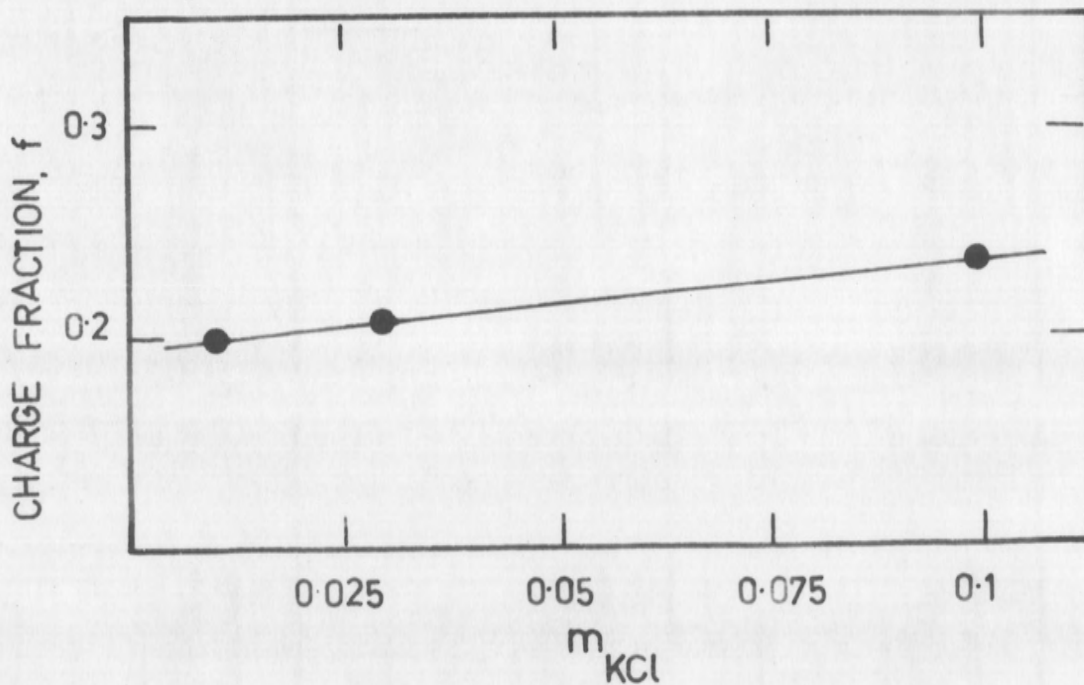


Figure 3-6.3. Charge fraction of the polyanion in potassium polyvinyl sulphonate solution as a function of the molality of potassium chloride from the results of Imai and Eisenberg.¹⁰⁴ Temperature 25°C.

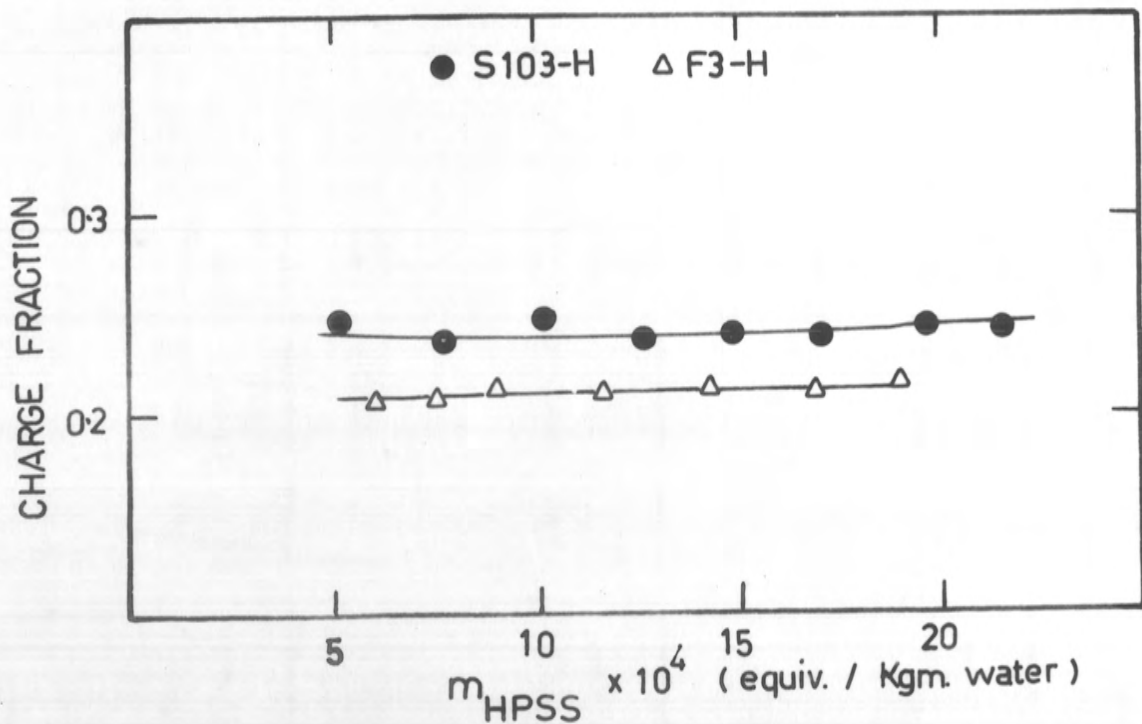


Figure 3-6.4. Variation of the charge fraction of the polystyrene sulphonate ion with the concentration of polystyrene sulphonic acid in the presence of hydrochloric acid. Cell without liquid junction. Temperature, 25.00°C.

F3-H with $4.56 - 4.08 \times 10^{-4} M$ HCl

S103-H with $4.78 - 4.37 \times 10^{-4} M$ HCl.

The charge fraction of the polystyrene sulphonate ion was independent of concentration for both types of polyacids.

(d) Comparison of results from cells with and without liquid junction

The charge fraction, f_J , of the polyanion of polystyrene sulphonic acid, found by using cells with liquid junction, is considerably higher than the comparable values of the charge fractions, f , determined using cells without liquid junction. Coupled with the values of 0.28-0.29 for the stoichiometric activity coefficient of the counterions in salt-free potassium polyvinyl sulphonate solutions - obtained by Crescenzi and co-workers¹⁰⁰ from membrane potential measurements - it is seen that the previously mentioned results of Imai and Eisenberg¹⁰⁴ support this finding.

Table 3-6.2

Comparison of charge fractions calculated from cells with and without liquid junction

	H-PSS	KPVS ^{100,104}
liquid junction	0.39-0.40	0.29-0.28
no liquid junction	0.23	0.19-0.20

In an endeavour to explain the discrepancy between the two sets of results the approximate error in the electromotive force which would be necessary to lead to the same charge fraction as that found

using cells without liquid junction was calculated for the cells with liquid junction from

$$f = m_{H^+} / m_p \quad \text{and} \quad pH = (E - E_{ref}) / 59.16$$

These calculations show that in all cases an error of about 10-15 millivolts at concentrations between 1×10^{-4} and 5×10^{-2} equivalents of polyelectrolyte per kilogram of water would be necessary to explain the results.

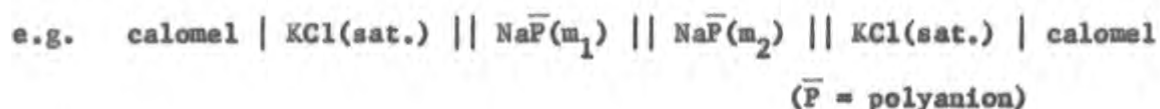
As measurements of single ion activity coefficients are subject to uncertainties which arise through the neglect of liquid junction potentials^{88,94,105} it is pertinent to consider whether any conclusions can be reached concerning the magnitude of liquid junction potentials in these cells.

Mock¹⁰⁶ determined the activity coefficients of the sodium ion in salt-free sodium polystyrene sulphonate solutions (0.22-0.26 for molalities of polysalt, $2.2-4.6 \times 10^{-2}$) by freezing point measurements and compared these values with those obtained by Nagasawa and co-workers⁹² for sodium polyvinyl alcohol sulphate (Table 3-6.1) using an electrochemical cell with liquid junction. He concluded that the latter measurements were thermodynamically valid.¹⁰⁶ It is doubtful, however, whether the comparison is justifiable owing to the considerable difference in the surface charge density of the different polyanions.¹⁰²

A comparison of the above cryoscopic results with those of Lyons and Kotin¹⁰² from membrane potential measurements using sodium polystyrene sulphonate solutions ($\gamma_{Na^+}^* = 0.31$ at the highest concentration used) would, in fact, lead to the opposite conclusion, viz. a high contribution

from liquid junction effects. It should be noted, however, that the significance of the above deductions from Mock's work is difficult to assess because of the self-admitted rough nature of the freezing point determinations.

The conclusion by Kotin and Nagasawa,¹⁰³ based on diffusion potential measurements, that the liquid junction potentials between a polyelectrolyte and saturated potassium chloride solution are zero, is open to question. In these cells,



two liquid junctions between saturated potassium chloride solution and polyelectrolyte solution are present as well as the junction between the two polyelectrolyte solutions. The electromotive force of the cell will therefore be the sum of the potentials which arise at the three junctions. Using the above cell Nagasawa and co-workers⁷⁵ measured the electromotive force, E , as a function of the concentration of sodium polyvinyl alcohol sulphate, m_2 , while the concentration, m_1 , in the other half-cell remained constant. From a knowledge of the activity coefficients of the counterion - obtained from membrane potential measurements - the transport numbers of the sodium ion were determined from gradients of a plot of E versus $\log a_{\text{Na}^+}$. By carrying out the experiment at a number of concentrations of standard solution it was found that, by shifting the axes vertically, the above plots were superimposable. This indicates that

(a) the two liquid junctions with potassium chloride cancel each other and that they are not greatly affected by the concentration of

polyelectrolyte solution in contact with the potassium chloride solution,

(b) accurate values of diffusion potentials can be measured with the cell.

It should be noted, however, that, contrary to the assertion by Kotin and Nagasawa,¹⁰³ this work does not indicate that the magnitude of the liquid junction potential is negligible. Moreover it does not indicate whether the liquid junction with the polyelectrolyte solution is the same as that with a simple 1:1 electrolyte solution.

From diffusion potential measurements Botre et al.⁸¹ found that the transference numbers of the sodium ion in solutions of sodium polyacrylate and sodium polyphosphate were 0.69 and 0.54 respectively by using the relation,

$$t_{\text{Na}^+} = -\frac{\Delta E}{58\Delta \log \gamma_+ c_+}$$

where $\Delta E/\Delta \log \gamma_+ c_+$ is the slope of the plot of the electromotive force of the cell against $\log \gamma_+ c_+$. These values compare favourably with those reported by Huizenga et al.,⁶⁴ 0.60, and Wall and Doremus,¹⁰⁷ 0.56, for the respective polysalts using conventional H-type transference cells. Since the liquid junction potentials between saturated potassium chloride and the polysalt solutions were shown by Nagasawa and co-workers⁷⁵ to cancel, it follows that any assumptions made in the calibration of the cell used to determine the activity coefficient of the counterion, γ_+ , must hold if agreement between the transference

numbers is complete. The above results, especially with the sodium polyphosphate, therefore indicate that the usual assumption made in measuring single ion activity coefficients - viz. that liquid junction potential between saturated potassium chloride and sodium chloride solution is the same as that with the sodium polysalt at the same sodium ion activity (section 3-6b(1)) - may be close to the truth.

A further attempt to estimate the effect of liquid junction potentials was made by using the Henderson equation¹⁰⁸ (section 4-13d). It seems, however, that the value of the calculated liquid junction potential is only likely to be 2-3 millivolts higher with a polystyrene sulphonic acid solution than with a hydrochloric acid solution at the same concentration. Although considerable uncertainty is involved in these calculations, it does not appear possible that the calculated difference could approach the magnitude, 12-14 millivolts, needed to explain the difference in the experimental values of the charge fractions, f_j and f , calculated from measurements with cells with and without liquid junction on the basis of the ion binding model. A possible explanation may be that the discrepancy arises from a breakdown of the simple ion-binding model possibly combined with errors from the existence of small liquid junction potentials.

3-7 Pycnometry

(a) Factors affecting the partial specific volume of a polyelectrolyte

By density gradient ultracentrifugation of atactic and isotactic polystyrene in a benzene-bromoform mixture, Buchdahl and

co-workers¹⁰⁹⁻¹¹⁰ found that the atactic form had a partial specific volume which was $0.025 \text{ cc.gm.}^{-1}$ higher than the stereoregular variety. In contrast Krigbaum et al.¹¹¹ had previously reported a difference of only $0.004 \text{ cc.gm.}^{-1}$ using a pycnometric method. There existed therefore, the possibility that some difference might be detected in the partial molal volumes of the sulphonic acid derivatives of the polystyrenes especially if the magnitude was as high as the $2.6 \text{ cc. mole}^{-1}$ found by Buchdahl's group of workers with polystyrene.

No previous results have been reported for polystyrene sulphonic acid but for the sodium polysalt values of 0.697 and $0.606 \text{ cc.gm.}^{-1}$ have been given by two groups^{8,82} in reporting the results of sedimentation studies in 0.2 molar sodium chloride. A considerable uncertainty arises in comparison of results because the magnitude of the partial specific volume is dependent on a number of factors:-

(1) The partial specific volume will be lower for high degrees of sulphonation because of the more bulky nature of the styrene residue than the sulphonate ion.

(2) Owing to the hygroscopic nature of polystyrene sulphonic acid and its sodium salt there is a possibility that neglect of hydration will lead to a value considerably higher than that for the anhydrous product (equation 4-14.3).

(3) As the partial specific volume varies with concentration,¹¹² the experimental value will depend on the concentration at which the measurement is made.

(4) The partial specific volume may depend on the presence of salt. Recent work by Andersson,¹¹³ for example, showed that the

partial specific volume of sodium polymethacrylate in 0.01M sodium hydroxide changed from $0.384_6 \text{ ml.gm.}^{-1}$ to $0.415_3 \text{ ml.gm.}^{-1}$ when the solution was also made one molar with respect to sodium chloride.

(b) Experimental results

The apparent specific volumes of the sodium salts and the polyacids were determined in salt-free solutions as described in section (4-14) and found to be $0.570\text{--}0.575 \text{ cc.gm.}^{-1}$ and $0.582\text{--}0.588 \text{ cc.gm.}^{-1}$ respectively for the anhydrous samples in the concentration range $1\text{--}4 \times 10^{-3} \text{ gm./cc. solution}$. (The value calculated for the polyacid when not allowing for the presence of one molecule of water for each sulphonic group was in the vicinity of $0.623 \text{ cc.gm.}^{-1}$).

The results for the sodium salts are difficult to compare with those previously reported^{8,82} at higher concentrations in 0.2 M sodium chloride for the reasons listed above. However, taking into account the probable lower degree of sulphonation (indicated from the equivalent weight, 195.7, of the polyacid and calculated from data supplied by assuming that the composition of the dried sample was the same as in this work) and using Andersson's results with sodium polymethacrylate as a rough guide to the effect of salt, the values found in this work are not inconsistent with those of Prini and Lagos.⁸²

(c) Effect of tacticity

The apparent molal volumes of three polyacids and two sodium salts are shown plotted against the square root of the molarity in figure (3-7.1) while the partial molal volumes at infinite dilution

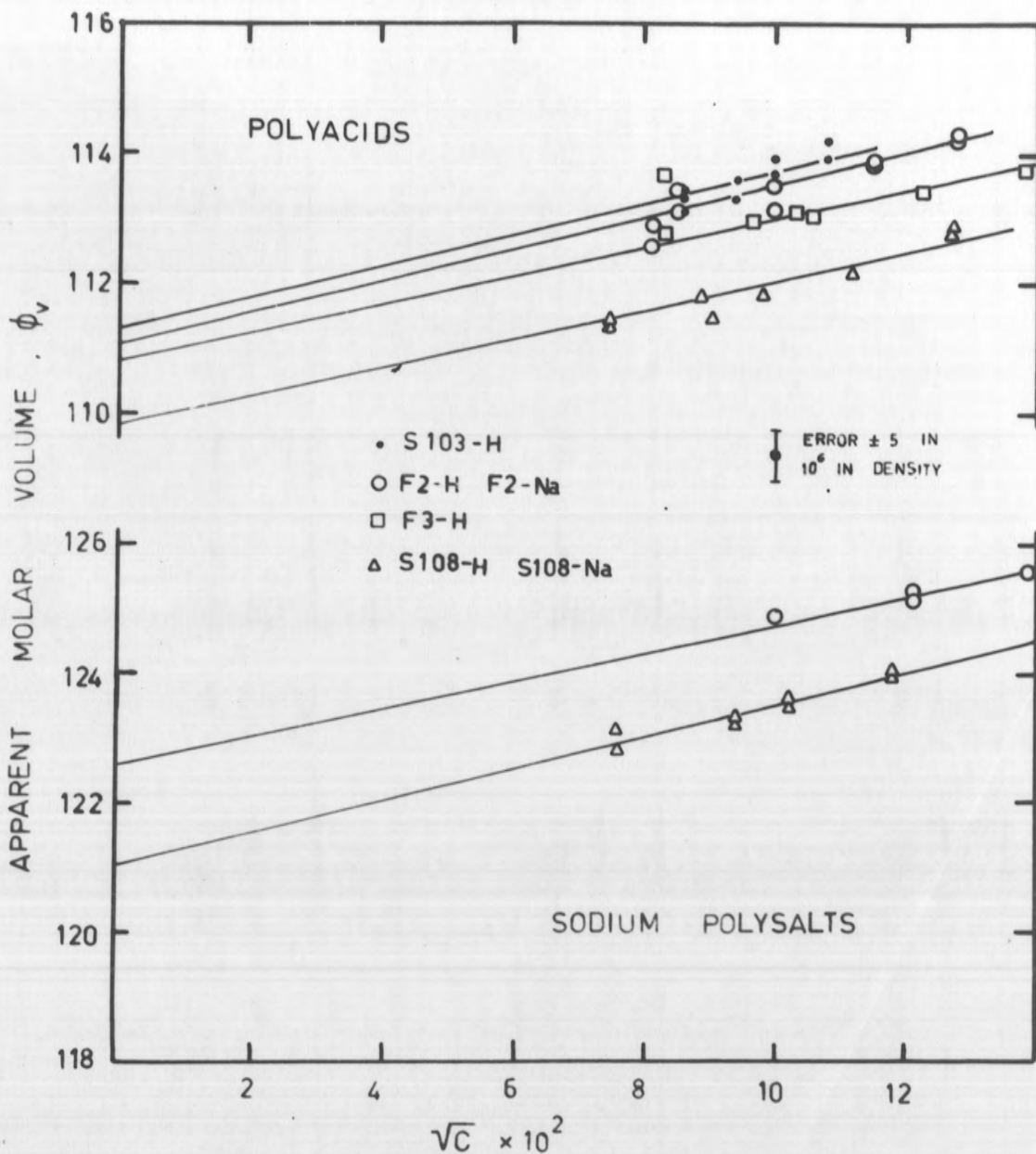


Figure 3-7.1. A plot of the Masson relation¹¹² for polystyrene sulphonic acids and their sodium salts from density measurements in salt-free solutions at 25.00°C. Concentration, c , in moles per litre. ϕ_v , in cc. mole⁻¹.

together with the molecular weight of the anhydrous monomeric units are shown in table (3-7.1).

Table (3-7.1)

Partial molal volumes of polystyrene sulphonic acids and sodium poly-salts at infinite dilution. Solvent, water at 25.00°C.

	F3-H	F2-H	S108-H	S103-H	F2-Na	S108-Na
\bar{V}_2^0 (cc.mole ⁻¹)	111.1	111.4	110.0	111.8	122.6	121.0
MW (anhydrous)	194.2	195.1	191.6	195.8	220.2	215.7

The experimental values of 110-112 cc.mole⁻¹ for the different polyacids agree with a rough estimate of 108 to 118 cc. mole⁻¹ by the method commonly used for proteins.¹¹⁴ The apparent molal volume of the -styryl, $-\text{C}_6\text{H}_4-\text{CH}-\text{CH}_2-$, group was calculated from data for amino-benzoic acid listed by Cohn and Edsall.¹¹⁴ Estimations indicated that the addition of a sulphonic acid group to the benzene ring was only likely to produce a small change in the apparent molal volume because of the compensating effect of electrostriction that results on ionization.¹¹⁴ Rasper and Kauzmann¹¹⁵ have pointed out that with proteins containing another charged ion near the carboxylate ion the electrostrictic effect, as far as the carboxylate ion is concerned, is increased by 5 ml. or more. It seems reasonable to expect a similar effect with the polystyrene sulphonic acid samples used in this work as the degree of sulphonation of benzene rings is in excess of unity (Table 4-8.1).

If all samples had been sulphonated to the same extent,

Buchdahl's results^{109,110} with uncharged polystyrene indicated the possibility that the partial molal volume of the atactic acid was likely to be greater than the isotactic form. The partial molal volumes of the polyacids at infinite dilution, \bar{V}_2^0 , were found, however, to parallel closely the variation in the molecular weight of the monomeric unit (Table 3-7.1) without any indication of an effect due to a difference in tacticity.

(d) Evidence for the nature of ion binding

Since electrostriction of solvent is a sensitive measure of the electrical state of molecules in aqueous solution Mukerjee¹¹⁶ suggested that differences in the partial molal volumes of polyacids and their corresponding salts can be used to distinguish between "site" and "ionic atmosphere" binding in polyelectrolyte solutions.

Although the principle is correct, however, the extent of electrostriction is influenced by a number of factors including the local ion concentration, the nature of the ion, the charge on the ion¹¹⁶ and the cooperative effects of ionized groups held covalently in close proximity on polyions.¹¹⁵ By comparing the results on simple electrolytes such as hydrochloric acid and its sodium salt with those for acetic acid and its sodium salt, a positive value for the difference in partial equivalent volumes of a polyacid and its sodium salt, $\Delta\bar{V}$, would indicate "site" binding whereas a negative value tends to suggest "ionic atmosphere" binding of counterions to the polyion.

The results in the present work with polystyrene sulphonic

acids and their sodium salts (Table 3-7.1) would therefore be qualitatively consistent with non-specific binding. This conclusion agrees with that reached by Strauss and Leung for sodium polystyrene sulphonate using a dilatometric technique,¹¹⁷ by Lapanje and Rice from studies of the Raman spectra of polystyrene sulphonic acid⁶⁰ and by Kotin and Nagasawa⁶¹ on the basis of nuclear magnetic resonance measurements on this same polyacid. Quantitatively the value of $\Delta\bar{V}_0$ - about -10 cc. per equivalent - is much greater than the value of -2 cc. per mole for hydrochloric acid and sodium chloride at 2 M concentration. The discrepancy, however, may be due to the fact that the difference will be influenced by the unknown concentration of counterions in the immediate vicinity of the polyion, the presence of two sulphonate groups on about 10% of the benzene rings and some variation in the nature of the binding of the two counterions.

3-8 General Discussion

(a) Differences in properties of atactic and isotactic polyions

Although in this present work a solid state examination of isotactic polystyrene sulphonic acid by X-ray diffraction revealed no evidence of the crystallinity which can be observed with the parent polystyrene, isotactic polyacrylic acid has been readily crystallized from solution.^{118,119} In the latter case crystallinity was verified by Kargin et al.¹²⁰ using electron microscopy and by Miller and co-workers^{118,119} from observations of both the sharpness of X-ray diffraction patterns and birefringence effects when specimens were viewed under a polarizing microscope. The above

solid state difference between the two isotactic polyelectrolytes is understandable. As discussed in section (3-1), the presence of the sulphonic acid group in the para-position of the benzene ring would be expected to prevent crystallization of the polyacid while the limited bulk of the carboxylic acid group near to the chain should not seriously hinder crystallization of the polyacrylic acid. Both isotactic polystyrene sulphonic acid and polyacrylic acid¹¹⁹ had identical infra-red spectra to their respective atactic forms but this was readily explained.

Studies with electrochemical cells, at least in the absence of liquid junctions, indicated that the charge fraction of the isotactic polystyrene sulphonate ion was significantly lower than that of the atactic polyanion. Similar evidence of strong counterion binding to another isotactic polyanion has been obtained from the potentiometric titration of atactic and stereoregular forms of polymethacrylic acid with sodium hydroxide. After Loeb and O'Neill¹²¹ had found, and the Sakaguchi group¹²³ had confirmed, that the isotactic acid was weaker than the atactic (probably mainly syndiotactic) form, a thorough investigation by Nagasawa, Murase and Kondo⁸⁶ showed that at all degrees of neutralization, irrespective of ionic strength, the potentiometric titration curves of isotactic polymethacrylic acid were above those of the syndiotactic acid with the atactic form occupying an intermediate position close to the syndiotactic acid. It followed therefore, that at the same degree of neutralization, the isotactic polyanion had the lowest charge fraction.

Evidence of a higher charge density of the isotactic polystyrene sulphonate ion in solutions of both the polyacid and its sodium salt by combined conductance and transference measurements was not as conclusive. The similarity in the mobilities of atactic and isotactic polystyrene sulphonate ions, however, appeared to agree with the electrophoretic mobility results of Anzuino et al.⁸⁵ for atactic and isotactic polymethacrylic acids at high degrees of neutralization.

Some of the physical methods which have proved useful in the study of solution properties of biopolymers were used in attempts to detect conformational differences between isotactic and atactic polystyrene sulphonate ions in solution. Although a rise in temperature of isotactic and atactic polyacid solutions produced insignificant changes in optical density and rather inconclusive evidence of changes in the reduced viscosity, optical rotation and dye-binding studies strongly indicated structural differences between the two types of polyelectrolytes.

In the optical rotation studies the quinine salt of isotactic polystyrene sulphonic acid was found to give a greater enhancement of optical rotation than the corresponding atactic salt at the same concentration in the same solvent at the same temperature. This agreed with similar evidence of structural differences of atactic and isotactic polyelectrolytes that had been reported earlier by Schulz and Schwaab³⁰ from optical rotation studies of the d-tartrates of isotactic and atactic poly-2-vinyl pyridine.

The observation that proflavine not only bound more strongly

to the isotactic polystyrene sulphonate ion at high polymer to dye ratio but that heating of the complex also caused a sudden rise in the extinction coefficient of the dye approximately to the value found for the almost temperature-independent atactic polyacid-proflavine complex, provided further evidence for structural differences between two types of polyanions.

The small difference that may have been expected between the partial molal volumes of isotactic and atactic polystyrene sulphonic acids, was not detected by pycnometry.

(b) Possible nature of the differences between atactic and isotactic polyions in solution

Although sulphone linkages between the linear sequences of isotactic macro-ions could possibly provide the conditions which would explain many of the above properties, sedimentation velocity studies have shown an absence of any abnormally high molecular weight species in both the atactic and isotactic polystyrene sulphonic acid samples. It appears therefore, that many of the properties reported in this work and in earlier publications were the result of conformational differences between linear polyions in solution.

In endeavouring to explain the difference in titration behaviour of the three types of polymethacrylic acid, Nagasawa et al.⁸⁶ observed that the measured pH values of the syndiotactic polyacid at various stages of the titration agreed closely with those calculated from the theoretical work of Kotin and Nagasawa¹⁰³ which was based on a planar zig-zag conformation of this polyacid in solution.



By postulating local helical regions in the isotactic chain with three monomer units per turn these workers showed that the calculated charge density of the isotactic polymethacrylate ion corresponded to the high value suggested by their experimental results. At the same time, however, they were careful to point out the caution that had to be exercised in attempting to explain the titration behaviour in this way, especially because of conflicting evidence for the existence of helical forms even in solutions of uncharged isotactic polymers.^{16,27} Whether Nagasawa's speculation can explain the experimental results in this work remains to be considered.

The presence of limited helical sections in the polyion chain would certainly be consistent with the above findings of a higher charge density for the isotactic polystyrene sulphonate ion than the atactic polyion. It also seems likely that a greater enhancement of optical rotation of the quinine salt of the isotactic acid could conceivably arise if some degree of helicity existed in the polymeric chain. Furthermore, the sudden rise in the extinction coefficient of the dye over a narrow temperature range when the isotactic polystyrene sulphonic acid-proflavine complex is heated, could be conveniently interpreted as a sudden change from limited helical regions of the chain to the random coil which is characteristic of atactic polyelectrolytes. However, until more positive evidence of helicity in isotactic polyelectrolyte solutions is obtained the above explanation can be regarded as no more than conjecture. Perhaps, as Morawetz has suggested,¹²⁴ stereoregularity may impose a restriction

on accessible conformations (conformational rigidity) of the chain, not necessarily helical, which could also lead to the observed differences in physical properties.

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CHAPTER IVEXPERIMENTAL DETAILS4-1 Polystyrene Samples(a) Atactic polystyrene

Samples S103, S108 and S109 were supplied by Dr. J.F. Rudd, Dow Physical Research Laboratories (Midland, Michigan, U.S.A.). They had weight average molecular weights of 124700, 267000 and 193000 with an M_w/M_n ratio of 1.05, 1.08 and 1.06. All gave amorphous X-ray diffraction patterns.

(b) Preparation of isotactic polystyrene

The preparation was carried out in a manner suggested by the results of Overberger et al.¹ using the heterogeneous catalyst formed from a 3:1 triisobutyl aluminium-titanium tetrachloride mixture.

After baking in an air oven for 2 days at 140-160°C, the apparatus (figure 4-1.1) was assembled as quickly as possible, evacuated immediately and then flushed with carefully purified nitrogen. The procedure was repeated on two further occasions after which the mercury-sealed Teflon blade stirrer was placed in position while a positive nitrogen pressure into the apparatus was maintained. Eighty ml. of triisobutyl aluminium (Ethyl Corporation, New York, U.S.A.) was distilled under reduced pressure at 114-116°C into funnel A while at the same time 17 ml. of titanium tetrachloride (B.D.H.) which had been previously refluxed with finely divided copper (E. Merck, Darmstadt, Germany) under nitrogen for three hours, was distilled at 136°C into funnel B. The two catalyst components were then added dropwise with stirring into the

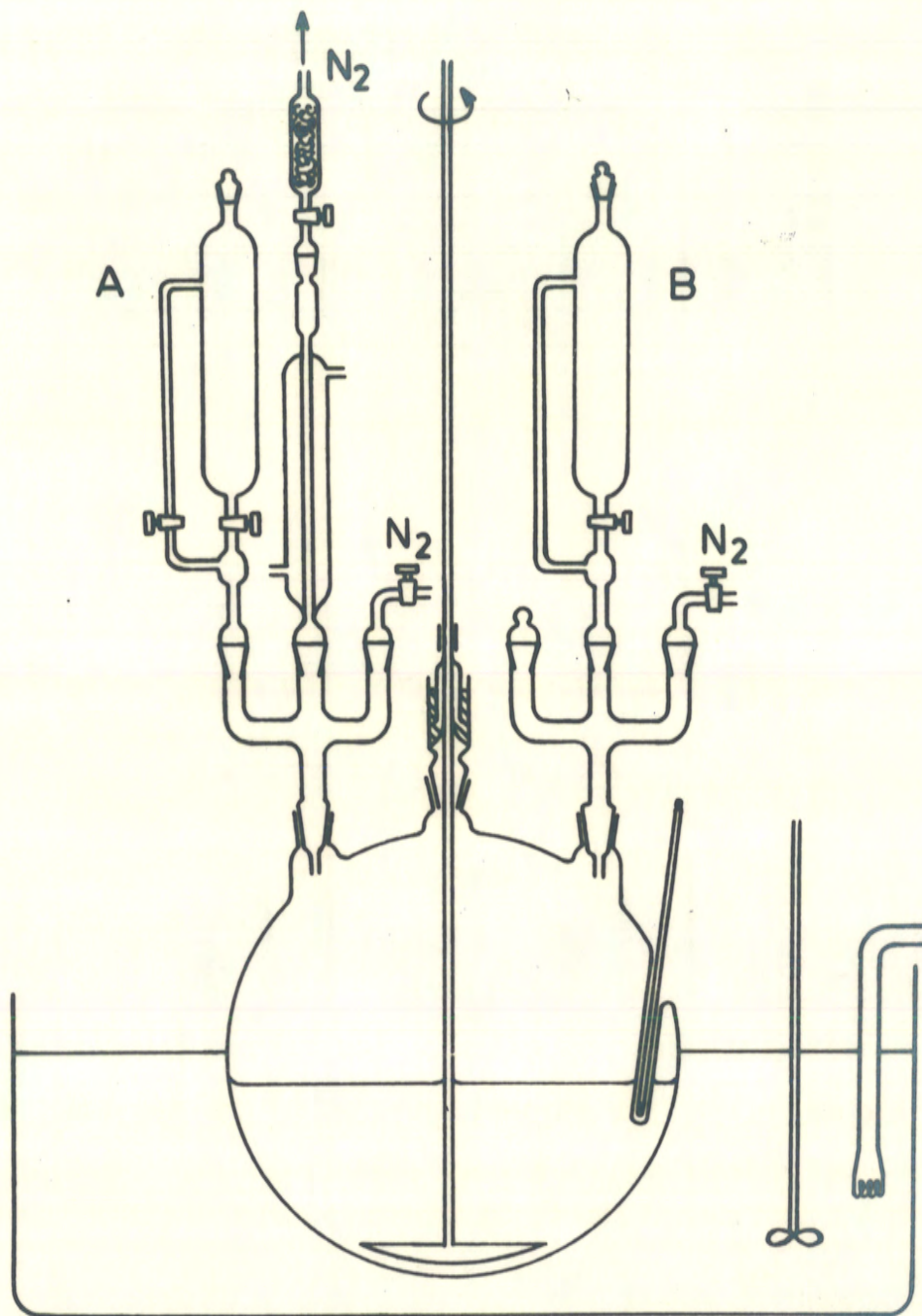


Figure 4-1.1. Apparatus for the preparation of isotactic polystyrene.

ice-cooled reaction vessel at such a rate that the temperature remained below 20°C as the brown solid catalyst formed. Two hundred ml. of purified n-heptane were fractionally distilled into funnel A and then added to the catalyst complex. Finally 200 ml. of purified styrene were introduced into the stirred catalyst suspension via funnel A while the temperature was maintained at 0-10°C. The temperature of the reaction mixture was gradually raised to $70 \pm 0.5^\circ\text{C}$ with a Sunvic controlled oil bath. After 21 hours at this temperature the reaction flask was cooled to 0-5°C and 400 ml. of methanol were very slowly added to the reaction product from funnel A followed by stirring for one hour. The crude polymer, after recovery by filtration, was washed repeatedly with 10% hydrochloric acid in methanol to remove the catalyst. After further washing with methanol to remove the acid the dried product was refluxed with boiling n-heptane for 10 hours. The filtered polystyrene, after drying, was repeatedly treated with methyl ethyl ketone² for periods of about 4 hours to remove atactic polystyrene from the insoluble isotactic form.

Two preparations were carried out and the product with the higher melting point was used in subsequent work. Verification of stereoregularity was made by X-ray diffraction and infra-red spectroscopy using annealed films (sections 2-2c and 2-5b). An attempt to determine the molecular weight by viscometry in toluene and benzene was unsuccessful due to the fact that a considerable proportion of the product was insoluble in these solvents.

(c) Purification of reagents

(1) Oxygen-free nitrogen (Commonwealth Industrial Gases, Torrens-ville, S.A.) was purified by passage through two liquid air traps, a Drierite (anhydrous calcium sulphate) tower and tri-isobutyl aluminium.

(2) After removal of the inhibitor by shaking repeatedly with 5% sodium hydroxide, styrene (C.S.R. Chemicals) was washed several times with water, dried by standing over fused calcium chloride in the dark at -5°C for several days and then vacuum distilled prior to storage at a low temperature over molecular sieves. Immediately before use the required quantity of styrene was re-distilled on a vacuum-line into a vessel which could be inverted directly over one of the funnels in the apparatus shown in figure (4-1.1).

(3) Normal heptane (May and Baker) which had been shaken several times with concentrated sulphuric acid and washed with water several times, was passed through an alumina column, ^{3a, 3b} collected over anhydrous magnesium sulphate and then fractionally distilled. The fraction coming over at $95-99^{\circ}\text{C}$ was stored over sodium wire for a day prior to refluxing for 6 hours over fresh sodium wire. It was used as described under section (4-1b).

(4) After a small quantity of fractionated AR methanol had reacted under reflux conditions with resublimed iodine and clean dry magnesium turnings, ^{3b} a large amount of methanol was added and then distilled to give the dry product. ³

(5) Methyl ethyl ketone was passed through an activated alumina column and then dried over anhydrous potassium carbonate for two days. The fraction of boiling point 79.5°C was collected on fractional distillation.

4-2 Fractionation of Isotactic Polystyrene

(a) Dissolution of the polymer

To the vacuum dried isotactic polystyrene was added a small volume of toluene which had been purified by refluxing over mercury and dried over sodium wire before distillation. After standing for two days the volume was made up to 500 mls. When dissolution was not apparent after some time, the mixture was heated at approximately 100°C for several hours. The considerable amount of gel^{4,5} which remained insoluble, was removed by centrifugation for 30 minutes at 20,000 r.p.m. using a Spinco model L preparative centrifuge. The centrifugate was then made up to 2.5 litres with toluene to give the stock solution which was used in the five subsequent fractionations.

(b) Fractionation procedure

As fractionation of isotactic polystyrene by the addition of methanol to a solution in toluene had been reported to present no difficulties,⁶ this method was used in the first attempt. The fractionation apparatus has been previously described.⁷

A measured volume of methanol was added to the isotactic polystyrene solution (500 mls. of stock solution made up to 2.5 litres with toluene) through a fine jet into the outer portion of the vortex created by stirring of the solution. The temperature was maintained at 30°C by means of a water-bath. A stage was eventually reached at which the solution suddenly became opalescent due to the onset of phase separation. After the addition of a slight excess of non-solvent the fractionation vessel was placed in another water-bath which was slowly

heated (usually to about 40°C) until the turbidity disappeared. The homogeneous solution was then run into a large flask which was placed in the water-bath at 30°C and left overnight. The re-precipitated phase, which had been separated from the supernatant solution by decanting the latter back into the fractionation vessel, was dissolved in hot toluene and then the isotactic polystyrene fraction was precipitated by spraying⁸ the resultant solution into methanol. Addition of more methanol to the original bulk solution yielded further fractions.

The use of methanol as a non-solvent led at all stages of the fractionation to the precipitation of a considerable amount of solid polymer on the stirrer due to a local high concentration of non-solvent at the point of entry to the solution. The problem was not eliminated by use of a spray technique.⁸ For this reason the remaining four fractionations were carried out using a 60% methanol-40% toluene mixture as non-solvent. Each fractionation yielded 8-10 fractions.

(c) Characterization and combination of fractions

A rough check on tacticity was obtained by determining the melting point (see section 4-3b) of each fraction, small quantities of which had been refluxed for 4-5 hours with boiling n-heptane. A sharp melting point of $230 \pm 2^\circ\text{C}$ was obtained in all cases.

Viscometry in benzene at 30°C (see section 4-4) yielded molecular weights which varied between 3.6×10^4 to 3.9×10^6 for the various fractions.

On the basis of their molecular weights, suitable fractions

were combined while still in solution to give seven final fractions, F1-F7. A rough check on dispersity by turbidimetric titration,¹⁰ using isopropanol as non-solvent, indicated the presence of a small amount of high molecular weight species in the low molecular weight fractions (figure 4-2.1). As a consequence the combined fractions were roughly re-fractionated by discarding the first trace of precipitant which appeared on addition of non-solvent to solutions of the fractions.

4-3 Solid State Characterization of Polymers

(a) X-ray diffraction

X-ray diffraction photographs were taken with a Philips PW1010 instrument.

(1) Polystyrene

Isotactic polystyrene powder specimens, which had been annealed in boiling n-heptane⁹ for 16 hours and dried in an oven at 160°C for several hours, were packed into quartz capillaries and rotation powder photographs were taken with nickel-filtered CuK α radiation on flat Industrial (Ilford) G, X-ray film. The sample to film distance was 4 cm. and the exposure time 1-2 hours. In some cases the X-ray photographs were taken with a Philips PW1024 powder camera. A small pellet was used in the case of atactic polystyrene.

The X-ray diffractograms were obtained from the films by using either a Spince Model RB Analytrol or a Joyce-Loebl densitometer (Gateshead, England). Analysis of the diffractograms to give the degree of crystallinity of each isotactic fraction was carried out in

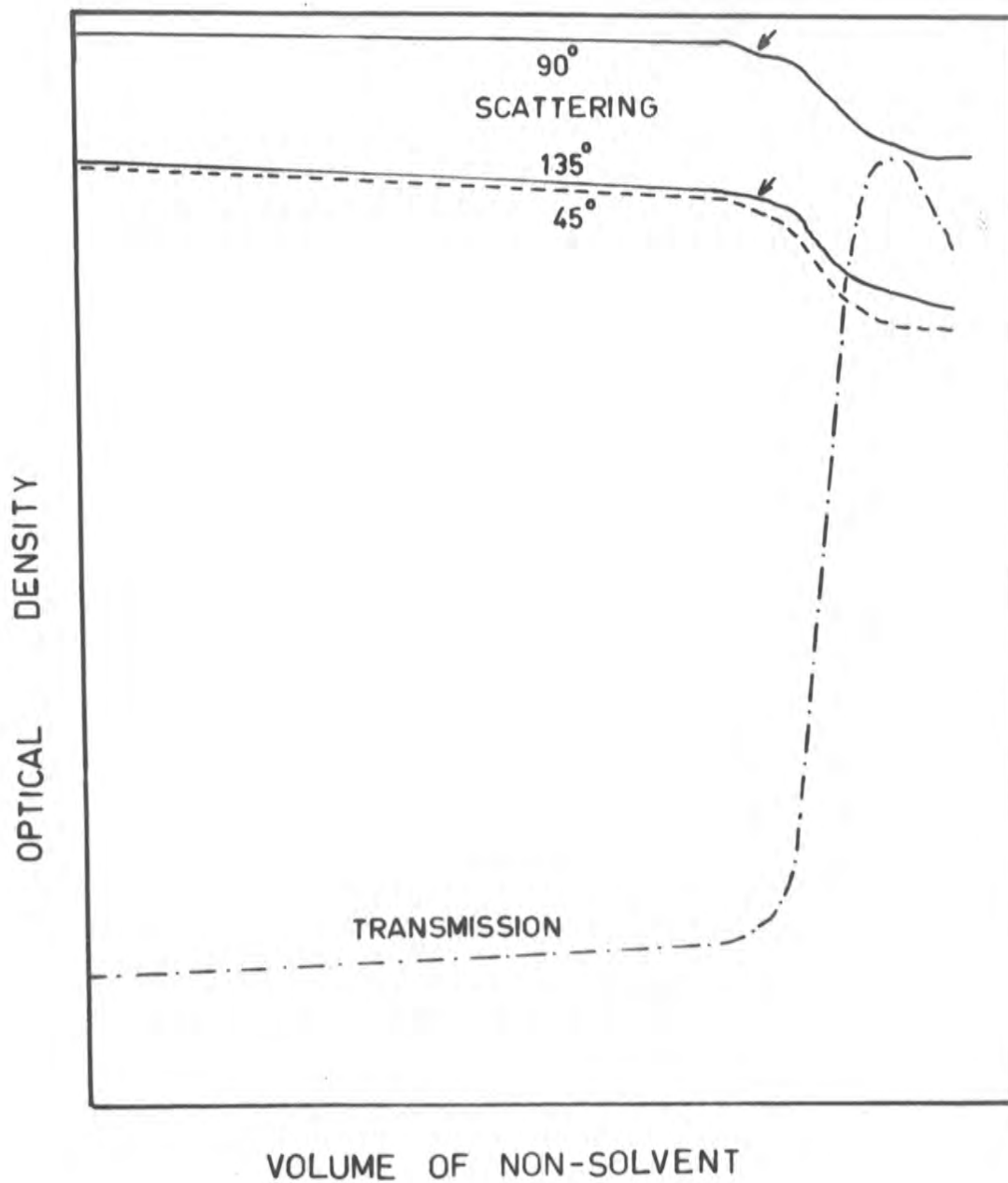


Figure 4-2.1. Turbidimetric titration of Y3 in benzene ($n = 1.50$) with isopropanol ($n = 1.38$) as non-solvent. Arrow indicates precipitation of a trace of high molecular weight species.

the manner proposed by Natta¹¹ and used subsequently by Takeda and co-workers.¹² Guided by the work of Challa et al.¹³ a diffraction curve for atactic polystyrene was constructed above the base line of the diffractogram for each isotactic sample.

(2) Polystyrene sulphonic acid

Short lengths (1.5-2 cm.) of quartz capillaries, sealed at one end, were inverted in small volumes of concentrated solutions of polystyrene sulphonic acid or the sodium polysalt. By momentary evacuation within a desiccator followed by restoration of the pressure, the capillaries were filled with the polyelectrolyte solution. They were then supported vertically in a desiccator over phosphorus pentoxide at room temperature until evaporation was complete and then the procedure was repeated on two further occasions. After heating the final samples over phosphorus pentoxide at 90-100°C for several days X-ray photographs were taken as described above. An attempt was made to obtain specimens suitable for X-ray analysis by evaporation of concentrated solutions on glass slides followed by transfer of the solid to the capillary tubes.

(b) Melting point determination

The melting points of the polystyrene fractions were determined with the aid of a Cooke polarising microscope while raising the temperature of an associated microfurnace⁸ by about 0.5-1.0°C per minute. The melting point was taken to be the temperature at which the polystyrene particles on the quartz slide of the furnace assumed globular shape and birefringent effects disappeared. The original

apparatus, described by McKeown,¹⁴ was modified and calibrated by Schultz.¹⁵

(c) Specific volume

The density of the same films that had been used for the infra-red analysis were determined by a flotation method^{12,16} using sodium chloride solutions of known density as the flotation medium. By dilution of 2.470 molar sodium chloride solution at 25°C, a series of eight sodium chloride solutions each differing in density by 0.002 gm.cc.⁻¹ were prepared with the lowest density being 1.069 gm.cc.⁻¹ at 25.0°C. Pyrex tubes, fitted with stoppers, were filled to 3 cms. from the top with these solutions and clamped vertically to a vibration-free support so that they were almost immersed in a water-bath at 25.00°C. After temperature equilibration of the solutions fragments of polystyrene film which had been washed in methanol to improve their wettability,¹⁷ were carefully immersed in the sodium chloride solutions. The density of the film (± 0.001 gm.cc.⁻¹) corresponded to that of the solution in which it remained suspended over a period of two to three hours. The densities of the solutions were determined by pycnometry and found to agree with the value calculated from the known molarity, c , using the equation,¹⁸

$$\rho = 0.997045 + 0.04210c - 0.002147c^{3/2}.$$

(d) Infra-red analysis

The infra-red analysis was carried out by using a Perkin-Elmer double beam spectrophotometer (model 21) with NaCl optics (1500-800 cm.⁻¹) and KBr optics (1050-400 cm.⁻¹).

(1) Polystyrene

The preparation of polystyrene films which gave consistent results proved troublesome,¹⁷ but the difficulty was satisfactorily overcome by adding three drops of a solution containing 0.04 gm. sample in 1.5 ml. of chloroform to a microscope slide and then, after evaporation was complete, adding a two further layers. The dried films were annealed in an air oven at 175°C for 16 hours and then slowly cooled to room temperature.

The relative intensities of the required absorption bands were determined by drawing base lines¹⁷ as shown in figure (4-3.1).

(2) Polystyrene sulphonic acid

Due to hygroscopic nature of the polyacid the potassium bromide-disc technique described by Hart and Janssen¹³ was used. Between 0.011-0.012 gm. of polystyrene sulphonic acid and 0.23 gms. of potassium bromide were dissolved in 4-5 mls. of conductivity water in a small freeze-drying tube. The freeze-dried products were dried for 2 days in vacuo over phosphorus pentoxide before being pressed into almost transparent discs in a hydraulic moulding press. The samples were stored in the dark in a desiccator over phosphorus pentoxide when not being used.

4-4 Viscosity

The Ostwald viscometer used was British Standards Specification²⁰ design (No. 1) with the exception that a mixing bulb was added above the solution reservoir to allow dilutions to be made within the viscometer. The dimensions of the viscometer were such that

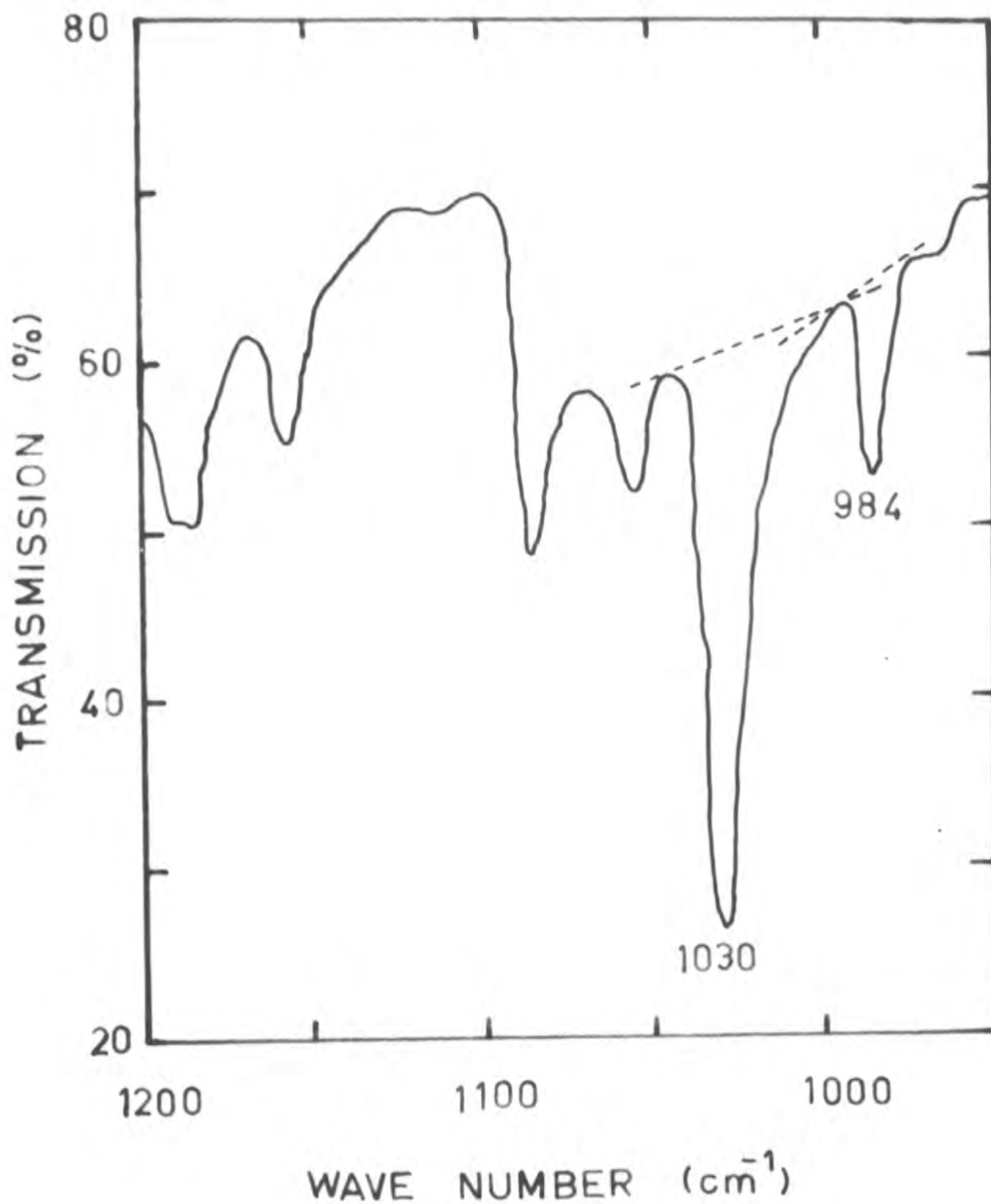


Figure 4-3.1. Infra-red spectrum of isotactic polystyrene showing the method of drawing base-lines for the determination of crystallinity (private communication with K. Iimura).

the kinetic energy correction and end effect could be regarded as negligible in the present work.

(Capillary length 12 cms.; working volume, 10.30 ml.; water flow-time at 30.00°C, 256.1 sec.)

(a) Polystyrene in benzene

Freeze-dried polystyrene samples which had been dried to constant weight at 60°C in vacuo, were dissolved in 50 mls. of benzene at 30.00°C in standardised flasks by the normal procedure.²¹ With fraction, F5, a trace of undissolved polymer was removed by pressure filtration at a slow rate through a sintered glass filter (porosity 4). Evaporation of portions of the filtered solution in gold-plated, stainless steel, weighing bottles showed that the insoluble material was a negligible part of the total fraction.

After determining the flowtime of benzene at $30.00 \pm 0.005^\circ\text{C}$ to ± 0.1 second, suitable volumes of stock polystyrene solution were added and, after thorough mixing with dry air or nitrogen and adjustment of the levels, the flowtimes, t , of different concentrations of the polymer were measured. With the reasonable assumption that the density of solvent and solution were equal at the concentrations used in this work, the relative viscosity, η_r , for each polymer solution was calculated from the ratio of flowtimes for solution and solvent. The intrinsic viscosity was then obtained from the common intercept²² of plots of η_{sp}/c and $\frac{1}{c} \ln \eta_r$ against concentration.

(b) Polystyrene sulphonic acid solutions

The Ostwald viscometer was also used to determine the temperature dependence of the reduced viscosity of atactic and isotactic polyacids.

The flowtime of double distilled de-ionized water was determined at a number of temperatures between 20°C and 85°C in a water bath using a closed circuit to minimise evaporation. The experiment was then repeated using isotactic (F3-H) and atactic (S103-H) polystyrene sulphonic acid solutions at a concentration ($5-6 \times 10^{-3}$ gm.dl.⁻¹) at which the rate of change of reduced viscosity with concentration²³ was small. Dissolved air was removed from the solutions at the beginning of each series of experiments by reduction of the pressure above the solution in the viscometer.

The relative viscosity of the solutions at each temperature was determined from the ratio of the flowtime for the solution to that interpolated for water from a calibration graph. Reduced viscosities were then calculated using concentrations which had been corrected for density changes²⁴ due to the variation in temperature.

4-5 Osmotic Pressure Measurements

(a) Apparatus

The osmometer used was the Pinner-Stabin³² type supplied by Polymer Consultants Ltd., England. After the reference and solution capillaries had been vertically aligned they were shown to be a matched pair by gradually adding solvent to the outer jacket and then measuring the solvent level in each capillary with a cathetometer reading to 0.001 cm.

Ultracella "feinst" membranes from Membranfilter Gesellschaft (Göttingen, Germany), supplied in aqueous ethanol, were conditioned by transferring at 24 hour intervals to solutions of 50% ethanol-water, 75% ethanol-water, ethanol (twice), ethanol-25% benzene, ethanol-50% benzene, ethanol-75% benzene and finally 100% benzene in which they were stored for 48 hours before use.

(b) Measurement of osmotic pressure

After assembling the osmometer in a water bath with temperature control to $30.00 \pm 0.005^\circ\text{C}$, the membranes were tested for leakages as suggested by Pinner.²¹ If they proved satisfactory (on most occasions this was not the case) a zero correction arising from surface inequalities of the membranes was determined by measuring the difference in capillary levels with benzene inside and outside the osmometer. When this zero correction was small (less than 0.02 cm.) and reproducible, the membranes were regarded as satisfactory. The solvent from within the osmometer was then replaced with the polystyrene solution (F3 in benzene) of lowest concentration using the procedure described by Pinner. The menisci were observed with a cathetometer over a period of several hours until the solution level remained constant. The operation was then repeated with progressively stronger solutions.

(c) Calculation of results

The osmotic pressure which was recorded for each solution as a height, h , in cms. of solution, was corrected for the zero error and then calculated in atmospheres using the expression,

$$\pi \text{ (atmos.)} = \frac{hp}{1033.3}$$

where ρ is the density of the solution in gms. per cc. With R set as 82.06 cc.-atm. deg.⁻¹ mole⁻¹, $(\pi/cRT)^{1/2}$ was plotted against c (gm.cc.⁻¹) to give a linear plot from the intercept and slope of which the number average molecular weight and second virial coefficient respectively were calculated.

4-6 Sedimentation Studies

(a) Experimental procedure

Sedimentation measurements were carried out with a Spinco Model E ultracentrifuge equipped with a schlieren optical system and an RTIC temperature control unit. The rotor speed was measured by taking odometer readings with a stopwatch over periods of at least 30 minutes during a run. The cells were of the aluminium centre-piece type with an optical thickness of 12 mm.

The experimental procedure was similar to that described by Billick.²⁵ Acceleration of the rotor was carried out at constant current until the final speed of 59,780 r.p.m. had been reached, with the zero time of sedimentation being taken as that when the rotor had attained two-thirds of its final speed. The automatic camera was started after the peak had resolved. Photographs of the schlieren pattern were taken on Kodak Scientific Plates, IIG. Some of these are shown in figure (4-6.1).

(b) Measurement of plates

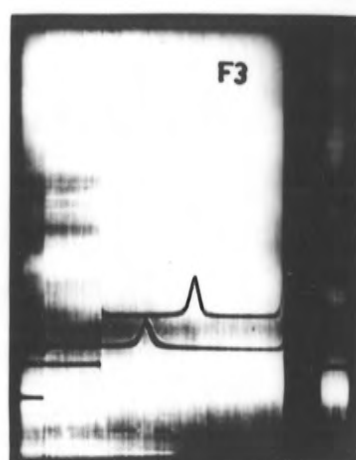
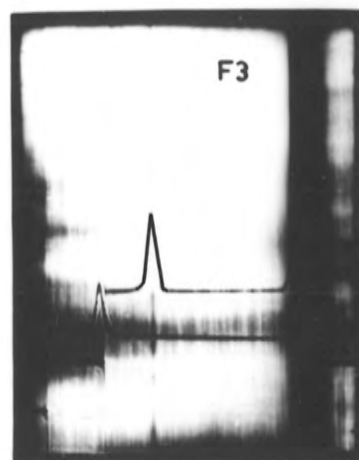
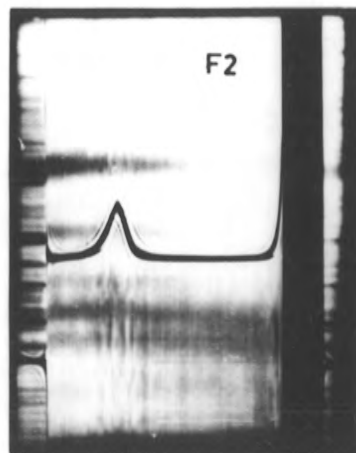
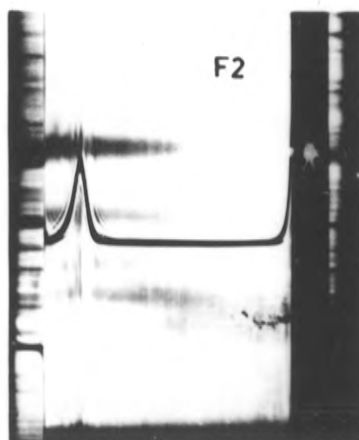
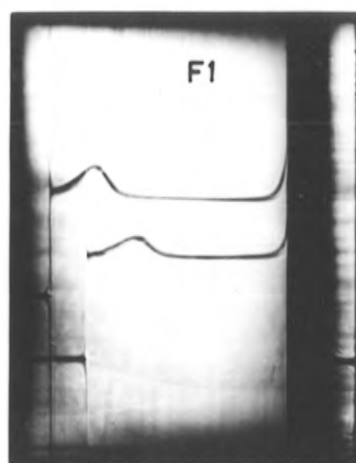
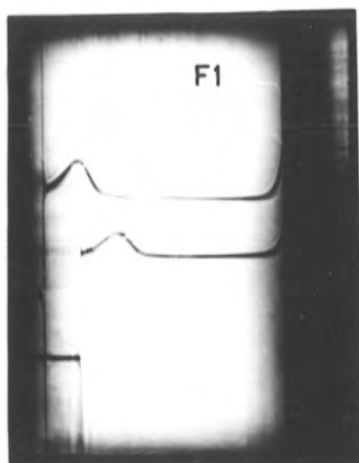
Measurements of the position of the maximum of the refractive

Figure 4-6.1a. Ultracentrifugation of isotactic polystyrene fractions in benzene at 30°C. Speed 59,650 r.p.m.

F1 Concentrations, 0.635₄ and 0.849₇ gm. dl⁻¹.
Time, 51 min. 8 sec. and 67 min. 8 sec.

F2 Concentration, 0.801₀ gm. dl⁻¹.
Time, 50 min. 19 sec. and 86 min. 19 sec.

F3 Concentrations, 0.476₈ and 0.625₂ gm. dl⁻¹.
Time, 52 min. 6 sec. and 100 min. 6 sec.



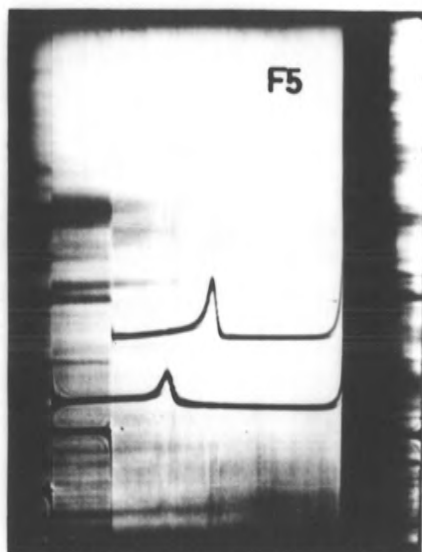
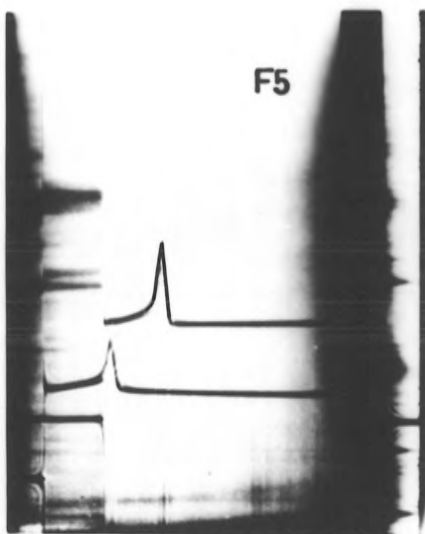
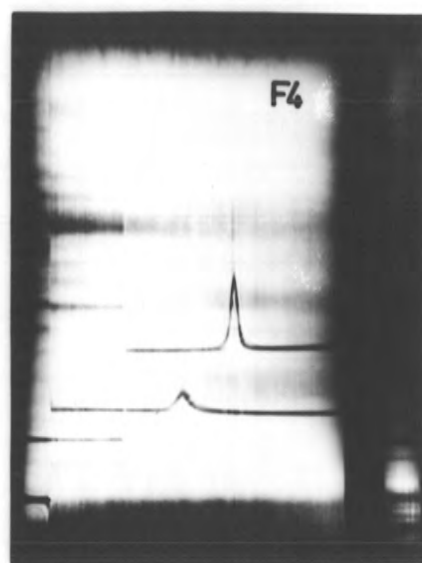
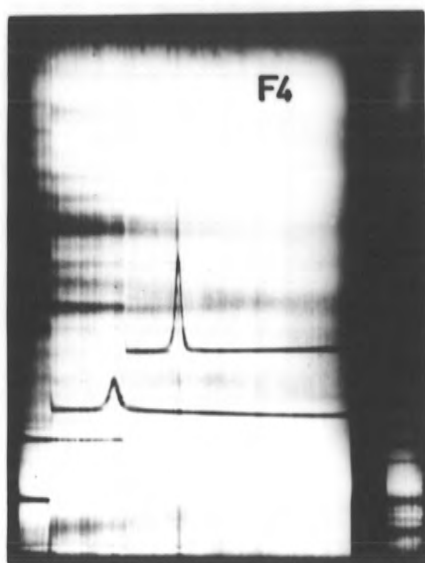


Figure 4-6.lb.

F4 Concentrations, 0.191_0 and 0.368_0 gm. dl.⁻¹.
Time, 36 min. 39 sec. and 76 min. 39 sec.

F5 Concentrations, 0.439_8 and 0.586_6 gm. dl.⁻¹.
Time, 43 min. 59 sec. and 79 min. 59 sec.

index gradient were made with either a Pye two dimensional comparator reading to 0.01 mm. or a two dimensional microcomparator (Optical Measuring Tools Ltd., Maidenhead, England) capable of reading to 0.002 mm. and fitted with a projection screen. Several readings were taken of the distance of the maximum of the schlieren peak from the reference line which was assumed to be 7.346 cms. from the axis of rotation as suggested by Schachman.^{26a} The distance, x , of the peak maximum from the axis of rotation was then calculated from the optical magnification factor.²⁷ The true position of the meniscus, x_0 , was measured by assuming that it was situated at a position one-third of the width of the meniscus image in from the top of the solution column.²⁸

(c) Calculation of results

Calculation of the values of $\ln x_0$, s^0 and B in equation (2-8.8) were determined from values of $\ln x$ and t using a least squares program with a 1620 computer.²⁹

A check on the effect of small errors, δ , in zero time was made by processing one set of results in which the measured time, t , was replaced by $(t + 30)$ seconds.

Time (secs.)	$\ln x_0$	Coefficient of $\omega^2 t$	Coefficient of $(\omega^2 t)^2$
t	1.791 ₆	4.400×10^{-13}	$12.18_1 \times 10^{-26}$
$(t + 30)$	1.790 ₅	4.430×10^{-13}	$12.05_9 \times 10^{-26}$

Even by the assumption of this abnormally high error in time the effect on the coefficients was small as had originally been pointed out by

Billick.²⁵ This was also suggested by substitution of $(t + \delta)$ in equation (2-8.8) to give

$$\ln x = (\ln x_0 + s_0^0 \omega^2 \delta - B \omega^4 \delta^2) + (s_0^0 - 2B\delta) \omega^2 t - B \omega^2 t^2 + \dots,$$
 and then substituting values of s_0^0 , B , ω^2 and δ for a given run.

The standard error, σ , of the pressure dependence parameter, μ , was calculated from the computed standard errors of s_c^0 , B and α using the following relation,⁵¹

$$\sigma^2 = \left(\frac{\partial \mu}{\partial s}\right)^2 \sigma_s^2 + \left(\frac{\partial \mu}{\partial B}\right)^2 \sigma_B^2 + \left(\frac{\partial \mu}{\partial \alpha}\right)^2 \sigma_\alpha^2$$

In determining the pressure dependence parameter of the sedimentation coefficient by the Cantow method, allowance was made for the fact that the distance of the meniscus from the axis of rotation varied slightly in different experiments. For the ultracentrifuge run in which the meniscus distance was greatest, sedimentation coefficients were calculated at distances of 0, 0.1, ... 0.7 cm. below the surface. For other experiments at different concentrations of polymer the distance below the meniscus at which the pressure was identical to that at each of the above positions was determined. This enabled the sedimentation coefficients (calculated from the least squares equation for the lines in figure 2-8.4) at the same pressure to be obtained as a function of concentration as shown by the plots in figure (2-8.5).

- (d) Data for calculation of molecular weight from the Mandelkern-Scheraga equation

\bar{v}_2 for polystyrene in benzene, 0.917₅ ml. gm.⁻¹ 30,31

ρ of benzene at 30°C, 0.8681_g gm. ml.⁻¹ found experimentally, agreed with the interpolated value given in Landolt-Börnstein,³²

η of benzene at 30°C, 5.61×10^{-3} poises,³³

and $0.97 \phi^3 P^{-1}$ for polystyrene in benzene was taken to be 2.60×10^6 as given by Kurata and Stockmayer.³⁴

(e) Calculation of the pressure dependence coefficient of the sedimentation coefficient

Andersson³⁵ has pointed out that the pressure dependence coefficient of the sedimentation coefficient is given by

$$\mu = \lambda' + [\bar{v}_o \rho_o (\beta - \varphi)] / (1 - \bar{v}_o^p \rho^p) \quad (4-6.1)$$

in which λ' , φ and β are the pressure coefficients of the solvent viscosity, the partial specific volume of the solute in the solvent and the density of the solution respectively with the value of φ being about one-fifth of the value of β .

A rough estimate of μ for the polystyrene-benzene system was obtained from the average of the interpolated values of 8×10^{-10} cm.² dyn.⁻¹ for λ' and 9.3×10^{-11} cm.² dyn.⁻¹ listed by Baldwin and van Holde³⁶ for the pressure range 0-200 atmospheres. Assuming that the value of $\bar{v}_o \rho_o$ (0.803) differs only slightly from that of $\bar{v}_o^p \rho^p$ (see Andersson's data for polystyrene in toluene below) equation (4-6.1) gives a value of 11×10^{-10} cm.² dyn.⁻¹ for μ . This value compares favourably with those previously reported for the polystyrene-toluene system:-

Andersson³⁷ - 9.9×10^{-10} at 1 atmosphere and 9.7×10^{-10}

at 100 atmospheres, calculated experimentally at 20°C,

Billick²⁵ and Cantow et al.³⁸ - 10×10^{-10} cm.² dyn.⁻¹,

calculated at 25°C from data listed in literature.

4-7 Sulphonation of Polystyrene Samples

Sulphonation of polystyrene has been achieved by a number of methods including the use of concentrated sulphuric acid at high temperatures in the absence^{39,40} and in the presence of silver sulphate^{41,82} as a catalyst as well as the use of a cold sulphonating mixture of anhydrous sulphur trioxide in suitable organic solvents.^{40, 42-44} Recently however a technique has been developed by Turbak⁴⁵⁻⁴⁷ using a triethyl phosphate-sulphur trioxide technique which gives water soluble products with a minimum amount of cross-linking due to sulphone formation.

(a) Preparation of liquid sulphur trioxide

Liquid sulphur trioxide was prepared by a technique similar to that described by Partington and Vogel.⁴⁸ This involved the heating of an excess of phosphorus pentoxide with 20% oleum (Adelaide Chemical and Fertilizer Co., South Australia) in an oil bath and condensation of the vapour to monomeric liquid sulphur trioxide with the temperature at 30°C in order to minimise the formation of the solid polymeric α -form which is unsuitable for use in the sulphonating procedure.⁴⁵

(b) Initial attempts to sulphonate polystyrene⁴⁰

A solution of either isotactic polystyrene, GPS II, or

atactic polystyrene in purified chloroform^{54d} was cooled in dry-ice, treated with a calculated amount of sulphur trioxide dissolved in a dichlorodiethyl ether-chloroform mixture⁴⁰ and then left for up to 5 hours. The product, which was vacuum dried for 1-2 days after repeated washings with chloroform, was added to a large volume of water but in many preparations always gave a viscous solution containing a high percentage of gel. In one case a sulphonated CPS II fraction in water was freed of both gel by centrifugation and simple ionic impurities by passage through a mixed bed resin column before recovery by freeze-drying. The small yield of product was soluble in water and by titration with standard sodium hydroxide was shown to have an equivalent weight of 271 ± 1 which corresponds to a low degree of sulphonation. The ultraviolet spectrum was typical of that for polystyrene sulphonic acid with molar extinction coefficients of 303 and 281 at 2615\AA and 2555\AA respectively. The charge fraction, found by Mock and Marshall,⁴⁹ was 0.38 ± 0.01 and independent of concentration while the equivalent conductance was found to vary from $137\text{--}142 \text{ cm.}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$ at concentrations of $8\text{--}30 \times 10^{-5}$ equivalents per litre at 25°C . For the latter measurements a conductance cell (cell constant $5.66 \times 10^{-2} \text{ cm.}^{-1}$) associated with an Ubbelohde viscosimeter was used. The reduced viscosity in water of specific conductance $0.3 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$ was $400\text{--}500 \text{ dl. gm.}^{-1}$ at 25°C . Because of the low degree of sulphonation and high gel content of the initial product the above sulphonation procedure was not used for the fractionated polystyrene samples.

(c) Sulphonation using the Turbak method

(1) Preparation

In the absence of detailed information from the patent literature⁴⁷ at the time and the desirability of obtaining the poly-acid rather than the sodium salt the original Turbak method was slightly modified.

An approximately 1% (w/v) solution of polystyrene was prepared by standing 0.5-1.0 gm. polystyrene samples over freshly purified chloroform in a desiccator in the dark for two days. A calculated quantity of triethyl phosphate (B.D.H., purified by distillation under reduced pressure in dry nitrogen at 75°C) was added to 20 mls. of chloroform^{54d} through a rubber seal into a two-necked flask fitted with a mercury-seal stirrer. After cooling the solution to -50°C in an ice-salt bath a calculated volume of liquid sulphur trioxide (S.G. = 1.92),⁵² slightly in excess of that required for 1:1 sulphonation of polystyrene, and sufficient to form a 3:1 complex with the triethyl phosphate, was then added with a syringe in about two minutes and the mixture was slowly stirred for 5 minutes.⁴⁷ The solution of polystyrene was then introduced in 2-3 minutes with stirring to give an immediate white precipitate. After a further 10-15 minutes stirring the sulphonated product was rapidly filtered with a sintered glass funnel and washed repeatedly with chloroform to remove triethyl phosphate and any excess sulphur trioxide. The faintly off-white solid was dissolved in double-distilled water and then passed through a mixed bed of Amberlite IR-120(H) and IRA-400(OH) resins to remove traces of sulphuric acid before dialysing for 6 days

against distilled water using Dexstar dialysis tubing No. 18/32. (The tubing had been previously warmed with 5% sodium bicarbonate solution at 80°C for 30 minutes to remove plasticizer and other impurities and then washed and soaked in distilled water for 1-2 days). The solid polystyrene sulphonic acid was obtained by freeze-drying and stored in a desiccator under reduced pressure over phosphorus pentoxide, in the dark. This procedure completely prevented the tendency of the polyacid samples to discolour on storage.

(2) Test for absence of crosslinking

The possibility of crosslinking due to sulphone formation was checked by sedimentation of solutions of polystyrene sulphonic acid in potassium chloride solution. Figure (4-7.1) shows that no high molecular weight material is present in the sample as no small peak in advance of the main peak is apparent in the sedimentation pattern.⁸² Small convection spikes, typical of those discussed by Schachman,^{26b} were evident in some sedimentation patterns.

(d) Preparation of the sodium polysalts

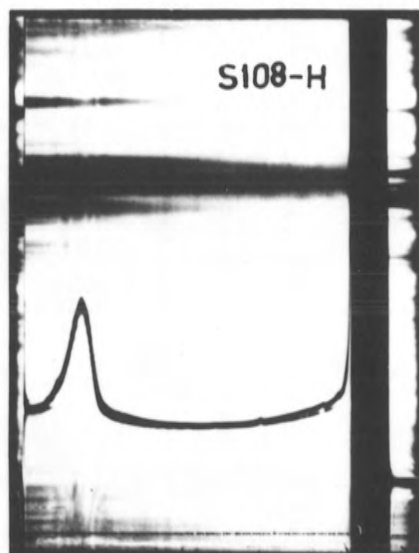
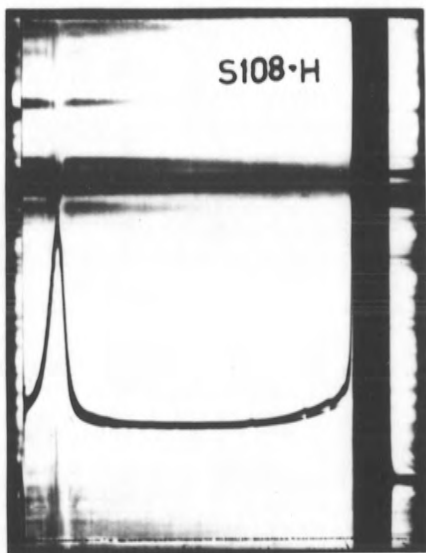
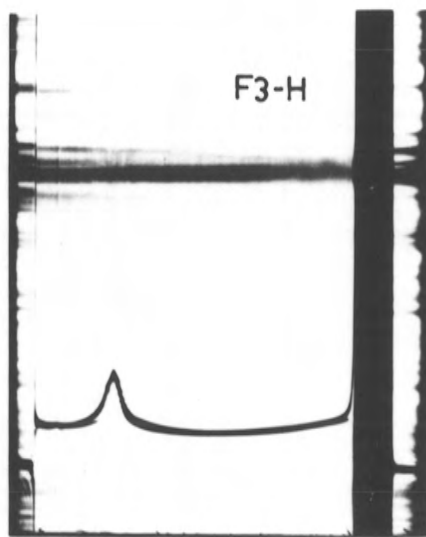
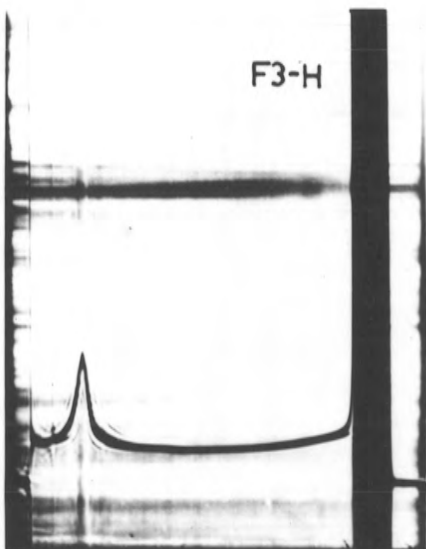
A small calculated excess of sodium hydroxide solution was added to a known weight of polystyrene sulphonic acid in water and the resultant solution was then dialysed for 6-8 days against distilled water. The solid samples were recovered by freeze-drying.

(e) Attempted hydrolysis of polystyrene sulphonic acid to polystyrene

Aqueous solutions of polystyrene sulphonic acid (1% w/v)

Figure 4-7.1. Ultracentrifugation of 0.44% isotactic polystyrene sulphonic acid, F3-H, in 0.84M KCl at 50,740 r.p.m. after 29 and 45 minutes.

Lower photographs with 0.52% 5108-H in 1.00M KCl after 31 and 47 minutes showing the convection that sometimes occurred. Temperature, 21°C. Diaphragm angles 70° and 60° respectively.



were heated with about 50% aqueous sulphuric acid or phosphoric acid in sealed glass tubes for 10-20 hours at temperatures ranging from 80°C to 140°C. No change occurred below about 110°C after which extensive degradation took place.

4-8 Analysis of Polystyrene Sulphonic Acid and its Sodium Salt

(a) Equivalent weight of the polystyrene sulphonic acids

A concentrated carbonate-free sodium hydroxide solution, prepared in the usual manner,^{54a} was diluted to a concentration of 0.017-0.02 molar with conductivity water. This solution was then standardised by titration against weighed quantities of stock solutions of potassium hydrogen phthalate^{54b} (A.R.) and potassium acid iodate^{54c} (made up by weight in conductance water) using thymol blue as indicator. In some cases standardised hydrochloric acid was also used as a check.

To avoid degradation^{49,50} the freeze-dried polystyrene sulphonic acid samples (usually 0.1-0.2 gm.) were dried in pyrex weighing bottles at 67°C in a vacuum oven over phosphorus pentoxide. The weighing bottles were always cooled in a desiccator over phosphorus pentoxide for twenty minutes prior to re-weighing. The samples, which were weighed to ± 0.0001 gm. with a Mettler B5 balance, were found to take 3-6 days to reach constant weight.

The polystyrene sulphonic acid solutions were made up by weight in steam-cleaned polythene vessels using conductance water ($0.15-0.25 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$) and stored in the refrigerator at 5°C when not being used.

To determine the equivalent weight of the polystyrene sulphonic acid, weighed portions of the stock solution were titrated against the standardised sodium hydroxide either potentiometrically or with thymol blue as indicator. The calculated equivalent weights and molecular weights of the polyacids are listed later in table (4-8.1).

(b) Ultraviolet spectrophotometry

(1) Ultraviolet spectrum

A Unicam SP500 spectrophotometer was used to obtain the ultraviolet spectrum of aqueous solutions of polystyrene sulphonic acid and its sodium salt.⁸² This is shown in figure (4-8.1) in the wave-length range required in this work. The accuracy of the optical density scale was checked by measurements with standard potassium chromate solution⁵⁵ in the required wave-length range. A small correction was found necessary at the two absorption maxima 255.5 and 261.5 m μ used in this work, in addition to that due to imperfect matching of the silica cells (0.5, 1.0, 2.0 and 4.0 cms.).

(2) Concentration dependence of the optical density

This was determined by the progressive addition of stock polyacid solution to a known mass of water contained in the cell by means of an "Agl" micrometer syringe (Burroughs Wellcome Ltd., London) fitted with a glass or stainless steel needle. Mixing of the solution was achieved by means of a small platinum stirrer onto which the tip of the needle was touched after each addition from the syringe. Reproducibility of measurements was good. From the results,

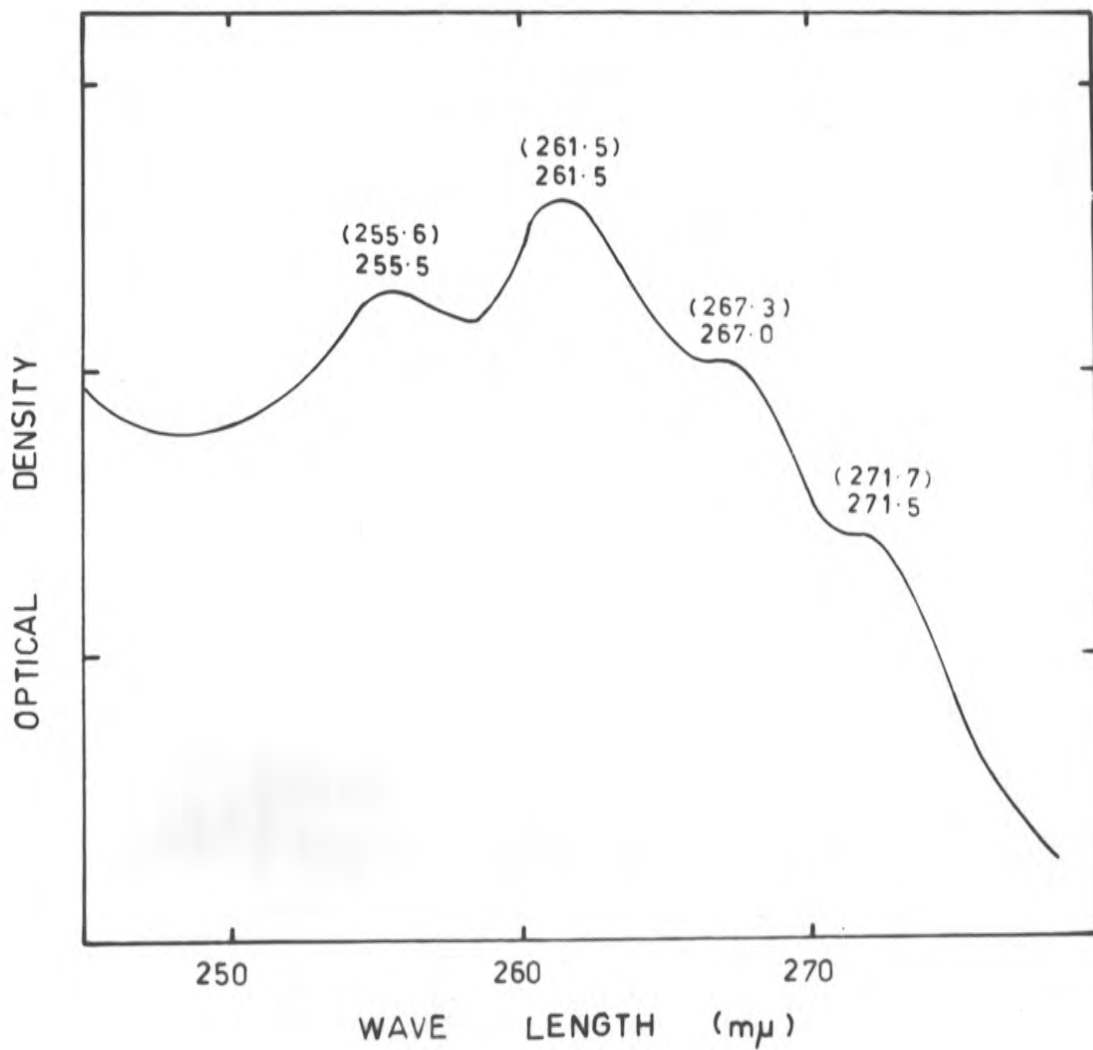


Figure 4-8.1. Ultraviolet spectrum of aqueous polystyrene sulphonic acid solutions using an Uvicam SP500 spectrophotometer. Bracketted values were the absorption maxima or shoulders found with an Uvicam SP700 spectrophotometer.

(1) Beer's Law was shown to hold over the concentration range used in subsequent experiments (figure 4-8.2),

(11) the extinction coefficients of the polyelectrolyte were calculated at 255.5 and 261.5 m μ (Table 4-8.1 later).

It is noteworthy that adherence to Beer's Law for both polystyrene sulphonic acid and its sodium salt supports the proposal by Darskus⁵⁶ that the existence of the discontinuity in the concentration dependence of the optical density of salts of weak polybases is due to hydrolysis at high dilution rather than aggregation at concentrations above the critical concentration.⁵⁷

(3) Relationship between the extinction coefficient of the polyacid and sodium salt

The extinction coefficient of the sodium polystyrene sulphonate was found to be the same as that for the corresponding polyacid by measuring the optical density of a solution of the polyacid and then adding weighed amounts of sodium hydroxide solution in stages until neutralization was complete. The solutions were stirred as described above. After making the necessary correction for dilution the extinction coefficients of the polyacid and the sodium salt were found to be the identical value.

(c) Composition of the dried samples of polystyrene sulphonic acid and the sodium salt - equivalent weights

Samples of polyacid and sodium salt were weighed to constant weight as described above and the optical densities of their aqueous solutions were measured in each case. The assumption that both

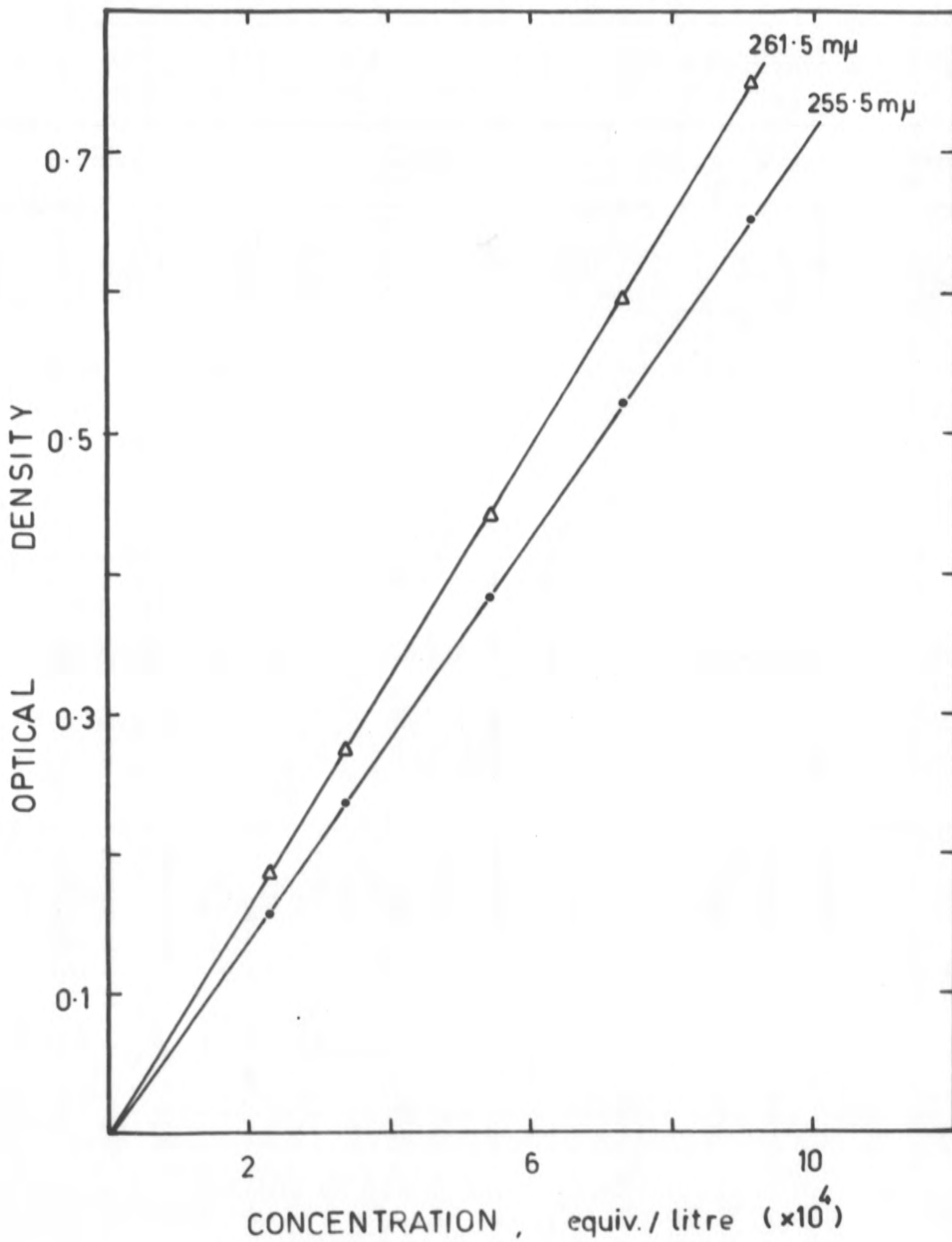


Figure 4-8.2. Concentration dependence of the optical density of aqueous polystyrene sulphonic acid (S108-H) solution. 2 cm. silica cells.

samples were anhydrous,

$$\text{i.e. } E.W._{\text{Na polysalt}} = E.W._{\text{polyacid}} + 22,$$

led to different values of the extinction coefficients which as shown above was incorrect. On the other hand if it was assumed that one water molecule was associated with each sulphonic acid group while the sodium salt was anhydrous then the molar and equivalent extinction coefficients agreed within experimental error as Table (4-8.1) shows.

Table (4-8.1)

Extinction coefficients of polystyrene sulphonic acids and their sodium salts. Solvent, water. Temperature, 25°C

Poly-electrolyte	EW*	MW*	Degree of sulphonation	ϵ_M (261.5 μ)	ϵ_M (255.5 μ)
S108-H	193.0	211.3	1.10	455 \pm 2	398 \pm 1
S108-Na	197.0	215.5		450 \pm 3	404 \pm 2
S103-H	188.6	216.5	1.15	466 \pm 1	410 \pm 2
S103-Na	192.6	221.1		460 \pm 4	408 \pm 4
F2-H	189.3	215.6	1.14	463 \pm 2	404 \pm 2
F2-Na	193.3	220.2		459 \pm 2	408 \pm 1
F3-H	190.3	214.6	1.13	459 \pm 1	402 \pm 1
CPS II-H	271.0	162.9	0.60	303 \pm 1	280 \pm 2

* acid, hydrated; salt, anhydrous

The above results were obtained from an average of ten to twenty

measurements of optical density at different concentrations for each polyelectrolyte sample. As the degree of sulphonation exceeded unity, an additional assumption in the above calculations was that each benzene ring carried either one or two sulphonate groups so that

$$EW = \left(\frac{300 - 98x}{2 - x} \right) \quad \text{and} \quad MW = 300 - 98x \quad \text{for the hydrated}$$

polyacid,

$$\text{and} \quad EW = \left(\frac{308 - 102x}{2 - x} \right) \quad \text{and} \quad MW = 308 - 102x \quad \text{for the sodium}$$

polysalt,

where x was the fraction of monosulphonated benzene rings.

4-8 Optical Rotation Studies

(a) The apparatus and chemicals

The Bellingham and Stanley spectropolarimeter was used in the visible region only and all operations were manually controlled. Corrections were applied to the wavelength scale of the SP500 monochromator with the aid of standard filters and using the specific rotations of a sucrose solution (26.00 gm. per 100 ml. solution) at several wavelengths as a check on the calibration.⁵⁸

The sucrose was either "Univar" analytical reagent or a standard sample supplied by the National Bureau of Standards, Washington, D.C.). Before use it was dried at 30°C in vacuo over phosphorus pentoxide for two days. The specific rotation at 589.3 μ was taken to be 66.53° for a solution containing 26.00 gm. of sucrose in 100 ml. of solution with the concentration dependence⁵⁹ being

$$[\alpha]_D^{20} = 66.43_5 + 0.00870c - 0.000235c^2$$

for concentrations between 0 and 65 gm. per 100 ml. of solution. The variation in optical rotation, α , of sucrose solutions with temperature in °C is so small⁵⁹

$$\alpha_T = \alpha_{20} [1 - 0.00037(T - 20)]$$

that thermostating of sucrose solutions was not considered necessary.

The solvents used were redistilled methanol and "Unilab" N-N-dimethyl formamide.

The free quinine was prepared by adding excess 2.4 molar sodium hydroxide to a solution of quinine hydrochloride in water. The filtered precipitate was dissolved in diethyl ether and shaken many times with water to remove traces of excess alkali and sodium chloride. After drying over anhydrous calcium sulphate the ethereal solution was evaporated to give free quinine. The product was purified by re-crystallization from a minimum volume of warm ethanol. It was obtained in the anhydrous state⁶⁰ by drying at 125°C for one day and checked for purity by determination of its molar rotation at 589.3 m μ in both methanol and dimethyl formamide.⁶¹

(b) Quinine salts of the polyacids and measurement of their specific rotation

(1) Methanol as solvent

Solutions of anhydrous quinine in methanol were made up by weight in A grade 100 ml. flasks (approximately 2 gms. quinine per 100 ml. of solution). The specific and molar rotations were determined at

30 ± 1°C using decimetre polarimeter tubes at wave-lengths between 400 and 600 mμ.

The quinine salts of the polystyrene sulphonic acids were prepared by adding a calculated weight of quinine solution to the known weight of polyacid dissolved in a small quantity of methanol such that a 1.005:1 equivalent ratio of base to acid was present. In the case of the less soluble quinine salt of the isotactic acid it was necessary to warm slightly, with magnetic stirring to hasten complete solution. The solutions of atactic and isotactic salts were finally diluted with methanol until the concentrations were approximately the same (concentration range, 1.41-1.48 gm. quinine per dl. solution). The densities of the solutions were determined by weighing 10.00 ml. of solution at 30°C. Measurements of optical rotation were made as a function of wavelength yielding the results discussed in section 3-2(c).

(2) N-N dimethyl formamide as solvent

Similar experiments to those described with methanol as solvent were carried out in dimethyl formamide. The specific rotations of the isotactic salt solutions, prepared directly as described above, agreed to within 1% of those obtained by low temperature evaporation of a weighed quantity of the above methanolic solution followed by dissolution of the resultant vacuum-dried salt in a suitable weight of dimethyl formamide.

4-10 Dye Binding Studies

(a) Spectrophotometric titrations

All optical density measurements were made by manual operation of a Gilford Model 2000 Absorbance Recorder set up with a Beckman DU Monochromator.

After washing with dry ethanol the proflavine used in this work was crystallized⁶² from water and dried in vacuo to constant weight. Stock solutions of proflavine of concentration $1-2 \times 10^{-4}$ molar were made up in conductance water and then diluted to a suitable concentration ($\sim 2 \times 10^{-5}$ molar) by the addition of either conductance water or sodium chloride solution. To reduce dye adsorption on the container and to prevent photoreduction,⁶³ proflavine solutions were prepared in polyethylene vessels under semi-darkened conditions and then stored at 4°C in the dark. The concentration of diluted proflavine solution was calculated from its optical density at $443 \text{ m}\mu$ taking the molar extinction coefficient of the dye to be $4.1_0 \times 10^4$ at this wave-length.⁶²

During the titration the optical density of the dye was usually measured at a number of wavelengths between 420 and $465 \text{ m}\mu$ as a function of the concentration of polystyrene sulphonic acid or its sodium salt. This was achieved by the addition, by weight, of small amounts of polyelectrolyte solution to 1 cm. silica cells containing a known weight of proflavine solution of measured concentration. Allowance was made for slight evaporation losses during each measurement. Solutions were stirred during addition of polyelectrolyte and then for a further $\frac{1}{2} - 1$ minute by means of a micromagnetic stirrer which was prepared by sealing 0.5 cm. of soft iron wire in 0.5 inch diameter polyethylene tubing ("Intramedic", Clay-Adams Inc., New York). The extinction coefficients of the proflavine were calculated from volume corrected optical

densities. Four or five spectrophotometric titrations using polyelectrolyte solutions of gradually increasing concentration were necessary to obtain the complete dye-binding curves.

(b) Temperature dependence of dye-binding

This was determined at high polymer to dye ratios in 1 cm. silica cells in the presence of an overlying paraffin layer to prevent evaporation losses. Heating of the cells was carried out either

(1) by circulating water through the jacket surrounding the cell compartment of the Gilford instrument and averaging the inlet and outlet temperatures which differed by less than 0.3°C, or (2) in an electrically heated and thermostatically controlled cell holder fitted to an Unicam SP500 spectrophotometer. In the latter case temperatures were obtained from a calibrated thermocouple. After allowing 20-30 minutes for temperature equilibration the optical density was measured at 452 m μ (or as a function of wavelength if spectra were required) and later corrected for volume changes during heating using listed values of the density of water.

4-11 Conductance Measurements

(a) Apparatus

One bridge which was used in this work solely to determine the resistance of the conductance water, has been previously described.⁶⁴ All measurements with polyelectrolyte solutions were made with a 4-decade resistance and capacitance bridge (Conductivity Bridge Type 6401, Eilco, Norwood, S.A.) capable of measuring resistances to 111,000

ohms. The conductance cell, which has been described by Daraskus,⁵⁶ was designed to avoid errors which might arise due to adsorption of the solute on the electrodes and to permit periodic additions of stock polyelectrolyte solution while working in an atmosphere of nitrogen. The electrodes were bright platinum discs about 2.6 cm. in diameter and spaced about 5 mm. apart by means of a tungsten seal through the pyrex glass wall of the cell (figure 4-11.1). The cell was occasionally cleaned with warm chromic acid, washed many times and soaked overnight in distilled water and finally steam-cleaned for several hours. In one series of experiments a conductance cell (cell constant, 5.66×10^{-2} cm.⁻¹), built into the central arm of an Ubbelohde viscometer, was used (section 4-7c).

The nitrogen used for conductance, transference and electromotive force studies was obtained by passing "oxygen-free" nitrogen (Commonwealth Industrial Gases, Torrens ville, S.A.) through a liquid air trap and moist potassium hydroxide pellets to remove carbon dioxide, through a copper spiral immersed in the water bath to bring the temperature to 25°C and finally through a sintered glass disc into conductance water to saturate it with water vapour.

(b) Determination of the cell constant

The cell constant was determined with 0.001000 molar potassium chloride solution which had been prepared by weight dilutions (with appropriate air buoyancy corrections) of potassium chloride in distilled water saturated with air. The A.R. potassium chloride was recrystallized from water and vacuum dried over phosphorus pentoxide.

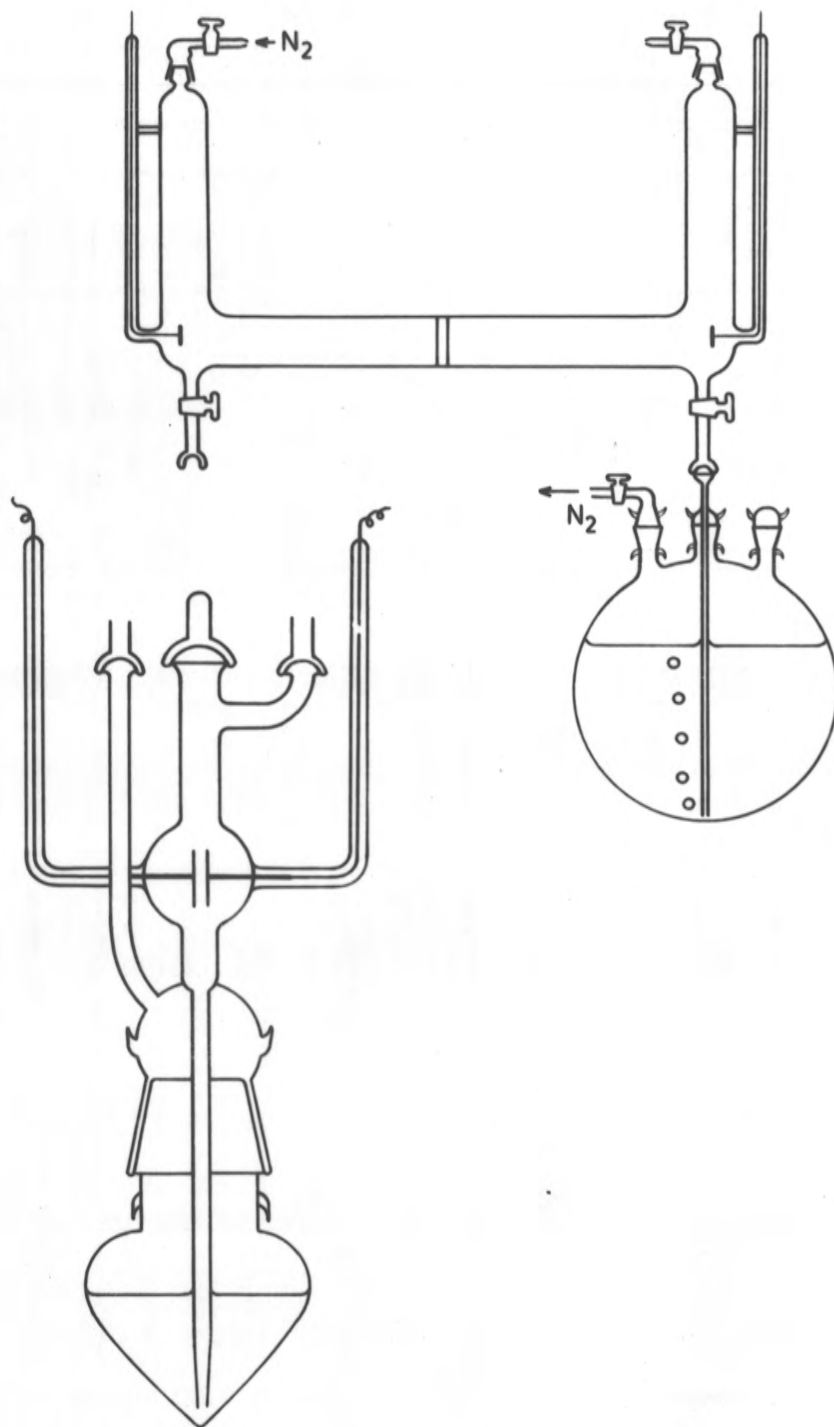


Figure 4-11.1. Transference and conductance cells.

Resistance measurements of both water and potassium chloride solution were made at frequencies of 0.4, 1 and 2.5 kilocycles per second with the cell immersed in a water bath at $25.000 \pm 0.003^\circ\text{C}$ (fig. 4-11.2). By taking the contribution of the potassium chloride to the specific conductivity⁶⁵ as $1.469_5 \times 10^{-4} \text{ ohm}^{-1} \text{ cm.}^{-1}$ and extrapolating resistances to infinite frequency, the cell constant was found to be $0.06572 \pm 0.0004 \text{ cm}^{-1}$. This value was confirmed by two later re-determinations. Air was used to force the solution from the lower reservoir into the upper cell compartment.

(c) Measurements with polyelectrolyte solutions

Approximately 40-60 ml. of conductivity water were run directly from a mixed-bed resin column through a suitable cap into the weighed, nitrogen-filled reservoir D. Immediately after reweighing, the cap was replaced by the upper part of the conductance cell through which nitrogen was passing. When the resistance, measured as a function of frequency, reached a maximum value at $25.000 \pm 0.003^\circ\text{C}$ (corresponding to $\kappa = 0.15-0.25 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$) stock polymer solution was added to the solvent through A while nitrogen was passed over the liquid surface through B, arm C being closed. After thorough mixing nitrogen was slowly bubbled through the solution until after 20-30 minutes the resistance reached a maximum value. The equivalent conductance of the polyelectrolyte was calculated by extrapolating the resistance to infinite frequency and making the usual solvent correction to the specific conductance. Further additions of stock solution were then made to determine the equivalent conductance as a function of

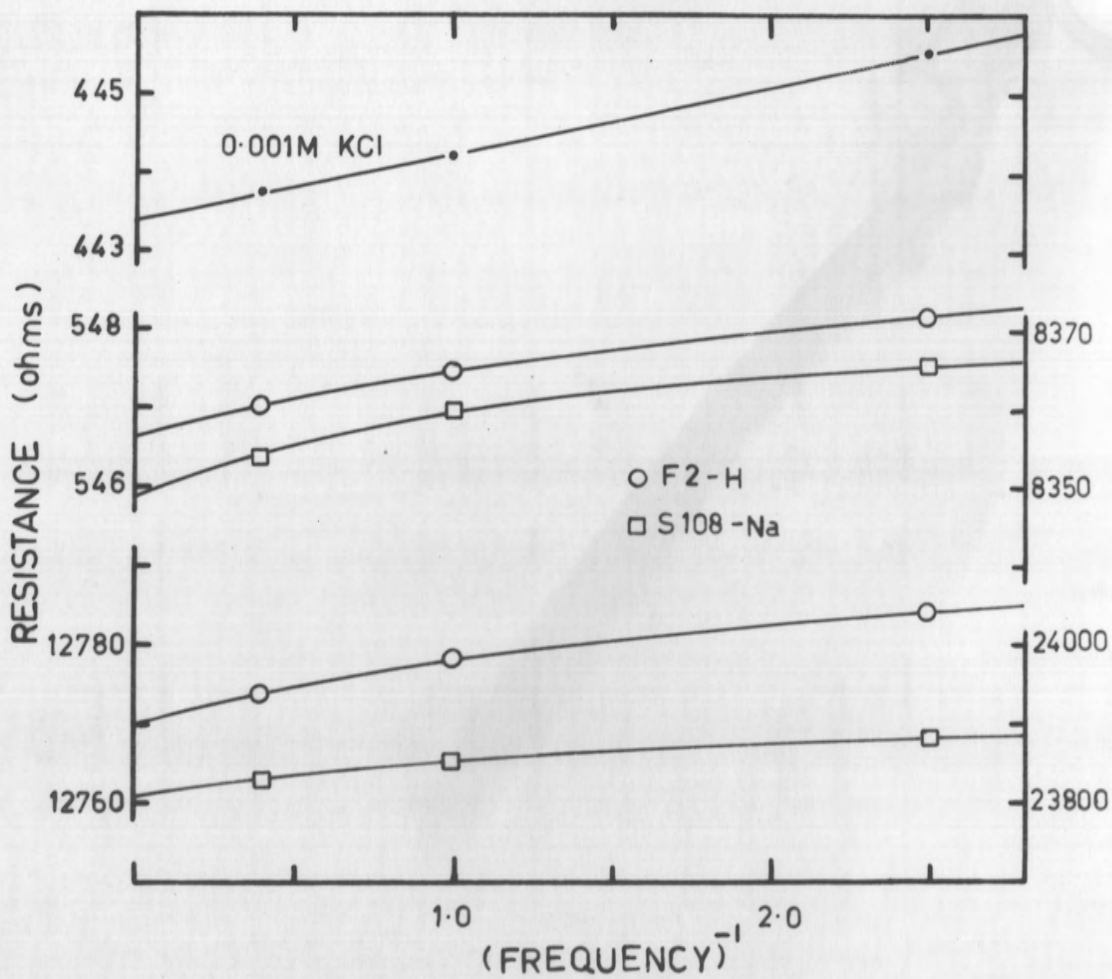


Figure 4-11.2. Extrapolation of resistances of solutions to infinite frequency.

concentration.

It should be noted that

(1) with perhaps the exception of very dilute solutions adsorption effects were shown to be negligible by the constancy of resistance over periods of several hours,

(2) results were generally reproducible to about $\pm 1\%$,

(3) the extrapolation of resistance to infinite frequency was not completely linear but the resultant error was unlikely to have been greater than 0.5% (figure 4-11.2).

4-12 Transference Studies

(a) Apparatus

The transference cell which was similar to that described by Huizenga et al.,⁶⁷ consisted of two compartments each of 50 ml. capacity separated by a coarse sintered-glass disc. The electrodes, situated 18 cm. apart, were bright platinum discs of about 1 cm. diameter.

A constant current was supplied from an electronically regulated power supply (Electronic Instrument and Lighting Co., Norwood, S.A.).

(b) Measurement of transference numbers

Weight dilution of stock polyelectrolyte solution with conductance water was carried out in a flask filled with nitrogen (section 4-11a). After removal of possible traces of carbon dioxide by a slow stream of nitrogen the diluted solution was transferred through a ball joint to the transference cell which had flushed out with the same nitrogen stream used above (figure 4-11.1). When the cell had been

rinsed out three times by moving the solution to and from the flask, the filled transference cell was detached and placed in a water-bath at $25.000 \pm 0.005^\circ\text{C}$. After temperature equilibration a suitable current (between 200 and 800 μA) was passed through the solution for 12-18 minutes so that 15-20% of polyelectrolyte was transferred from the cathode to the anode compartment during the electrolysis. The quantity of electricity passed through the solution was calculated from measurements of time and current.

One compartment at a time was drained and then rinsed with the original solution into a weighed flask. The change in concentration was measured spectrophotometrically with an Unicam SP500 using 1-4 cm. silica cells by determining the difference in optical density between the original and electrolysed solutions at 255.5 $\text{m}\mu$ and 261.5 $\text{m}\mu$. Transference numbers (section 3-5d) of the polyanion were then calculated in the usual way. Results were generally reproducible to better than $\pm 3\%$.

4-13 Measurements with Electrochemical Cells

(a) Apparatus and solutions

The glass electrodes used in this work were the Radiometer Type G222B (reversible with respect to hydrogen ions) and Sodium Responsive Electrodes Type GEA33 (Electronic Instruments Ltd., England). When not in use these electrodes were stored in water and 0.1M sodium chloride respectively.

The reference electrode was a saturated calomel electrode with the liquid junction being made through a fine asbestos thread.

The variation of the conductance of water in which the tip of the calomel electrode was immersed (measured with a Philips Bridge and conductance cell) was used to show that the junction resulted in negligible contamination of the polyelectrolyte solution during the time taken for a series of measurements. To show the effect of potassium chloride contamination on the stoichiometric activity coefficient of the hydrogen ion in polystyrene sulphonic acid solutions a series of pH measurements was carried out in the presence of 1×10^{-4} molar potassium chloride. The polyacid was prepared from a sample of sodium polystyrene sulphonate (ET-409 supplied by Dow Chemical Co.) by passage through a mixed-bed resin column. The activity coefficient of the hydrogen ion increased to the high constant value of 0.71 in the presence of the small amount of simple electrolyte (figure 4-13.1) in contrast to the constant value of 0.41 in salt-free solutions. This compares favourably with the findings previously reported by Eisenberg and Ram Mohan⁶⁸ for a similar system.

The silver-silver chloride electrodes were prepared electrolytically by a method similar to that described by Ives and Janz.⁶⁹ Cleaned platinum gauze cylinders welded to platinum wire were silver-plated by electrolysis of potassium silver cyanide solution and about 25% of the silver was then converted to silver chloride by electrolysis of pure hydrochloric acid solution (see below). The electrodes were stored in conductance water at 25°C for two days before use with no precautions being taken to exclude light.⁷⁰

Measurements of pH and electromotive force were made with a

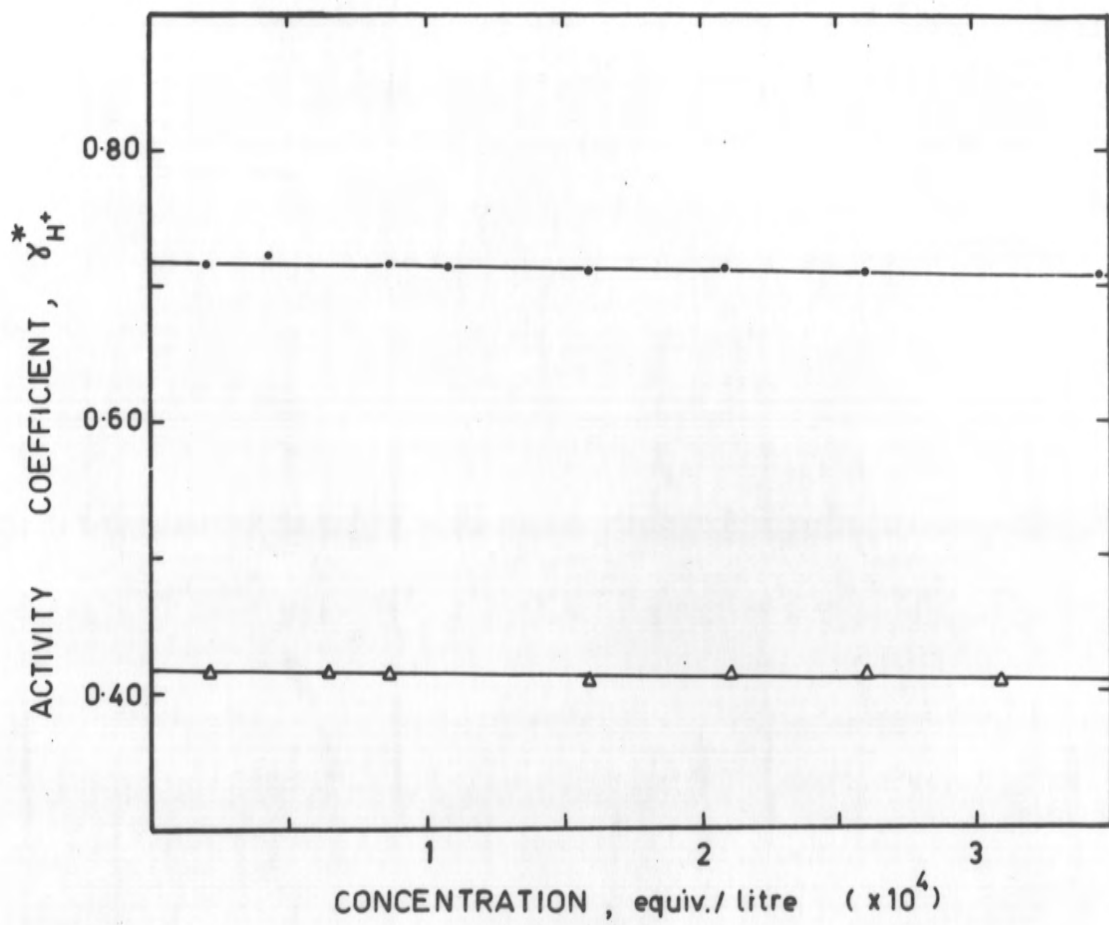


Figure 4-13.1.

Effect of potassium chloride on the stoichiometric activity coefficient of hydrogen ions in polystyrene sulphonic acid solutions. Temperature 25°C.

Upper curve: in 5×10^{-4} M KCl.

Lower curve: in absence of simple electrolyte.

Radiometer pH meter 4 (Copenhagen, Denmark).

The hydrochloric acid was prepared by weight dilutions of the constant boiling mixture which was obtained by distillation of suitably diluted A.R. hydrochloric acid.^{71a} The calculated molarity^{71a} was in agreement within 0.2% of the value obtained by titration against a known weight of recrystallized sodium tetraborate^{71b} which had been stored for some weeks over a solution saturated with sucrose and sodium chloride.

Sodium chloride solutions were prepared from A.R. sodium chloride which was further purified by recrystallization and by fusion in a platinum dish.⁷²

Cylindrical vessels of approximately 150 ml. capacity, fitted with a perspex lid for entry of electrodes and purified nitrogen (section 4-11a), were used for electrochemical measurements. Conductance water was run directly into the weighed nitrogen-filled vessel and, after reweighing as quickly as possible, was equilibrated under nitrogen for 20 minutes in a water bath at $25.000 \pm 0.003^\circ\text{C}$ with both electrodes immersed except when the saturated calomel electrode was being used.

(b) Cells with liquid junction

(1) The hydrogen ion glass electrode-calomel system was standardised at 25°C with 0.0500 M potassium hydrogen phthalate^{71c} solution and then checked with 0.0500M sodium borate buffer. The pH values of solutions of polystyrene sulphonic acid were determined by the progressive addition of small amounts (0.100-1.000 ml.) of stock polyacid solution to weighed amounts (about 40-50 gm.) of temperature-

equilibrated water. Solutions were mixed by bubbling nitrogen through the solution with a drawn-out silica tube for about two minutes. It was found that the system rapidly reached equilibrium after the addition of the polyelectrolyte.

In the absence of values for the variation of the pH of hydrochloric acid solutions with concentration, the following empirical relation, reported by Hitchcock and Taylor⁷³ for the same electrochemical cell, was used in the treatment of the results in the manner described under section (3-6b),

$$(\text{pH})_{\text{HCl}} = (E^{\text{HCl}} - E_o^{\text{HCl}})/k = -\log c_{\text{HCl}} + A\sqrt{c_{\text{HCl}}} - Bc_{\text{HCl}} \quad (4-13.2)$$

where E_o^{HCl} includes contributions by E_{glass}^o , E_{calomel} and ϵ_{1j} . Taking E_o^{HCl} equal to E_o^{HP} , the pH of the polystyrene sulphonic acid can be written as

$$(\text{pH})_{\text{HP}} = (E^{\text{HP}} - E_o^{\text{HP}})/k = \log f_J c_{\text{HP}} + A\sqrt{f_J c_{\text{HP}}} - Bf_J c_{\text{HP}}$$

Setting $A = 0.509$, calculating B to be approximately⁷¹ 1.2 and taking f_J to be 0.4, the contribution of the terms $A\sqrt{f_J c_{\text{HP}}}$ and $Bf_J c_{\text{HP}}$ respectively to the pH can be shown to be approximately 3×10^{-3} and 5×10^{-5} for 1×10^{-4} molar polystyrene sulphonic acid and 1×10^{-2} and 5×10^{-4} for a 1×10^{-3} molar solution. The contribution of the $Bf_J c_{\text{HP}}$ term is therefore negligible over the concentration range used.

An approximate value of the charge fraction, f'_J , with neglect of the activity coefficient term was first calculated from

$$(\text{pH})_{\text{HP}} = -\log f'_J c_{\text{HP}} \quad (4-13.3)$$

and finally the value of f_j was obtained from

$$(\text{pH})_{\text{HP}} = -\log f_j c_{\text{HP}} + 0.5 \sqrt{f_j' c_{\text{HP}}} \quad (4-13.4)$$

The stoichiometric activity coefficient, γ_+^* , of the hydrogen ion was calculated as described in section (3-6b).

(2) The electromotive force (to ± 0.3 m.v.) of the sodium ion glass electrode-calomel system was measured as a function of the molality of sodium chloride by the progressive addition of small quantities of stock sodium chloride solution to water using the procedure outlined in (1) above. A graph of the electromotive force against $(-\log_{10} m \gamma_+)$ was linear to concentrations of about 4×10^{-4} molal with the slope agreeing to within 98-99% of the theoretical value of 59.16 millivolts. The mean ionic activity coefficient, γ_{\pm} , for sodium chloride was assumed to be equal to f_{\pm} , the value on the molarity scale which was calculated by the Guggenheim equation,^{74a}

$$-\log_{10} f_{\pm} = -\frac{A |z_1 z_2| \sqrt{I}}{1 + \sqrt{I}} + bI \quad (4-13.5)$$

where A and b were taken to be 0.5115^{74c} and 0.16^{74b} litre mole⁻¹ respectively.

As soon as possible after the calibration the experiment was repeated with the addition of the sodium salt of the polyacid. For each sodium polystyrene sulphonate concentration the molality of sodium chloride, $m_{\text{NaCl}}^{\text{P}}$, which in the cell produces the same electromotive force as that of the polysalt solution, was determined. The charge fraction, f_j , of the polyion or the stoichiometric activity

coefficient of the sodium ion, γ_{+}^{Na} , was then calculated as described in section (3-6b) and previously reported in figure (3-6.1).

(c) Cell without liquid junction

After temperature equilibration of the conductance water at 25.00°C the electromotive force of the hydrogen ion glass-silver, silver chloride cell was determined as a function of the molality of hydrochloric acid. After each addition of stock hydrochloric acid solution the cell was left for 15-20 minutes for the system to come to equilibrium. The results of the calibration were represented graphically by a plot of the electromotive force against a suitable concentration scale such as the square root of the molality. Between the concentrations of 3×10^{-4} and 6×10^{-3} molal the slope of the graph of E against $-\log_{10} m\gamma_{\pm}$ was linear and corresponded to 97-99.5% of the theoretical slope of 118.3 millivolts at 25.00°C (figure 4-13.2). For this calculation the mean activity coefficient of hydrochloric acid was interpolated from values listed in Harned and Owen.⁷⁵ Corrections which allowed for the solubility of silver chloride made no significant difference to the calculated value of $\log m\gamma_{\pm}$.

In subsequent experiments the electromotive force, E_2 , of the cell was measured as a function of the concentration of

- (1) hydrochloric acid which was progressively added to a suitable known quantity of polystyrene sulphonic acid in the conductance water,
- (2) polystyrene sulphonic acid which was progressively added to a suitable known quantity of hydrochloric acid in the conductance water.

The charge fraction of the polystyrene sulphonate ion was

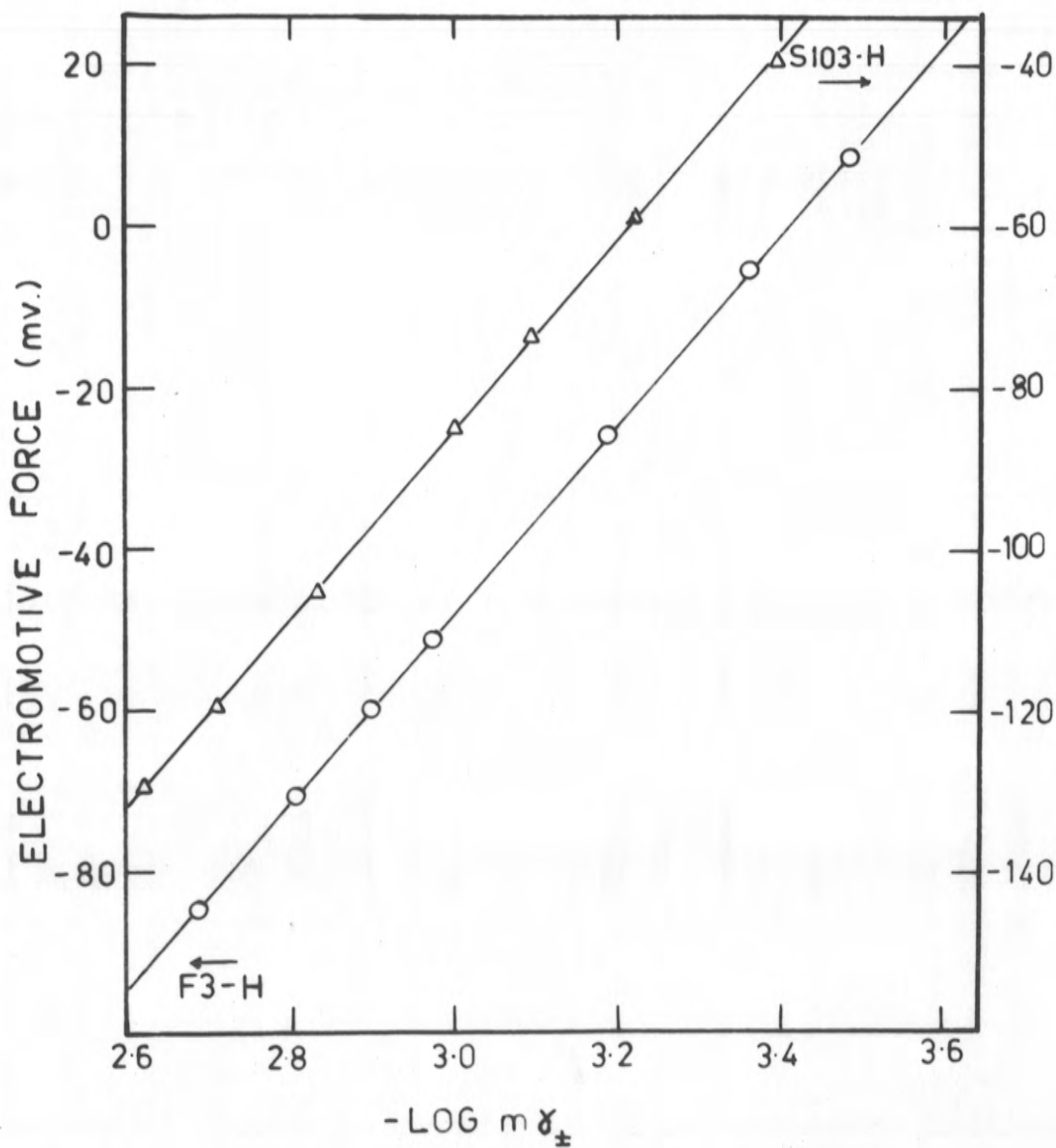


Figure 4-13.2. The electromotive force of the hydrogen glass- silver silver chloride cell against $\log m \gamma_{\pm}$ of hydrochloric acid solutions at 25.000°C. After calibration the cells were used with polystyrene sulphonic acid solutions, S103-H and F3-H.

calculated as described under section (3-6c) using equation (3-6.8).

(d) Estimate of liquid junction potentials

An estimate of the liquid junction potential between solutions of polystyrene sulphonic acid and saturated potassium chloride solution (4.2 molar) was made from the Henderson equation,⁷⁶

$$E_{lj} = \frac{4.2(u_{K^+} - u_{Cl^-}) - c_1(u_{H^+} - u_{PSS^-})}{4.2(u_{K^+} + u_{Cl^-}) - c_1(u_{H^+} + u_{PSS^-})} \cdot \frac{RT}{F} \ln \frac{4.2(u_{K^+} + u_{Cl^-})}{c_1(u_{H^+} + u_{PSS^-})} \quad (4-13.6)$$

where the u_i are the mobilities of the ions and c_1 is the concentration of the polyacid. Taking the equivalent conductance of a saturated potassium chloride solution^{77a} to be $93 \text{ cm.}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$ and the transference number of the potassium ion^{77b} in this solution as 0.488, equation (4-13.6) gives the liquid junction potential for a cell containing 10^{-4} to 10^{-3} molar polystyrene sulphonic acid to be approximately 5 to 6.5 millivolts. The corresponding value involving 1×10^{-3} molar hydrochloric acid (equivalent conductance, $421 \text{ cm.}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$) is approximately 4 millivolts. MacInnes⁷⁶ has referred to the uncertain accuracy of the above calculations as several assumptions involved in deriving equation (4-13.6) do not hold in practice.

4-14 Pycnometry

(a) The pycnometers

From selected mould-blown bulbs, precision bore capillary tubing and B10 cones and sockets, four almost identical pycnometers were constructed. The weight of glass in the pycnometers and volumes

to the graduation mark were within ± 0.006 gm. and ± 0.015 cc. respectively for all pycnometers. By weighing and measuring the length⁷⁸ of mercury in a piece of the capillary tubing it was shown that 1 cm. of tubing had a volume of 0.008766 cc. At the same time a tare was constructed so that the weight of glass, the shape, the size and the weight of water sealed within were almost identical to those of the pycnometers containing water to the graduation mark. The averaged results of four calibrations against the tare are shown in the following table with the reproducibility ± 0.00005 gm. or better. Δm_1 is the difference in the weight in air of the pycnometer filled to the mark with water and the weight in air of the tare.

	A	B	C	D
Δm_1	0.00655	0.01874	-0.00714	-0.01234
volume (in cc.)	32.5242	32.5361	32.5098	32.5056

It is noteworthy that the pycnometers were so designed that when filled with any solutions used in this work no further weights had to be lifted from the supports of the Mettler balance (Type B5C1000) when comparing them with the tare.

(b) Principle of the tare

It can be shown⁷⁹ that the relationship between the density of the solution, ρ , and the density of water, ρ_0 , for this pycnometer-tare method is given by

$$\rho = \rho_0 + \frac{\Delta m_{12}}{V} \quad \text{with} \quad \Delta m_{12} = \Delta m_2 - \Delta m_1, \quad (4-14.1)$$

where V is the volume of the pycnometer in cc.,

Δm_2 is the difference in weight of the pycnometer filled to the mark with solution and the weight of the tare under the same air conditions,

and Δm_1 is the corresponding difference with water in the pycnometer.

It is necessary, however, to correct the above difference in weights for the buoyancy effect of air on the stainless steel weights which are used with the Mettler balance. Taking the density of steel and air to be 7.76 and 1.2×10^{-3} gm. per cc. respectively gives

$$\rho - \rho_0 = \frac{0.999845 \Delta m_{12}}{V} \quad (4-14.2)$$

It should be noted that since the pycnometer and the tare are equal in surface area, the effect of changing air humidity will always produce identical variations in weight due to adsorbed water in both the pycnometer and the tare. Furthermore it can be shown that the assumption that the density of air is constant leads to negligible errors owing to the small magnitude of Δm_{12} . It follows, therefore, that Δm_{12} will always be constant for a given solution even if Δm_1 and Δm_2 are determined under different air conditions.

(c) Experimental technique

Before use the pycnometers were cleaned with chromic acid in the normal manner (section 4-15a) and then sucked dry by inverting,

while warm, over a stainless steel capillary connected to a filter pump. After rinsing with a small volume of the solution to be used they were filled by means of a Luer syringe to slightly above the graduation mark with the solution which had been previously warmed to about 28°C. This procedure helped to overcome the necessity of removing air bubbles which otherwise tended to collect in the pycnometer bulb later in the experiment. The pycnometers were then mounted vertically in a water-bath controlled to $25.000 \pm 0.002^\circ\text{C}$ (allowance was made for variations of the bomb calorimeter thermometer reading with atmospheric pressure). After 15-20 minutes the level of the liquid was adjusted as close as possible to the mark with a syringe and then the upper part of the capillary was dried with thin strips of No. 50 wet strength filter paper twined around a fine piece of steel wire. With the cap replaced, a further 15 minutes was allowed before the position of the meniscus and the graduation mark were measured with a cathetometer (Precision Tool and Instrument Co. Ltd., Surrey, England) fitted with a suitable telescope (Gaertner Scientific Corp., Chicago, U.S.A.).

The outside of the pycnometers and the tare were washed with distilled water, cleaned with cheese cloth several times between washings and finally wiped with well-worn cotton cloth. After standing inside the balance case for one hour the difference in weight of the pycnometer and tare was determined to ± 0.00002 gm. The correction due to the meniscus of the solution being above or below the graduation mark then gave Δm_2 from which the density of the solution

was calculated using equation (4-14.2). The density of water at 25.000°C was taken to be 0.997048 gm. per cc.

(d) Calculation of the apparent specific volume of the polyelectrolyte

Since the vacuum dried, solid polystyrene sulphonic acid was shown to contain one molecule of water for each sulphonic acid group the concentration of the solution, which had been prepared by weight, was converted to that for the anhydrous acid. From the calculated concentration, c , in gm. per cc. of solution the apparent specific volume, ϕ_v/M , was determined by substitution in the relation,⁸⁰

$$\phi_v/M = \frac{1}{\rho_0} - \frac{(\rho - \rho_0)}{c\rho_0} \quad (4-14.3)$$

where ϕ_v is the apparent molar volume of the polyelectrolyte. The results were recorded graphically by plotting ϕ_v/M against \sqrt{c} .

4-15 Miscellaneous

(a) Cleaning of glassware

Glassware was cleaned with either chromic acid for several hours or alkaline potassium permanganate for a few minutes. After washing several times with distilled water and soaking for several hours, the glassware was steam-cleaned whenever necessary.

(b) Purification of water

Water from a continuous still using de-ionized rain water

was distilled over acidified potassium dichromate solution and then alkaline potassium permanganate solution. It was stored in well-seasoned pyrex containers. For the preparation of salt-free poly-electrolyte solutions and for electrochemical and conductance studies this water was passed through a mixed-bed resin column and used directly. The specific conductance of this water was $0.15-0.25 \times 10^{-6}$ ohm⁻¹ cm⁻¹.

The de-ionized water was tested for the presence of small fragments of resin by electron microscopy. Samples of water were sprayed by means of a nebuliser onto freshly cleaved mica together with reference Dowex polystyrene spheres (2570Å). After shadowing with platinum and backing with collodion the specimens were mounted on copper grids and examined at high resolution with a Philips EM/100 instrument.⁸² There was some evidence of resin particles immediately after preparation of the column but after washing with 2-3 litres of water (~ 200 ml. mixed bed resin) no further traces were detected.

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NOTE:

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