SURFACE PROPERTIES
OF
HYDROPHILIC POLYMERS.

by

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SYNOPSIS.

Polymers based entirely or substantially on hydrophilic monomers have achieved importance in recent years largely because of their ability to absorb water and form (in the case of cross-linked polymer) soft, elastic gels ('hydrogels').

The surface properties of this group of materials are important in both the dehydrated and hydrated state and yet no thorough-going study has been previously made of this aspect of these polymers. The surface properties in the dehydrated state govern such important aspects of manufacturing technology as particle fusion and adhesion (to the mould surface). In the hydrated state the surface properties govern inter alia the biocompatibility of the polymer. Since hydrogels are important in such diverse biomedical fields as artificial liver support systems and contact lenses this represents an important field of knowledge.

In order to determine the surface energy of the hydrophilic polymers a series of samples was prepared and the surface energy of each sample was determined by means of wetting experiments. These measurements were performed on both hydrated and dehydrated samples but only the surface energy of the dehydrated samples could be calculated. The problems were too great to allow unambiguous values for the hydrated samples to be determined, although a method for determining only the polar component of the surface energy was used with the hydrated samples and provided useful results.

These experimental results were compared with results obtained by two different predictive methods, Parachor and CED, each of which used different parameters to estimate the surface

energy of a copolymer. The predictive method which best matched the experimental results was extended to predict the surface energy of hydrated samples.

Since surface energy controls both the rate of fusion of particles and the degree of mould adhesion seen with the polymer an attempt was made to use the experimental surface energy results to illuminate these two areas which had been found to be a problem with hydrophilic polymers.

Modification of the base polymer was also carried out in an attempt to lower the surface energy, modify some aspects of biocompatibility and to impart antibacterial properties to the polymer.

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ABBREVIATIONS.

HEMA - Hydroxyethyl methacrylate.
HEA - Hydroxyethyl acrylate.
HPMA - Hydroxypropyl methacrylate.
HPA - Hydroxypropyl acrylate.
NVP - N-vinyl pyrrolidone.

γ - Surface free energy or Surface tension of a sample.
γ_d - Dispersive component of the surface energy.
γ_p - Polar component of the surface energy.

INTRODUCTION.

1.1. General Introduction.

Contact lenses are devices which correct defects of vision. They are placed in contact with the cornea, as opposed to spectacles, in which the lenses are held away from the eye. Although the first record of the concept of correcting visual defects with a lenticular device which is in contact with the eye was that of Leonardo da Vinci in the 16th century[1], they did not come into widespread use until much later.

The first material to be employed for the construction of contact lenses, namely glass, persisted in use until the late 1940's. Following the Second World War, however, poly (methyl methacrylate) (PMMA) came into use having been developed during the war as a replacement for glass, proving advantageous in terms of toughness and impact strength.

1.2. Methods of Construction.

Lenses are conventionally produced from PMMA by a machining process commonly called lathe cutting[2] in which a section of a polymer rod is mounted on a lathe and the required curves are cut by a diamond stylus. The back curve is a fit to the curvature of the patient's cornea, whilst the front curve gives the lens its power. In order to give high wearer comfort, the edges of the lenses need to be smoothed and shaped. This is achieved by hand grinding, followed by buffing to remove the machining marks. A different approach is to compression mould discs of PMMA into the lens shape using polished moulds to give the required curves. However, these lenses still need to be edged by hand.

Even with a correct fit of lens, most patients find that there is a long period of discomfort before all day wear can be achieved. In this period of build up the patient is conditioning the eye to accept a foreign body. In the open eye, without a lens being present, the oxygen needed for corneal metabolism is obtained from the blood vessels in the sclera and from the tears. In placing a lens on the eye, the second route for providing oxygen to the cornea is curtailed. Good lens design produces a lens which rocks with eye movements. This rocking has the effect of pumping tears under the lens and into contact with the cornea, thus bringing more oxygen to the eye and preventing a thickening of the cornea as the aerobic mode of metabolism is replaced by anaerobic.

When the wearer is asleep this pumping mechanism is not so active as the eye movements are less. Thus any oxygen needed by the cornea must be provided by the scleral blood vessels or by direct diffusion through the lens. PMMA has a low oxygen diffusion coefficient and so during sleep the eye is receiving insufficient oxygen for aerobic metabolism.

1.3. Development of Hydrogel Materials.

In 1960 Wichterle and Lim[3], in Czechoslovakia, developed a material which was capable of swelling in polar solvents to give a gel. The material was a polymer of 2-Hydroxyethyl methacrylate (HEMA) and was found to swell in water to give a flexible, transparent gel which was found to be suitable for contact lenses. Investigation of the material showed that the water in the gel matrix increased the compatibility with the eye, so wearer comfort was improved and the period needed to achieve all day wear was reduced. Additionally it was shown that the amount of oxygen which the cornea received was increased due to the higher permeability of the material.

In order to produce contact lenses from hydrogel polymers a new fabrication technique was devised[4]. This was to rotate rapidly in a circle a mould in which had been placed catalysed monomer. The required backcurve was obtained by varying the rate of rotation whilst the primary surface was given by the mould itself. Poly (2-hydroxyethyl methacrylate) is also suitable for being lathe cut in the dehydrated state, although account has to be taken of the swell of the material in cutting out the lens shape.

Further research developed gels derived from monomers other than hydroxyethyl methacrylate[5]. These gels were made from monomers which also had an affinity for water, the so-called hydrophilic monomers, although sometimes these were combined with a hydrophobic monomer, e.g. Polystyrene or PMMA, to impart special properties, such as higher tensile strengths in the swollen state. The name Hydrogels was used to describe these water swellable gel materials. A correlation between oxygen permeability and water content was found[5] and so new copolymer systems came to be formulated which had high water content and thus good oxygen permeability. This good permeability led to the suggestion that hydrogels could find application[6] in the fields of reverse osmosis, kidney dialysis and haemo-perfusion, where a membrane permeable to certain molecular species is required. In the last two applications it is important that there is good compatibility with human tissue and blood since close contact with blood and tissue is a prerequisite of efficient toxine removal.

The water in the gel renders the system fairly bio-compatible with human blood[7]. The normal test for bio-compatibility is to record the time a blood sample takes to clot when in contact with the polymer sample. Some workers, however have tried to study bio-compatibility in polymers from the viewpoint of wetting, surface tension and adhesion of those polymers[8,9,10].

1.4. Surfaces and Interfaces.

The study of wetting is not a new endeavour. Many workers have tried to correlate a material surface, and the interface formed with a second phase, with the bulk properties of the species involved.

1.5. Thermodynamic Approach.

The oldest attempt was made by Gibbs[11], who described a system in which the two bulk phases are homogeneous up to the interface. He then used a residual thermodynamic property of an interface of zero volume for the mathematical surface between the phases. Although complete mathematically, this model gives no physical insight into the properties of interfaces. It should be noted that an interface is defined as the boundary between any homogeneous phases which are in thermodynamic equilibrium.

More recently Guggenheim[12] has introduced a model in which the mathematical interface has been replaced by a molecular interface with a small but finite thickness (Fig. 1). Two bulk phases α and β are separated by an interfacial layer σ with thickness t. The lines AA$'$ and BB$'$ are the arbitrary limits of phases α and β.

It can be shown that:-

$$F^{\alpha} = n_1^{\alpha} \overline{F_1} + n_2^{\alpha} \overline{F_2} \qquad - 1$$

$$F^{\beta} = n_1^{\beta} \overline{F_1} + n_2^{\beta} \overline{F_2} \qquad - 2$$

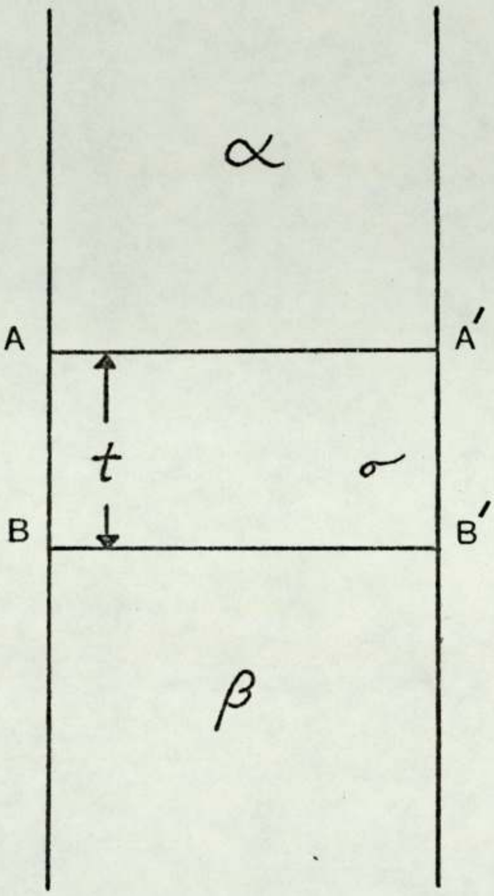


Fig. 1

and $$F^{\sigma} = \gamma\Sigma + n_1^{\sigma}\bar{F}_1 + n_2^{\sigma}\bar{F}_2 \qquad - 3$$

where:- n_1^{α} = No. of moles of component 1 in phase α

n_2^{α} = No. of moles of component 2 in phase α

n_1^{β} = No. of moles of component 1 in phase β

n_2^{β} = No. of moles of component 2 in phase β

$\bar{F}_1$ = Partial molal free energy of 1 in both phases

$\bar{F}_2$ = Partial molal free energy of 2 in both phases

γ = Interfacial tension

Σ = Area of boundary plane

Equation 3 points out that the interfacial tension, γ, describes the free energy increase of the whole system described by phases α, β and σ when a unit area of interface is created at constant T and P. This gives the basic definition of interfacial tension from which the more familiar one of force per unit area is derived. Additionally one can see that it is immaterial whether the interfacial phase σ is created from molecules of bulk phases α or β, since $\bar{F}_1$ and $\bar{F}_2$ are independent of the phase.

1.6. Surface Tension and Structure.

It has been pointed out [13] that an apparent surface of a liquid or solid is just an interface in which one phase is a gas. Five types of interface can be formed:-

1.	Liquid - Gas	γ_{LV}
2.	Solid - Gas	γ_{SV}
3.	Liquid - Liquid	γ_{LL}
4.	Liquid - Solid	γ_{LS}
5.	Solid - Solid	γ_{SS}

Interfaces of types 1 and 2 are those normally called surfaces. From a thermodynamic position, to maintain a stable surface requires a positive value for γ_{lv} or γ_{sv}. When these diminish to zero or become negative, there is no resistance to unlimited expansion of the surface. This occurs at the critical temperature for the liquid or solid under investigation.

Surface tension is normally defined as an energy per unit surface area. The work needed to produce an additional increment of surface area $d\Sigma$ is given by:-

$$\text{Work} = \gamma . d\Sigma \qquad - 4$$

As long as γ is positive then work has to be done to extend the surface. Consequently liquids tend to form volumes of minimum surface area, i.e. spheres.

Using a quasi-lattice model for the bulk it is possible to introduce a quantity called the cohesive energy density, δ^2 This was defined by Hildebrand[14] as:-

$$\delta^2 = - \frac{u}{\nu} \qquad - 5$$

where u is the molar internal energy and ν is the molar volume. A working definition is given by

$$\delta^2 = \frac{\Delta H_{vap} - RT}{\nu} \qquad - 6$$

where Δ Hvap is the molar heat of vaporization and ν is the molar volume. The gas law term, RT, presumes the vapour to be an ideal gas.

Thus the simplest correlation between bulk and surface properties would be a plot of γ, an energy per unit area, versus δ^2, an energy per unit volume for a range of liquids[15]. A plot of surface tension versus cohesive energy density where both vary considerably is given in Fig. 2. The linearity of the correlation works well for non-associated liquids. However, the alcohols present an independent trend because of their polar-nonpolar

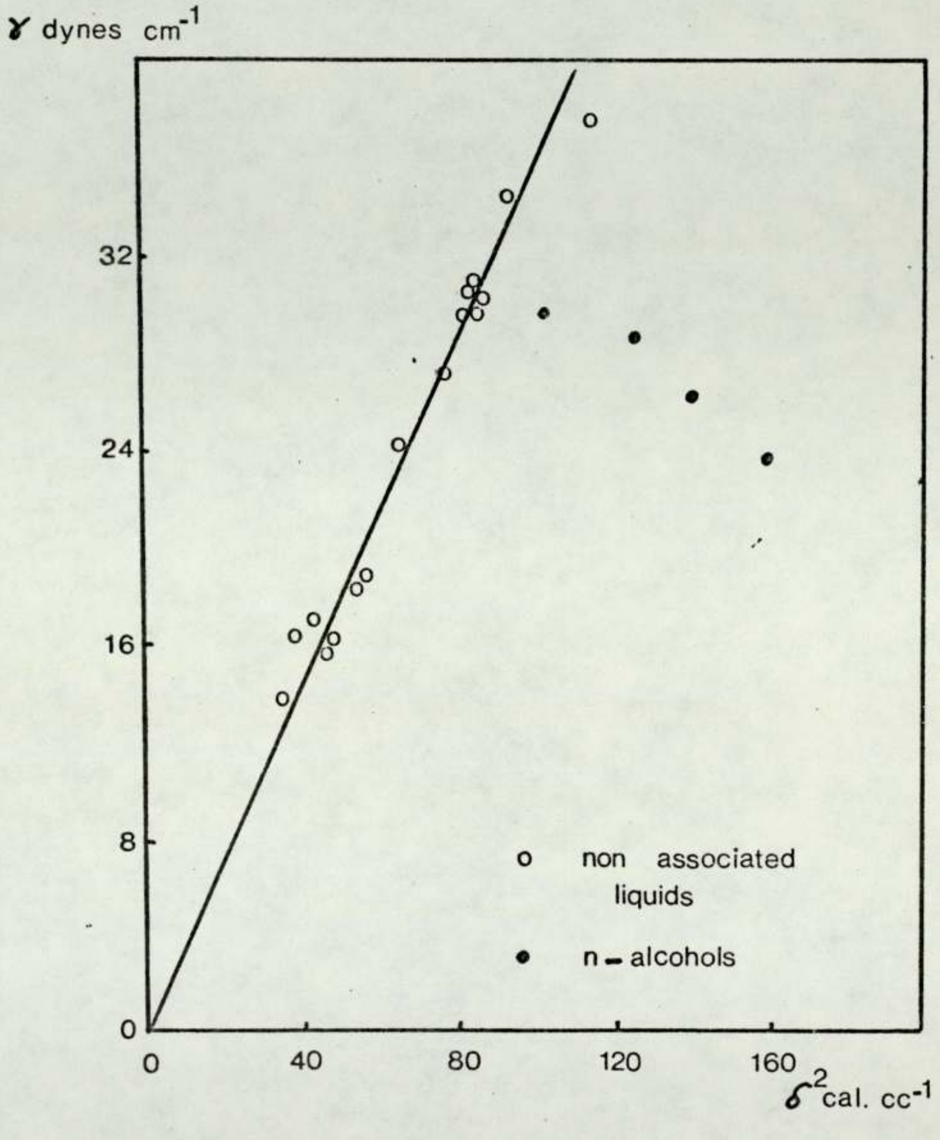

γ dynes cm^{-1}
32
24
16
8
0
0
40
80
120
160
δ^2 cal. cc^{-1}
o non associated liquids
● n – alcohols

Fig. 2

nature and the way that they orientate at surfaces.

This orientation is an example of distinct surface structure. Since both surface and interfacial tensions are free-energy properties they tend to minimise through molecular orientation when allowed to do so. That is provided the energetics are favoured and the rheological restraints to molecular motion do not inhibit reorientation. Surface tension is minimised by orientation of the nonpolar part of the molecule toward the vapour phase. With the alcohols this orientation produces a minimum surface tension with low energy methyl groups at the surface; the hydroxyl group being associated with bulk interactions. As the chain is lengthened, the bulk hydroxyl interactions are maintained but some of the surface is now occupied by slightly higher energy methylene groups. So the surface tension increases with molecular weight.

At the interface molecules tend to orientate so as to reduce the interfacial tension to a minimum. This can be illustrated by:- [13]

n-octane - water = 50.6 dynes cm^{-1}

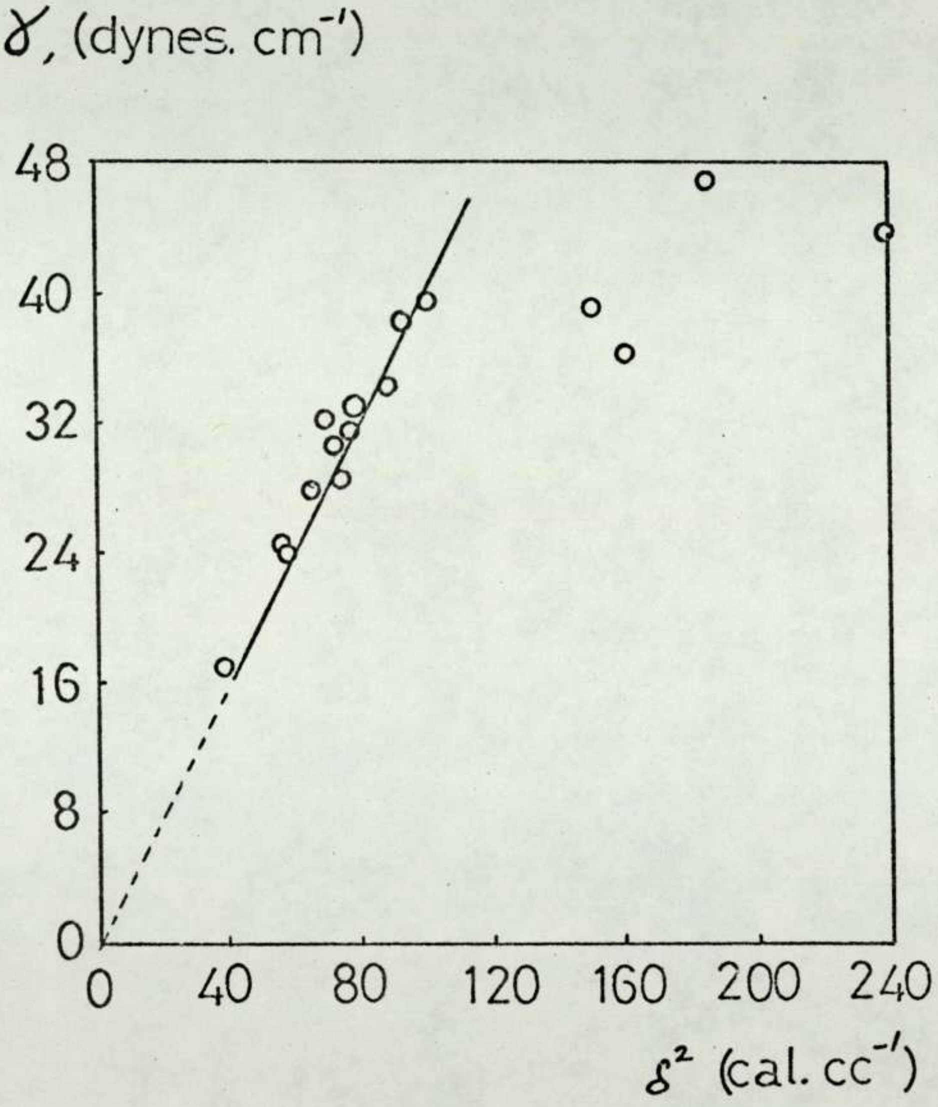
n-octanol - water = 8.8 dynes cm^{-1}

The high value for the octane-water interface is characteristic of other hydrocarbons. The reduction with the octanol-water interface can be explained by the orientation of the hydroxyl group of the octanol to the water surface.

Plots of γ versus δ^2 for polymers (Fig. 3) indicate that there is a direct proportionality. For polymers of $\delta^2 < 100$ the following equation holds:

$$\gamma = 0.44\,\delta^2 \qquad - 7$$

Fig 3


γ, (dynes. cm^{-1})
48
40
32
24
16
8
0
0
40
80
120
160
200
240
δ^2 (cal. cc^{-1})

When the value of δ^2 exceeds 100 then the value of γ becomes nearly independent of δ^2. Surface orientation of groups provides a reasonable explanation for this independence. This simple proportional relation between γ and δ^2 is apparently independent of the physical state of the polymer, i.e. whether amorphous, crystalline or elastomeric.

Hildebrand and Scott[14] applied an empirical but accurate relationship to connect surface tension, cohesive energy density and molar volume for non-polar liquids. This was modified by Wu[16] to provide accurate predictions for polymers based on molecular constitution. The relationship can be stated thus:-

$$\gamma = 0.327 \left[\frac{(\Sigma F)_s}{n_s}\right]^{1.85} \left[\frac{n_s}{\nu_s}\right]^{1.52} - 8$$

where n_s is the number of atoms, $(\Sigma F)_s$ is the summation of Small's force constants [17] for the segments, and ν_s is the molar volume of the repeat unit. In developing this equation Wu presumes that Small's values of F gives the dispersion force contribution to surface tension and that the value of γ given by this equation is equal to the dispersion part of the total surface free energy. The values obtained are in close agreement with the so called critical surface tension of Zisman [18].

1.7. Critical Surface Tension.

This technique represents the best documented approach to characterizing solid-surfaces. Zisman and his co-workers[19,20,21,22] plot the surface tension of a series of liquids against the cosine of the contact angle of a sessile drop of the liquids on a polymer surface. Extrapolation of the graph to Cos $\theta = 1$ (θ is the contact angle as measured through the liquid) gives a value for a liquid surface tension. This liquid, if it existed, should just completely wet the solid surface and it is this value which is called the critical surface tension of the solid (Fig.4). This idea can also be expressed as an equation:-

$$\cos\theta = 1 + b\,(\gamma_c - \gamma_L) \qquad - 9$$

Many of Zisman and his co-workers earlier results were obtained using, as wetting liquids, hydrocarbons. This is a reason why the values from Wu's equation which used data based on dispersion forces are in such close agreement with the critical surface tension values of Zisman, who used liquids with only dispersive forces capable of operating at the interface. Later[19] he started to use liquids which had some polar component in their surface tension. This produced much more scatter in the results and some deviation from linearity. In order to take into account these factors Zisman proposed that the narrowest possible rectilinear band should be constructed around the results and this used to give the value for critical surface tension. Recently Kitazaki and Hata[23] have proposed that wetting liquids used in Fox-Zisman plots should be divided up into 3 classes. One comprising non-polar solvents such as the n-alkenes, a second composed of polar liquids, for example esters and halogenated liquids, and the third group hydrogen bonding liquids such as water and formamide. These groups would yield three values of the critical surface tension to be designated A, B and C. It can be seen from the example given in Fig. 5 that a maximum value of γ_c is given by the non-polar liquids and that a minimum is given by the hydrogen-bonding liquids. Zisman seems to have regarded the smallest value of γ_c as the

Fig 4

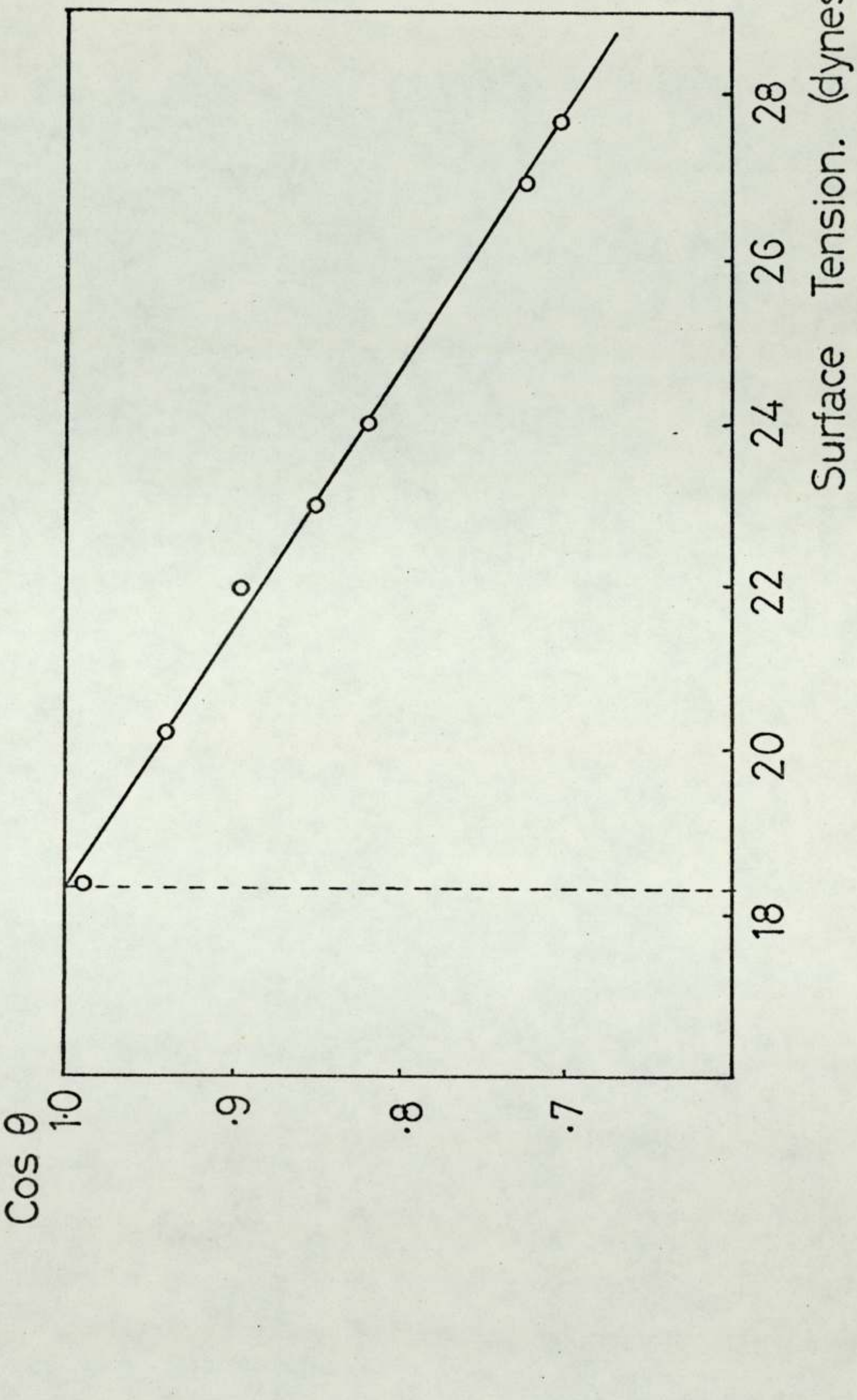
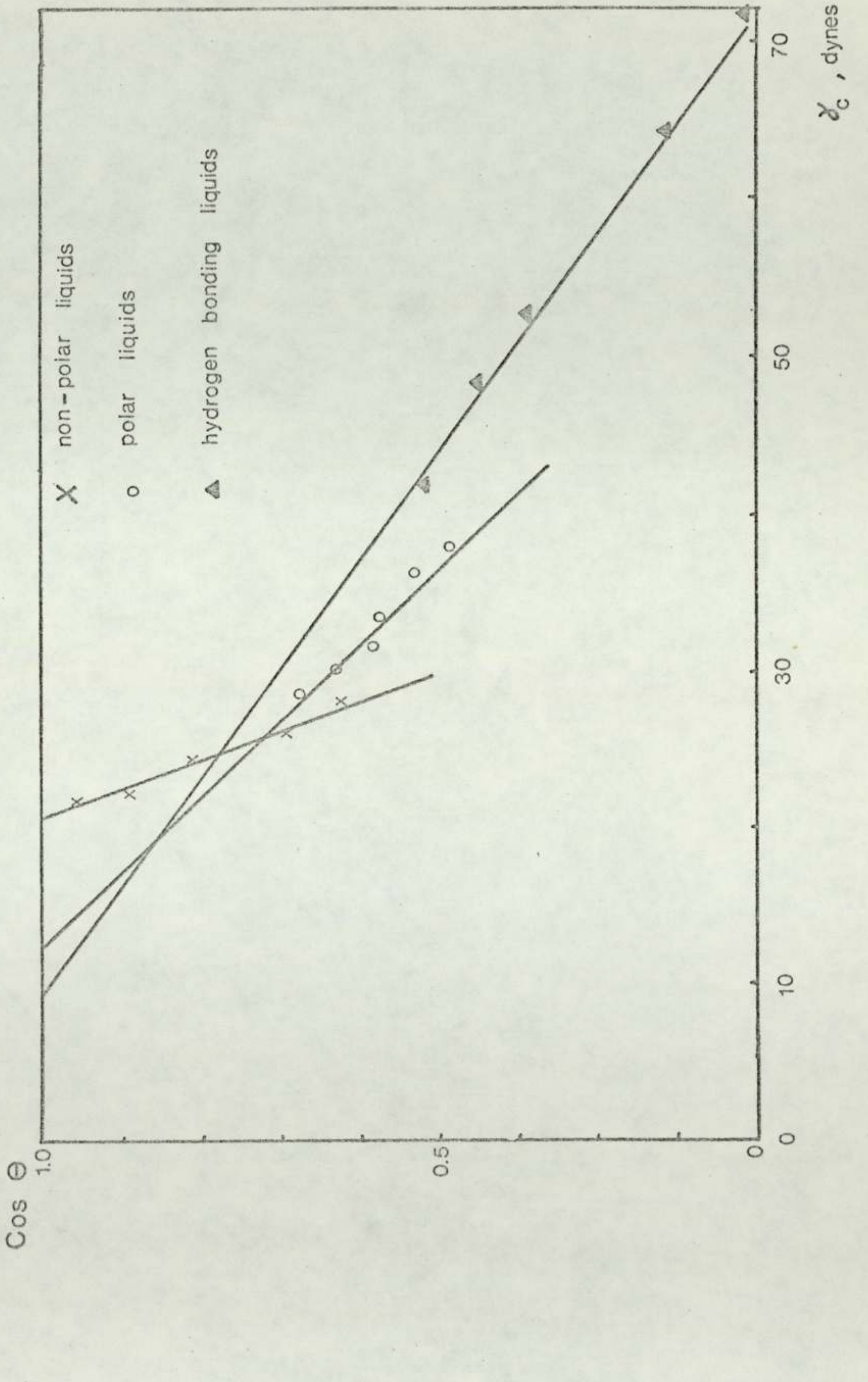


Fig. 5


Cos Θ
1.0
0.5
0
0
10
30
50
70
γ_c , dynes cm^{-1}
X non-polar liquids
o polar liquids
▲ hydrogen bonding liquids

critical surface tension, although recently[24] he has used the difference in γ_c values to explain conformational changes in samples of synthetic polypeptides.

1.8. Wetting and Contact Angle.

Historically it was Young[25] who provided the first of a number of important equations on wetting when he defined the equilibrium which quantifies the boundary of a liquid drop in contact with a solid. This equilibrium is expressed mathematically as:-

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \qquad - 10$$

This equation was obtained by resolving the forces at the point of contact of a sessile drop and a solid. (See Fig.6)

Later, Dupre[26] demonstrated that the work of adhesion could be defined in terms of Young's equation:-

$$W_a = \gamma_s + \gamma_{lv} - \gamma_{sl} \qquad - 11$$

Where γ_s is now the surface tension of the solid in vacuum. Combining Equations 10 and 11 in terms of the interfacial tension yields the Young - Dupre equation:-

$$W_a = (\gamma_s - \gamma_{sv}) + \gamma_{lv}(1 + \cos \theta) \qquad - 12$$

The first term of Equation 12 accounts for the drop in the surface free energy of the solid when it comes into contact with the saturated vapour of the wetting liquid which forms the drop. It is usually referred to as the spreading pressure, π_e. Bangham and Razouk[27] applied general adsorption equations in an attempt to elucidate π_e. They found that it was possible to express it in

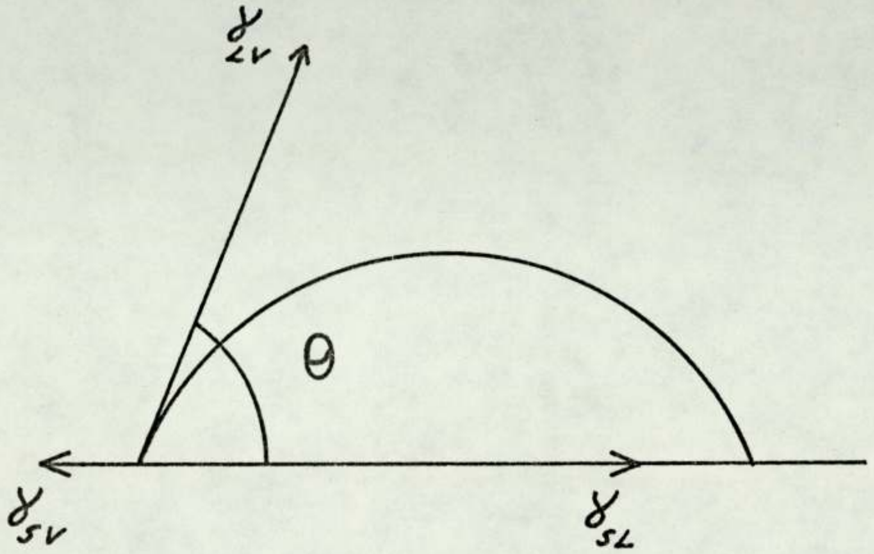


Fig. 6

terms of the concentration of absorbed vapour from the liquid and the vapour pressure of the liquid. Harkins[28] and his fellow workers used vapour adsorption studies to find values for π_e when the solid had a high surface free energy. With low energy solids, such as polymeric materials, it has long been assumed that π_e is equal to zero when the liquid forms a finite contact angle on the solid. Melrose has reviewed[29] the evidence for the assertion that the spreading pressure, π_e , is negligible and has concluded that if this is not the case then the actual value will be small.

1.9. Work of Adhesion.

It has been known for some time that one could consider the forces which operate between two solids or a solid and a liquid from the molecular point of view. Good and his co-workers[30-35] developed a molecular theory of work of adhesion using similar molecular force interaction parameters. The theory provides the following relationship for the work of adhesion, W_a

$$W_a = 2\phi_v\phi_a(\gamma_1\gamma_2)^{\frac{1}{2}} \qquad - 13$$

where γ_1 and γ_2 are the surface tension of the two adjacent phases at the interface. The parameters ϕ_v and ϕ_a identify the factors which cause a deviation from ideal interfacial behaviour. ϕ_v is given by an expression which depends on the molar volumes of the two phases; whilst the parameter ϕ_a is given by an expression:-

$$\phi_a = \frac{a_{12}}{(a_1\ a_2)^{\frac{1}{2}}}$$

The constants a_{12}, a_1 and a_2 are molecular attraction constants and are given by equations derived from the theories which cover basic molecular interactions, such as London and Keeson forces.

It is possible[15] to redefine ϕ_a in terms of the geometric means of the polar and dispersive fractions of the energy density of the adjacent phases.

$$\phi_a = (d_1 d_2)^{\frac{1}{2}} + (p_1 p_2)^{\frac{1}{2}} \qquad - \quad 14$$

where d is the dispersive and p is the polar component. Assuming that the molar volumes of the two phases are not vastly different then ϕ_v tends towards unity. Thus Equation 13 can be re-written as:-

$$Wa = 2 (\gamma_1 \gamma_2)^{\frac{1}{2}} \left[(d_1 d_2)^{\frac{1}{2}} + (p_1 p_2)^{\frac{1}{2}} \right] \qquad - \quad 15$$

Fowkes[36-39] has independently arrived at an expression for the dispersion force part of the total work of adhesion, W_a^d :-

$$W_a^d = 2(\gamma_1^d \gamma_2^d)^{\frac{1}{2}} \qquad - \quad 16$$

Good's derivation of the work of adhesion may be correlated with Fowkes' by re-writing Equation 15 in the following form:

$$W_a = 2 \left[(\gamma_1^d \gamma_2^d)^{\frac{1}{2}} + (\gamma_1^p \gamma_2^p)^{\frac{1}{2}} \right] \qquad - \quad 17$$

where $\gamma^d = \gamma.d$

$\gamma^p = \gamma.p$

and $\gamma = \gamma^d + \gamma^p$

with the appropriate subscript defining each phase.

By combining Equations 12 and 17 with respect to the work of adhesion an equation is obtained in which the measured contact angle and a known characterised liquid can be used to obtain a value for the surface free energy of a solid phase:

$$\cos\theta + 1 = \frac{2}{\gamma_{LV}}\left[(\gamma_l^d\gamma_s^d)^{\frac{1}{2}} + (\gamma_l^p\gamma_s^p)^{\frac{1}{2}}\right] \qquad - 18$$

Owens and Wendt[40] have used this expression to find the surface free energy of a number of polymers. The method relies upon having two wetting liquids, both fully characterised for polar and dispersive component and solving the equation for γ_s^p and γ_s^d. A number of liquids have been so characterised (Table 1) but the two normally chosen are water and methylene iodide, mainly because of ease of purification.

Recently Wu[41] has proposed a modification of Equation 18 in which the geometric mean terms, $(\gamma_l^d\,\gamma_s^d)^{\frac{1}{2}}$ and $(\gamma_l^p\,\gamma_s^p)^{\frac{1}{2}}$ are replaced by 'harmonic mean' terms:-

$$\frac{4\gamma_s^d\,\gamma_l^d}{\gamma_s^d + \gamma_l^d} \quad \text{and} \quad \frac{4\gamma_s^p\,\gamma_l^p}{\gamma_s^p + \gamma_l^p}$$

He claims that his modification renders Equation 18 more correct theoretically.

Alternatively Kaelble[42] has proposed a computational approach which uses a determinant form of Equation 18.

1.10. The relevance of Surface and Interfacial properties to biomedical applications.

The situations in which interfacial phenomena are important to biomedical or more specifically contact lens applications of polymers can be summarised from the following:

TABLE 1.

Dispersive, γ^d, and polar, γ^p, contributions to liquid surface tension, γ.

Liquid	γ (dynes cm^{-1})	γ^d (dynes cm^{-1})	γ^p (dynes cm^{-1})
Water	72.8	21.8	51.0
Glycerol	63.4	37.0	26.4
Formamide	58.2	39.5	18.7
Diiodomethane (Methylene Iodide)	50.8	49.5	1.3
n-Hexadecane	27.6	27.6	0.0
n-Octane	21.8	21.8	0.0

Fabrication of polymer	In vivo behaviour of polymers
Flow properties	Physical acceptance and comfort (e.g. physiological compatibility of lens and patient)
Coalescence of polymer particles in the melt	Bio-compatibility (e.g. Deposition of platelets, proteins etc. from blood)
Adhesion of polymer melt and solid to mould surface	Deposition of mucous debris from tear fluid

Polymers need first to be fabricated into the required shape for use. This means that particles of polymer are fused into a continuous phase which then must be made sufficiently fluid to flow into the mould shape. On cooling, the forces of cohesion between the polymer chains must be greater than the adhesion of the solid to the mould to allow release of the moulded object. This release cannot be achieved by the use of processing aids and lubricants as these would subsequently come into contact with human tissue; thus mould release has to be a property of the basic polymer structure. Once the polymer is in use in the human body the same low adhesion surface would play a large part in imparting a highly biocompatible surface to the polymer.

Many workers have tried to correlate the surface properties of a polymer with the biocompatibility criteria outlined above. Salzman[43] has published a review on how biocompatibility and surface properties interrelate. General observations have led to the proposal of Lambert's rule in the field of blood coagulation, which states, ". . . . the coagulation time is inversely proportional to water wettability."

Lyman et al[44] claimed to have found a correlation between surface free energy of hydrophobic polymers and their thrombus-inducing properties. This conclusion was refined later by Lyman[45,46] to the statement, ". . . . platelet adsorption increases with increasing critical surface tension." Bischoff[47] has postulated a relationship between the work of adhesion at the blood-polymer interface and coagulation time. Baier[48] has suggested that Zisman's critical surface tension, γ_c, for polymers can be related to their biocompatibility, concluding that polymers with γ_c of about 25 dynes cm^{-1} are the most biocompatible. Andrade[49-52] has postulated that it is the interfacial tension between the polymer and the human fluid in which the polymer is to be placed which is the important factor in biocompatibility.

1.11. Melt Processability of Hydrogels

Despite the fact that hydrogels were initially processed by either machining the dehydrated, cross linked polymer or by polymerising in a shaped mould to a product which is, in both cases, subsequently hydrated to a gel, melt processing does offer, as in the case of other polymers, the most versatile method of producing articles in a variety of different shapes and for different applications.

Although hydrogels share with other thermoplastics the potential ability to undergo melt processing by fusion of a powder which is then made to conform to the shape of an appropriate mould, they differ from conventional thermoplastics in two important respects. The first of these is the need to insert cross-links during the processing stage, a technique which is not intrinsically difficult and which is well known in other fields of polymer technology. The second reflects the facet in which hydrogels are unique, namely that the fabricated article must then be swollen by water to give the final product. Structural features which affect the hydrophilicity of the solid are also likely to affect the melt behaviour of the solid, such as mould release.

In passing from solid state to melt, a polymer differs from a liquid in that on cooling in contact with a solid surface, such as a mould surface, its own surface properties can be modified. Thus a given polymer moulded against a series of different surfaces can exhibit a range of surface properties. Generally this effect is small when compared to structure-surface relationships.

1.12. Scope and Objectives of Work

Since dehydrated hydrogel polymers are intermediate between polymer melts and the hydrated gels their properties may, in principle, be related to those of both the melt and the gel.

In the present work the surface properties of the dehydrated, solid polymer have been studied in an attempt to predict the surface behaviour of these two related states. The relevance of this is seen in the fact that whereas behaviour of the melt and the final gel are most important (e.g. in fabrication and in subsequent applications), the dehydrated solid hydrogel material provides the most convenient and reproducable type of surface to study.

In order to relate surface properties of dehydrated hydrogel polymers to the polymer melt and the hydrated polymer a knowledge of the surface free energy of the polymer and of the various polar and dispersive components of the surface energy is required.

The application of this knowledge is important in:-

i) Hydrogels in the eye. (Physiological compatibility.
Prevention of mucous build-up)

ii) Biocompatibility. (Platelet adhesion to the polymer
leading to a thrombus forming)

iii) Mould release. (Ease of release from a steel mould)

iv) Particle fusion.

In addition the question of surface modification either by inclusion of species having greater surface than bulk activity or by species which have specific surface effects are considered.

EXPERIMENTAL.

2.1. Purification of Monomers and Catalysts.

All the monomers and catalysts used were purified by conventional methods, using GLC to monitor the purity and are listed, with the suppliers, below.

Monomers.	Supplier.
Hydroxyethyl Acrylate.	B.P. Ltd..
Hydroxyethyl Methacrylate.	B.P. Ltd..
Hydroxypropyl Acrylate.	B.P. Ltd..
Hydroxypropyl Methacrylate.	B.P. Ltd..
N-Vinyl Pyrrolidone.	Koch-Light Ltd..
Styrene.	B.D.H. Ltd..
Acrylic Acid.	Koch-Light Ltd..
Methacrylic Acid.	Koch-Light Ltd..
Acrylamide.	Koch-Light Ltd..
Diacetone Acrylamide.	Koch-Light Ltd..
Initiators.	
α,α′-Azobisisobutyronitrile.	B.D.H. Ltd..
Uranyl Nitrate.	B.D.H. Ltd..

2.2. Preparation of co-polymer films.

i. Polymerised thermally.

The films were prepared in the cell shown in Fig. 7 . The glass plates G, were covered with sheets of poly(ethylene terephthalate) film, (Mylar) which allowed for easy separation; for it had been found previously that if the Mylar film was left out the adhesive bond formed between the polymer and the glass made it very difficult to separate the cell without destroying the surface of the sample. The covered glass sheets were separated by a polyethylene gasket, P, and the whole cell was held together by spring clips.

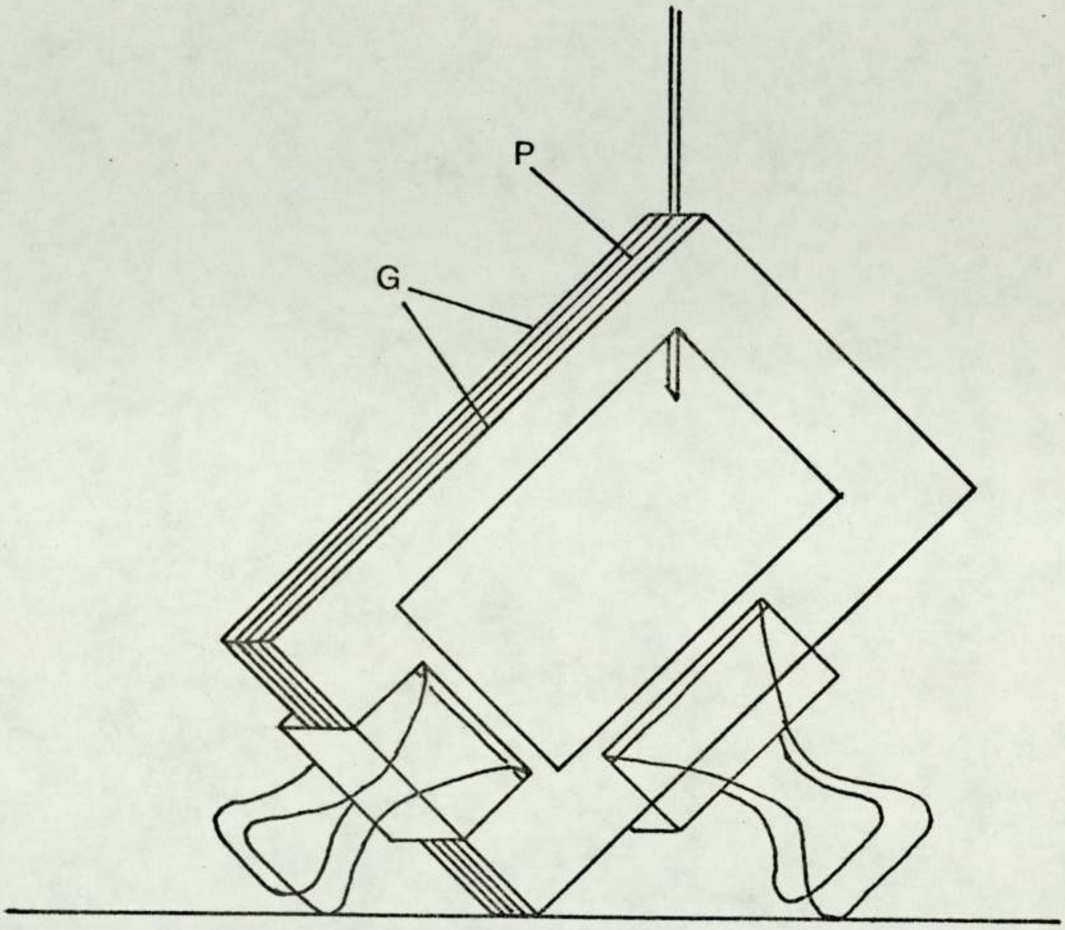


Fig. 7

Outgassed monomers with added catalyst were injected through a G25 syringe needle into the cell which was then placed in a 60°C oven for 3 days to allow the polymerisation to take place. Typically, 90 molar percent (5.22g) of **hydroxyethyl** acrylate and 10 molar percent (0.52g) of styrene were mixed together and 0.03 percent by weight of AZBN was added. The mixture was bubbled through with nitrogen to remove oxygen from the mixture and the solution was added to the cell via the syringe needle. Following a post-cure of 3 hours at 90°C, the glass plates were removed from the cell to leave the polymer film sandwiched between the Mylar sheets. If possible the Mylar sheets were carefully removed, if this was not possible the film was placed in distilled water to allow the hydrogel film to swell off of the Mylar. All films were allowed to hydrate for at least 3 weeks to ensure complete hydration, during which time the water was changed frequently to facilitate total removal of water soluble residues in the film.

ii. Polymerisation using UV radiation.

Several series of films were made using UV radiation with uranyl nitrate as the initiator. Films were also prepared for comparison with films produced by thermal polymerisation.

The cell used was the same as in thermal polymerisation and the monomers were also outgassed with nitrogen. Although the use of AZBN as a UV initiator is well known the more efficient initiator uranyl nitrate was used in this work. Typically, 90 molar percent (3.88g) of hydroxypropyl methacrylate and 10 molar percent of styrene were mixed together with 2 percent by weight of uranyl nitrate and the whole was outgassed with nitrogen. The mixture was added to the cell and placed under a UV lamp which emitted radiation of 365nm until polymerisation had taken place. In all cases no post-cure was used with the UV polymerised samples.

Following polymerisation the films were treated in the same way as the thermally initiated samples.

2.3. Preparation of Samples for testing.

From each hydrated polymer film two samples were cut, both were washed first with soap solution and then with copious volumes of distilled water to remove all the soap from the surface of the sample.

One sample was then stored in distilled water whilst the other was carefully dehydrated in a vacuum desiccator over phosphorous pentoxide. In order to keep the dehydrating samples flat they were sandwiched between sheets of Mylar held tightly together by spring clips.

2.4. Preparation of Polymer Rods.

In addition to films, a number of the copolymer formulations were prepared in the form of rods suitable for being lathe cut into lenses.

The rods were made in cells which consisted of a polyethylene tube sealed at its lower end. Catalysed monomers were introduced into the tube and the upper end sealed with a rubber stopper covered in polyethylene film. This coating prevented any possible attack by the monomers on the rubber stopper. PVC tape was used to secure the stoppers in the tubes and this also served to prevent any water leaking into the tube from the water bath used to maintain the required polymerisation temperature.

Following polymerisation the rods were post-cured for 4 hours at 90°C to ensure complete conversion. The polyethylene tubes were cut away from the polymer rods prior to the period of post-cure. Sample discs were cut from the rods, polished and used for contact angle work.

2.5. Techniques used to investigate surface properties.

Several techniques were used to investigate various surface properties of the prepared samples.

2.5.1. The measurement of Contact Angles.

The measurement of contact angles was carried out by a number of different methods.

i. Sessile Drop Method.

The cell used is shown in Fig 8. A square glass cell, O, had, standing in it, a stainless steel support, G, which carried a glass cover slip, C, to which the dehydrated sample, S, had been attached. A small volume of the sessile drop forming liquid was placed in the bottom of the cell, thus ensuring that the air around the sample was saturated with the vapour of the drop forming liquid once the cover, T, was in place. A small hole in T allowed a G25 syringe needle held in place by a Prior micromanipulator to enter the cell. This needle was connected to an 'Agla' microsyringe which was attached to a micrometer, so that small volumes of liquid could be placed accurately on the sample surface. The needle had had its point removed to ensure that the drop was formed symmetrically.

The cell was placed in the light path of a Rank Aldis Tutor 2 slide projector which had been fitted with a long focal length, 5cm, lens and an image of the drop was thrown onto a back projection screen. This image was then photographed to provide a permanent record.

The developed photographic film was placed in an enlarger

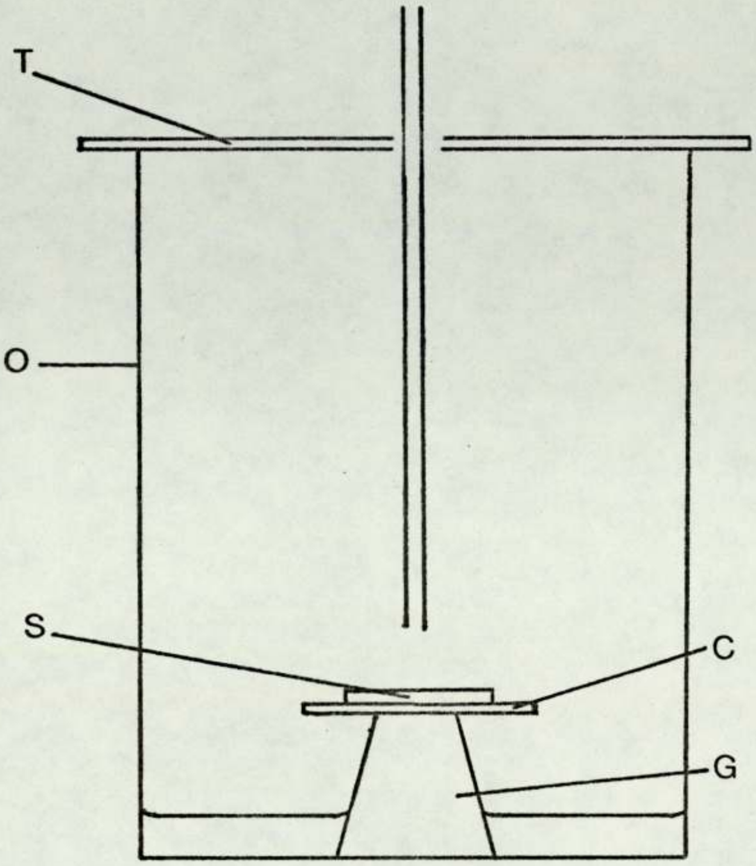


Fig. 8

and a large image of the drop was produced. The contact angle was determined by drawing the tangent to the drop at the surface of the sample and measuring the included angle with a protractor.

ii. Hamilton's Method.[53]

The apparatus is shown in Fig 9 . The sample, S, was glued to a glass cover slip, G, which was held in contact with a hollow tube, T, by a suction bulb contained in the tube. This apparatus was inverted and placed in the optical cell, C. Sufficient water, previously saturated with n-octane was added to the cell to cover the sample.

The wetting liquid which was delivered by the bent syringe needle, N, was n-octane. Control of the volume of the drop was achieved as in the Sessile Drop Method. Photographs of a projected image were taken and the contact angles were measured as before.

2.5.2. Goniophotometry.

This technique was used to investigate the samples for any surface roughness and is fully discussed in a later chapter.

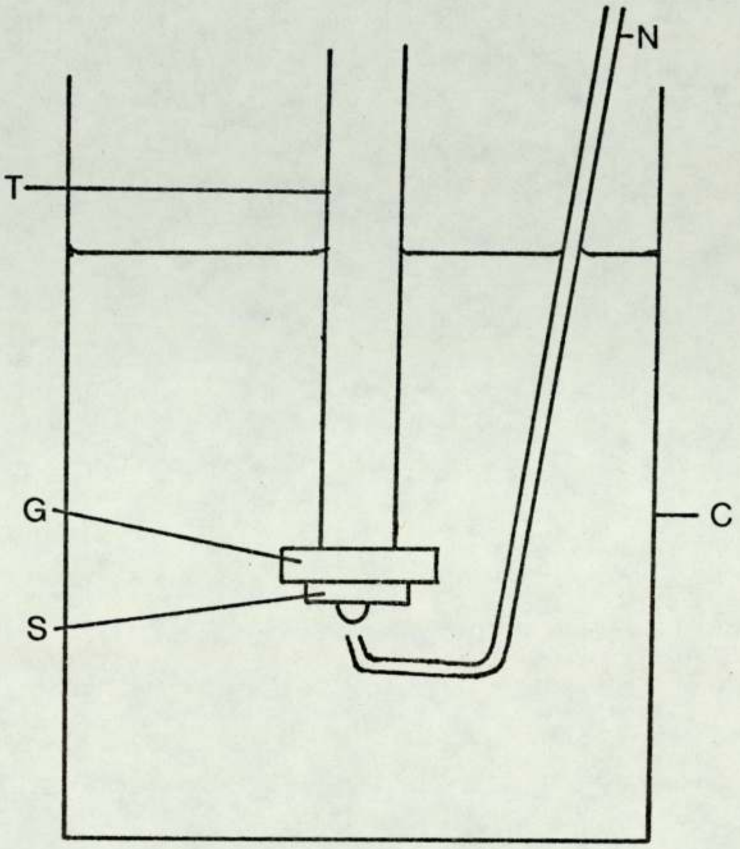


Fig. 9

CALCULATION METHODS.

3.1. Background and Applications.

One of the great aims of the chemist has always been to correlate the structure of molecules with their chemical and physical properties. To be able to predict a range of properties from only knowing the structure of the molecules involved would enable the best of a range of possible formulations to be selected without the need for production and testing of that entire range. Thus a material which ought, on theoretical grounds, to show advantageous surface properties could have its surface properties predicted from its molecular structure and if these then proved to be advantageous a sample could be prepared for testing; if not, no sample need be prepared and tested and so a considerable saving in time and materials would acrue.

Several theoretical methods are available by which the surface properties of liquids and polymers may be estimated. Free-volume theory gives a general equation relating surface properties to bulk properties. Wu[54] used this free-volume concept in Macleod's equation to obtain the following expression:-

$$X_s^{-1/n} - X_{s\infty}^{-1/n} = K(X_{b\infty} - X_b)$$

where X_s is a surface property, $X_{s\infty}$ is that property at infinite molecular weight, X_b is a bulk property, $X_{b\infty}$ is that property at infinite molecular weight, n is Macleod's exponent (normally taken as 4) and K is a constant. This equation indicates that surface free energy can be correlated to various bulk properties such as glass transition temperature, refractive index, mechanical strength and modulus. Good correlation has been shown between surface free energy and the glass transition temperature for some polymers although the above equation does not lend itself to simple or easy elucidation of an unknown surface property from known bulk properties.

The corresponding state theory of Prigogine[55] has been used by Roe,[56] Patterson and Rastogi,[57] and Siow and Patterson[58] to correlate the surface tension of liquids and polymers. In particular Siow and Patterson have shown that corresponding state theory gives similar results to those obtained with the parachor for some polymers. However this method is not as powerful as the parachor because it requires both the isobaric thermal expansion coefficient and isothermal compressibility data whereas the parachor only needs density data.

3.2. Parachor.

In 1923 Macleod[59] discovered the simple relationship which connects surface tension or free energy of a liquid and its density,

$$\gamma = C\,(D - d)^4 \qquad - 19$$

where D and d are the densities in the liquid and its vapour, γ is the surface tension at the same temperature, and C is a constant characteristic of the liquid. More recently Fowler[60] has shown that this expression may be deduced theoretically.

Sugden[61] revised the Macleod equation to express the constant in molar proportions and called this new constant the parachor. His revised form of the Macleod equation has the following form:-

$$\gamma = \left(\frac{P(D - d)}{M}\right)^4 \qquad - 20$$

where M is the molecular weight and P is the parachor. When the vapour density is very small in comparison with that of the liquid, the expression reduces to

$$\gamma = \left(\frac{PD}{M}\right)^4 \qquad - 21$$

$$= \left(\frac{P}{Vm}\right)^4 \qquad - 22$$

where Vm is the molar volume of the liquid.

At first the parachor was considered to be an additive function and atomic constants were calculated. For organic compounds the most important value was that of the $-CH_2$ unit. By comparing the members of various homologous series Sugden was able to arrive at a value of 39 for the methylene unit. From this he was then able to progress to obtain values for C and H, and by assuming that these values were correct and additive he calculated other elements' parachor values. Sugden also saw that in addition to the additive elemental constants certain constitutive features such as a double bond or ring could be assigned a value.

Mumford and Phillips[62] detected shortcomings in Sugden's simple treatment of the parachor as an additive function. They examined anomalies in the parachors of fatty acids which had been reported by Hunten and Maass[63] and concluded that they were probably due to an incorrect value being assigned to the methylene increment. Sugden had failed to distinguish between isomers and had also ignored the effects of branches in the chain. By using for their calculations only values from series of the same type - all primary, all secondary, etc. - Mumford and Phillips calculated a mean value for the methylene group as being 40. In addition they proposed assigning a value to any branch present in the molecule to allow for the 'strain' it introduced. This was an important step in establishing the value of the parachor for the methylene increment and, also, in further suggesting the constitutive nature of the parachor.

Recently Quayle[64] has extensively reviewed the parachor values which have been ascribed to constituent parts of various molecules and has produced a table of values for a large number of elemental units.

Roe[65] and Safonov and Entelis[66] suggested that the parachor could be applied to polymers. Yagnyatinskaya et al.[67] have used the parachor in determining the surface tension of a number of amorphous polymers and Wu[41,68,69] applied equation 21 to many homopolymers over a wide range of temperatures and has shown that it can predict both the surface free energy and its temperature dependence for polymers. He has also compared parachor calculated values with those obtained by direct measurement of the surface tension of polymers in the melt state and has found that there is good agreement. In all Wu's work the values used to calculate the parachors were those given by Quayle and these values have also been used by the author in this work. Table 2 gives a comparison of the parachor calculated surface free energy and the literature values for the critical surface tension for a number of homopolymers. As can be seen, the values obtained from the parachor calculation do not agree very closely with the values given in the literature for the critical surface tension. However when the parachor values are compared with values obtained for the

TABLE 2

A comparison of Parachor-calculated surface free energy, γ with literature values for critical surface tension, γ_c .

Polymer.	Parachor.	M.W	Density.	γ	γ_c
PTFE	122.4	100	2.2	53	18
Polyethylene	80	28	0.91	44	31
Polystyrene	245.4	104	1.07	40	36
Poly(methyl methacrylate)	216.4	100	1.19	44	38
Poly(ethyl acrylate)	223.8	100	1.1	36	35

surface tension of polymers in the melt state, Table 3, the agreement is much closer.

TABLE 3

A comparison of Parachor calculated surface free energy, γ_p, with values of surface free energy obtained from melt studies.

Polymer.	Surface free energy. Parachor-calculated.	Measured.
Polyethylene	44	35
Polystyrene	40	40
Poly(methyl methacrylate)	44	41
Poly(n-butyl methacrylate)	38	31

Table 4 lists the various monomers used in this project along with their parachors, molecular weights, densities and the calculated surface free energies of the homopolymers.

TABLE 4

Monomer.	Parachor.	M.Wt.	ρ	γ
HEA	234.4	116	1.36	57.0
HEMA	270.7	130	1.28	50.5
HPA	274.4	130	1.16	35.9
HPMA	310.7	144	1.19	43.46
NVP	230.1	111	1.21	39.6
Acrylic Acid	135	72	1.37	43.5
Methacrylic Acid	171.2	86	1.26	39.6
Acrylamide	136.1	71	1.3	38.6
Styrene	245.4	104	1.07	40.6

Rastogi and St. Pierre[70] have shown that the parachor could also be applied to random copolymers:

$$\gamma_{co} = x_1 \left[\frac{P_1 \rho_1}{M_1} \right]^4 + x_2 \left[\frac{P_2 \rho_2}{M_2} \right]^4 \qquad - \quad 23$$

where γ_{co} is the surface tension of copolymer, x_i is the mole fraction of component i, P_i is the parachor of a repeat unit of component i, ρ is the density of component i and M_i is the molecular weight of the repeat unit of component i. This equation implies that surface excess behaviour is absent, a better equation is, perhaps, given by

$$\gamma_{co} = \frac{(x_1 P_1 + x_2 P_2)^4 \cdot (x_1 \rho_1 + x_2 \rho_2)^4}{(x_1 M_1 + x_2 M_2)^4} \qquad - \quad 24$$

which allows for any surface excess behaviour.

The equation of Rastogi and St. Pierre, Equation 23, and the version modified to take account of surface excess behaviour, Equation 24, were both converted to computer programs to allow for easy processing of large amounts of data. These programs are listed in Appendix 2 , Table 1.

The data listed for the monomers in Table 4 was inserted into both programs and the surface free energies of a range of copolymers compositions were calculated. These corresponded to the copolymers prepared for testing by sessile drop techniques, however, several ranges of copolymer compositions not selected for testing were also calculated.

3.3. Cohesive Energy Density.

As discussed in the introduction it is possible to progress from the use of cohesive energy density to the work of Hildebrand and Scott,[14] who produced an equation which connected the surface free energy with data based on molecular constitution, such as molar volume, Vm and molar cross-sectional area, A. Although the work of Hildebrand and Scott gives fairly accurate results for non-polar liquids it is not so good for polar liquids and polymers.

Wu[16] reassessed Hildebrand and Scott's work with respect to polymers and found that because polymers are chainlike the relationship between molar volume and molar cross-sectional area was not as simple as supposed. He replaced A, the molar cross-sectional area, by a term he called the 'effective' molar cross-sectional area given by:-

$$A = k.N^{\frac{1}{2}}.n_s.(V_m^s/n_s)^{\frac{2}{3}} \qquad - \quad 25$$

where; n_s is the number of atoms in a segment,

V_m is the molar volume of a segment,

N is Avogadro's number.

and k is a parameter determined by the structure and packing geometry of the polymer molecules.

Equation 25 may be arrived at by assuming that polymer molecules may be represented by a series of 'equivalent spheres', each sphere being an interacting unit whose volume is Vm/n_s. By considering only dispersive contributions Wu arrived at a final equation which was given by:

$$\gamma = 0.327 \left[\frac{(\Sigma F)_s}{n_s}\right]^{1.85} \left[\frac{n_s}{\nu_s}\right]^{1.52} \qquad - \ 26$$

As this derivation uses only the dispersive contributions to all the parameters used, the final surface free energy will only be equivalent to the dispersive component of the total surface free energy. This in turn may be equated with the critical surface tension of Zisman. Table 5 shows the values for molecular weight, density, Small's sigma F values and the number of atoms in a repeat unit for a range of homopolymers and compares the calculated values for surface energy with the literature values for critical surface tension. Table 6 lists the values used in Equation 26 for the monomers employed in this work; also listed is the value obtained for the surface energy of the homopolymers.

TABLE 6.

Monomer.	M. Wt.	ρ	ΣF	No. Atoms in repeat Unit, n_s.	γ
HEA.	116	1.36	907	16	45.0
HEMA.	130	1.279	1000	19	39.1
HPA.	130	1.164	1016	19	34.9
HPMA.	144	1.19	1109	22	39.5
NVP.	111	1.208	910	17	39.7
Acrylic Acid.	72	1.37	551	9	45.2
Methacrylic Acid.	86	1.26	644	12	36.9
Acrylamide.	71	1.303	581	10	45.6
Styrene.	104	1.07	896	16	36.2

TABLE 5

A comparison of C.E.D. calculated surface energy, γ,
with literature values for critical surface tension, γ_c.

	M.Wt.	ρ	ΣF	No. Atoms in Repeat Unit	γ	γ_c
Polytetrafluoroethylene	100	2.19	300	6	21	18
Polyethylene	28	0.95	266	6	32	31
Polystyrene	104	1.04	896	16	36	36
Poly(methyl methacrylate)	100	1.19	778	15	36	38

A large number of co-polymers were investigated using Equation 26. To enable rapid processing of large amounts of data Equation 26 was converted in to a computer program which calculated the values of surface tension for varying co-polymer compositions. The program is given in Appendix 2 , Table 2 .

3.4. Discussion.

As can be seen by comparing Table 2 with Table 5 the calculation based on the parachor gives values which are not in very close agreement with the critical surface tension results of Zisman, whereas the work based on cohesive energy density gives values which are in very good agreement. This is because the work of Zisman used wetting liquids which had only dispersive forces causing their surface tension. Thus they could only interact through the dispersive forces in the material they were wetting and the critical surface tension obtained on extrapolation of the results back to zero contact angle leads to a value which is only a function of the dispersive forces present in the material.

The derivation of the cohesive energy density equation, Equation 25, by Wu used only the dispersive components of the parameters involved and so one would expect that the value obtained would be the dispersive component of the material under test and would be thus closely allied to the values obtained for that material by Zisman's methods.

With the parachor technique this does not occur as the important parameter, P, the parachor, has been found by methods which do not isolate either the dispersive or the polar components of the surface energy. Thus the parachor derived value of γ does not compare very favourably with the value obtained by Zisman's method for equivalent polymers, whereas it does compare favourably with values obtained by extrapolating values for the surface tension of polymers in the melt state.

As was to be expected the equation of Rastogi and St. Pierre, Equation 23, gave surface energy results for copolymers which were purely additive for each change in composition. With Equation 24 a deviation was seen from this straight line behaviour, this was because the equation allows for surface excess behaviour. At the extremes of any copolymer series, i.e. homopolymers, both equations yield the same value for surface energy.

Fig.10 shows a typical set of results for Equation 23 where the composition of hydroxyalkyl acrylate and methacrylate copolymers with styrene were plotted against the calculated surface energy. Fig.11 shows a comparison of Equations 23 and 24 for a copolymer of HEMA and styrene. All the copolymer systems studied have shown deviation from linearity, i.e. some surface excess behaviour of one of the components, although all the copolymers studied do not deviate towards the same component.

More detailed discussion of molecular interactions and other features will be given at a later stage in the thesis, in the light of experimental results to be subsequently presented.

Fig. 10

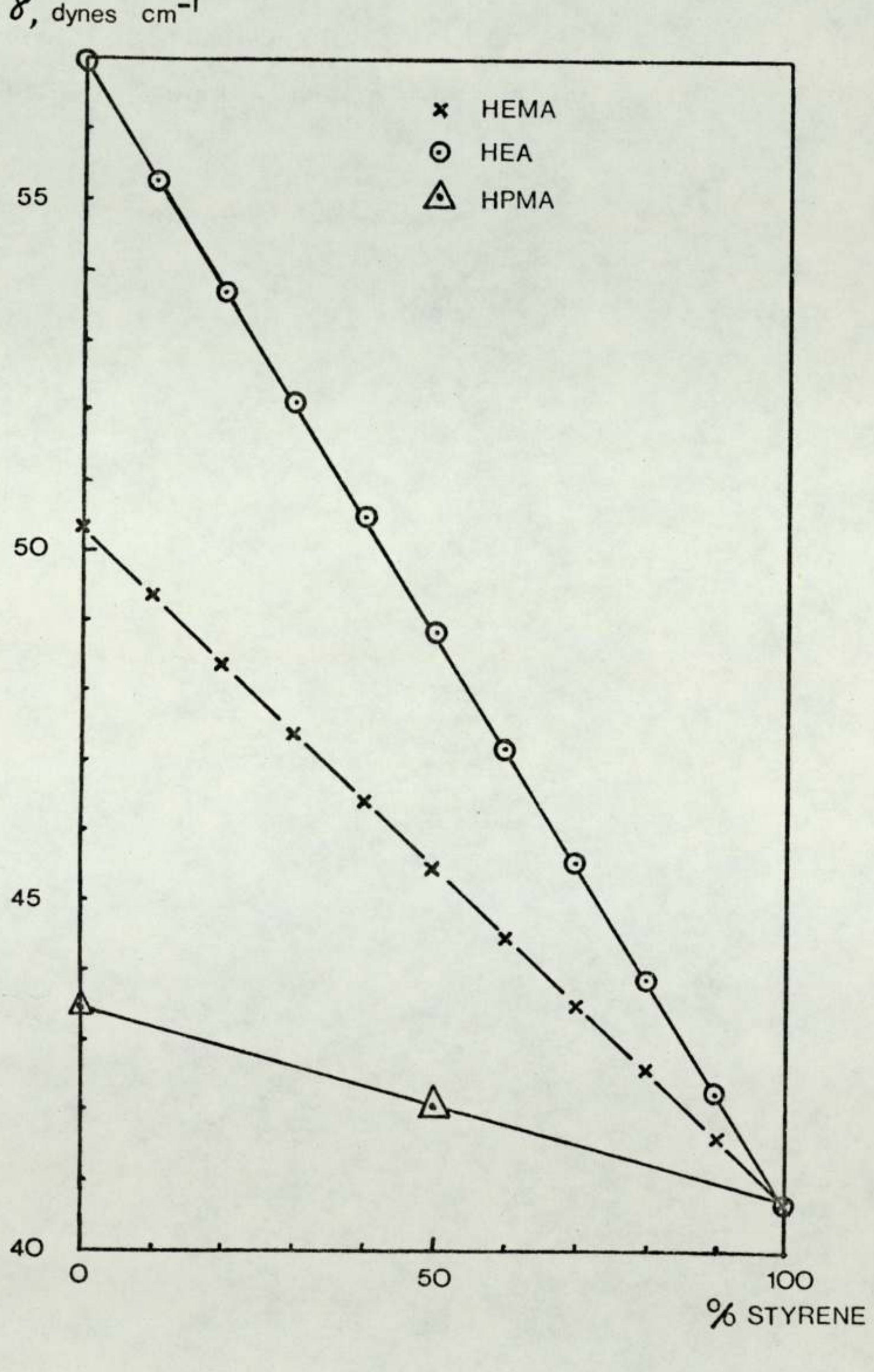
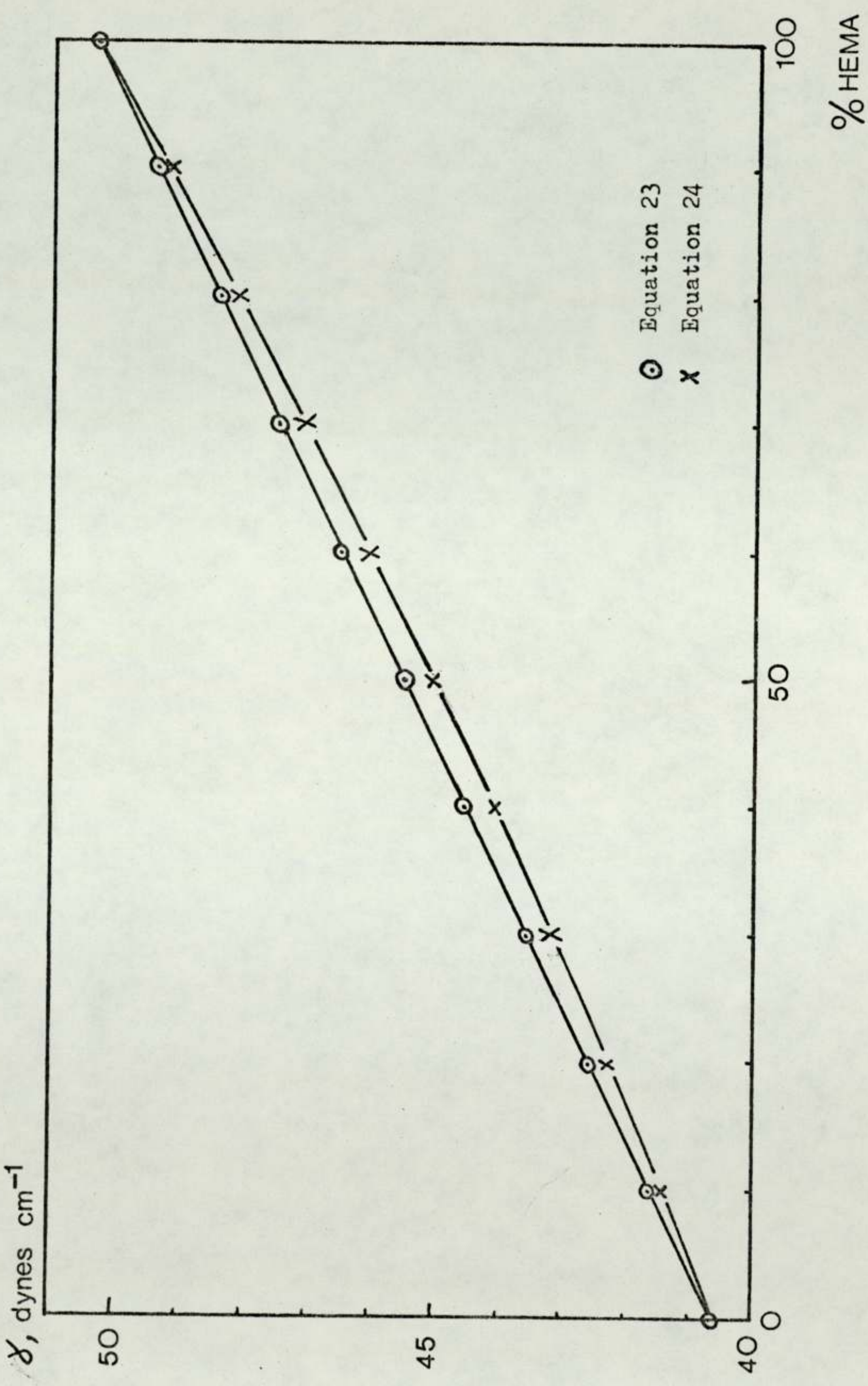


Fig. 11



EXPERIMENTAL TECHNIQUES
FOR
DEHYDRATED SURFACES.

4.1. Preliminary Studies.

4.1.1. Introduction.

The polymers used in the experimental work were prepared as described in a previous chapter (Chapter 2). It had been shown[71] that the detergent used to clean the surfaces was completely removed by washing with distilled water and so all the samples were cleaned by this method prior to dehydration.

Tests were carried out on the dehydrated samples in order to assess the surface roughness. Wenzel[72] has shown that surface roughness affects the contact angle and he has provided a relationship which connects the surface roughness, r, with the measured contact angle for rough, θ_r and for ideally smooth θ surfaces.

$$r = \frac{\cos \theta_r}{\cos \theta}$$

To reduce the roughness factor Zisman[18] has described special techniques which may be employed in the preparation of samples.

4.1.2. Goniophotometry.

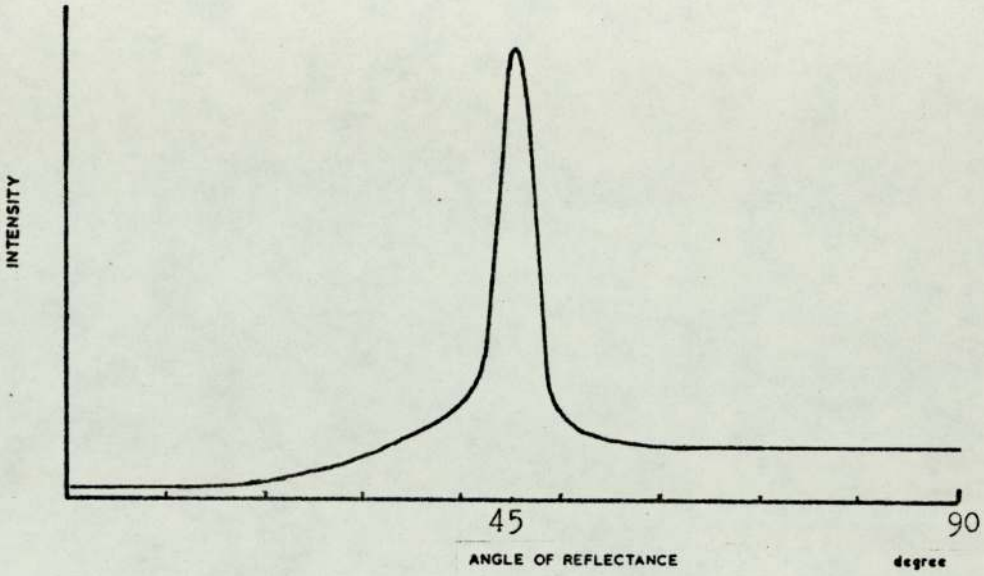
To examine the samples produced for surface smoothness specimens were subjected to Goniophotometric analysis. The technique of goniophotometry has been described in a series of papers [73,74,75] but consists, essentially, of a collimated beam of monochromatic light hitting the sample at a given angle of incidence together with a photomultiplier tube scanning the light reflected from the surface. As the photo-tube scans the surface, light intensity is recorded automatically in the form intensity versus angle of reflection.

For a planar smooth surface the angle of reflection equals the angle of incidence and the intensity of the light will appear as a sharp peak with rapid fall-off of the intensity as the tube scans away from that angle (Fig. 12). For surfaces which have large irregularities the peak will remain sharp but the angle of reflectance moves to a different value from that of the angle of incidence. With surfaces containing small irregularities the peak becomes diffuse and broadens, although the angles of reflectance and incidence remain substantially equal (Fig. 13).

The specimens were mounted in the machine using a glass slide as a support. Also tested was a sample of the poly(ethylene terephthalate)(Mylar) used as the release sheet against which all the samples were polymerised. Fig. 14 shows the trace obtained for the Mylar, Trace A, along with those obtained for poly(hydroxyethyl acrylate), Trace B, and poly(hydroxyethyl acrylate-co-styrene) (90:10), Trace C. Other samples tested gave similar results. The results were consistent with a sample which was microscopically smooth.

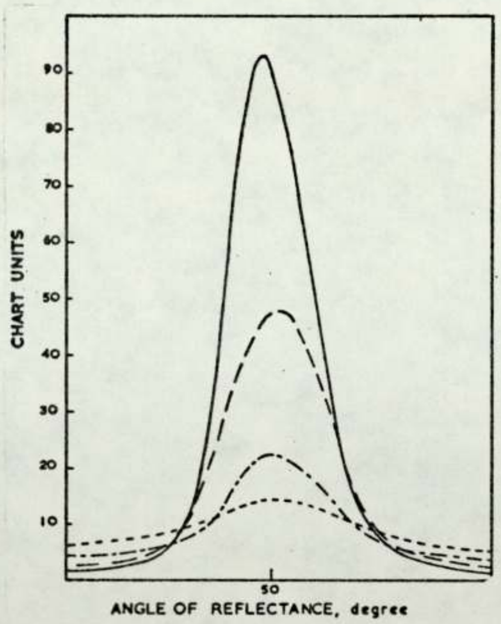
4.2. Sessile drop technique on hydrogel polymers.

The dehydrated hydrogel polymers were studied by the sessile drop method as described in an earlier chapter. Contact angles were measured for each sample using, initially, two contact liquids, water and diiodomethane. Later a third liquid, formamide was added to check on the generality of the method for analysing the results obtained from the contact angles. All the liquids were purified by reduced pressure distillation, except for the diiodomethane which was used as supplied. The surface tensions of the liquids were found by the use of a wetting balance and these results were



Angle of incidence = 45°

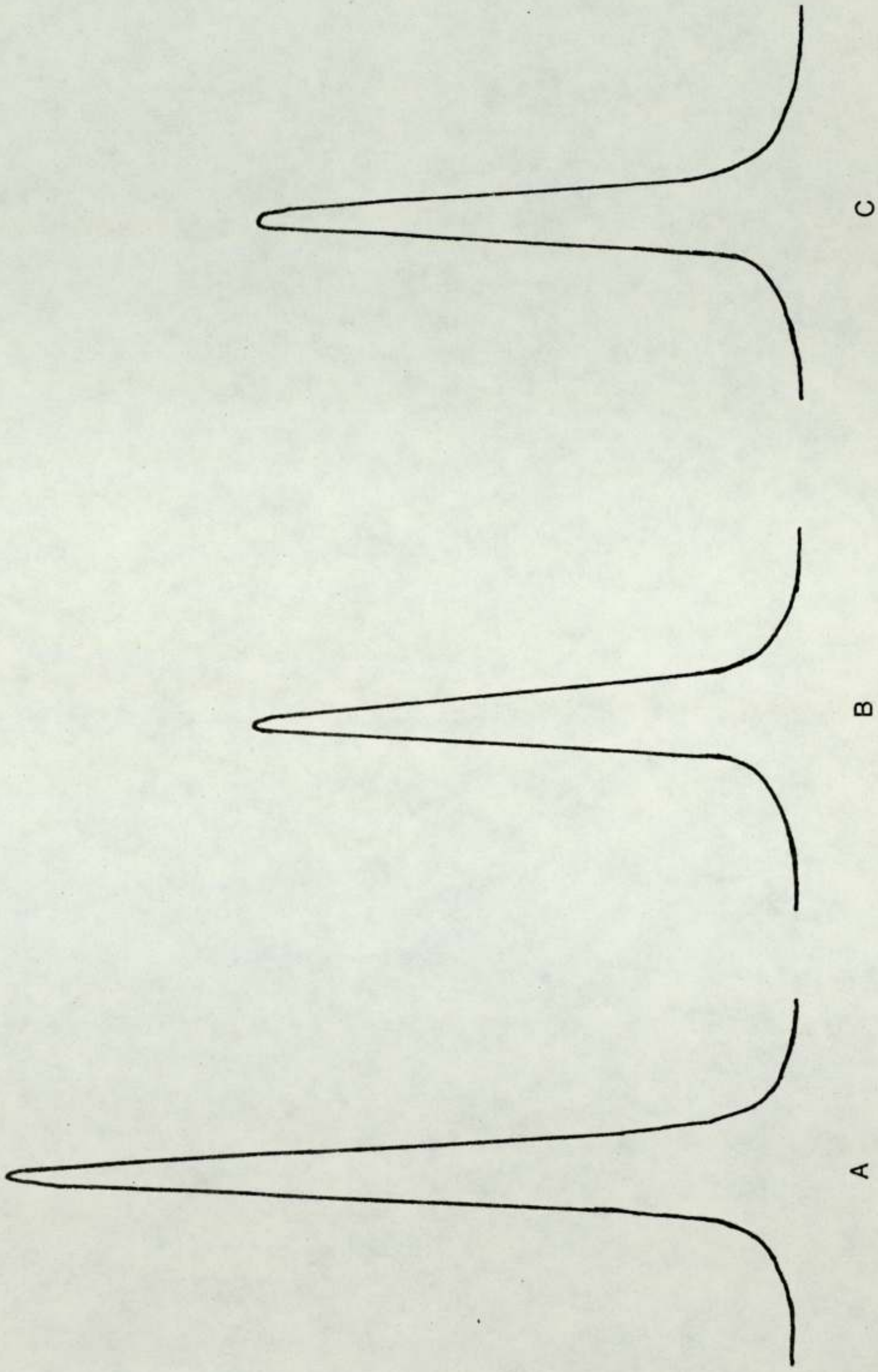
Fig. 12



Angle of incidence = 50°

Fig. 13

Fig. 14



compared with the literature values, see Table 7.

TABLE 7.

SURFACE TENSION. (dynes cm^{-1})

Liquid.	This work.	Literature value.[76]
Water.	71.4	72.8
Diiodomethane.	49.1	50.8
Formamide.	56.8	58.2

All three liquids had been fully characterised with respect to the polar and dispersive components of their surface tension (Table 1) and these values were used in all subsequent work.

The contact angles and the literature values for the components of the surface tension of the liquids (Table 1) were inserted into the equation of Owens and Wendt (Equation 18) to yield two simultaneous equations which were then solved to yield estimates of the surface energy components of the hydrogel surface. To assist in the rapid processing of the contact angle data and in solving the equations the necessary mathematical steps were reduced to a computer program, which is given in Appendix 2 , Table 3.

The Wu modification of the Owens and Wendt equation (Equation 18) has also been used to produce a further value for the surface free energy of the samples investigated. Wu's equation uses a harmonic mean term in place of the geometric term in the standard Owens and Wendt equation and in addition uses different values for the polar and dispersive components of both water and diiodomethane; see Table 8.

By solving Wu's equation with his data but using the same results for contact angle as were used previously a comparison could be made between the two calculation methods. Table 9 shows a typical set of results for a range of hydrophilic - hydrophobic copolymers and Fig. 15 shows a comparison of the results obtained by the two methods along with those obtained when the two sets of data are transposed.

As can be seen the trends are the same as with the Owens and Wendt equation although the results are slightly different, this being caused by the difference between a geometric and a harmonic mean and the difference in importance given to the two components of the surface tensions of the wetting liquids.

The method of Owens and Wendt was used throughout this project because it has a greater volume of supporting theory.

4.3. Sessile drop technique on non-hydrogel polymers.

Several non-hydrogel polymers were included in the investigation to act as controls and to serve as a comparison with literature work. The polymers selected were:- polyethylene, poly(methyl methacrylate), polystyrene, poly(tetrafluoroethylene) and poly(ethylene terephthalate). These samples were cleaned and dried in the same way as the hydrogel samples and were stored in a vacuum desicator until needed. (See Table 11.)

One sample of polyethylene was used to ensure that each set of contact angle determinations, which were carried out at

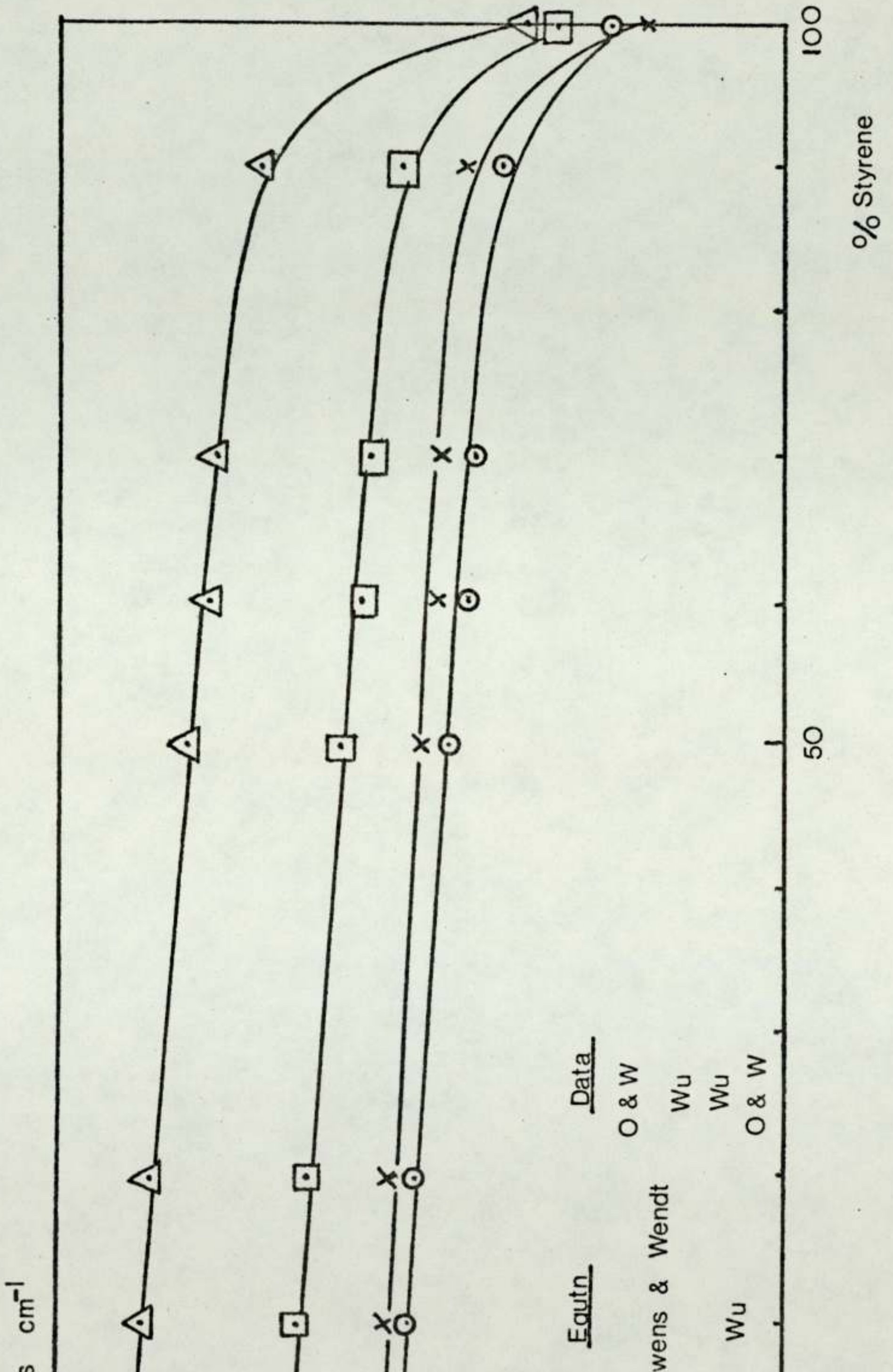
TABLE 8

Liquid	Owens & Wendt γ	Owens & Wendt γ^d	Owens & Wendt γ^p	Wu γ	Wu γ^d	Wu γ^p
Water	72.8	21.8	51.0	72.8	22.1	50.7
Diiodomethane	50.8	49.5	1.3	50.8	44.1	6.7

TABLE 9

Equation type	Owens & Wendt		Wu	
Data type	Owens & Wendt	Wu	Wu	Owens & Wendt
Sample HEA : Styrene				
0 : 100	42.1	47.8	39.6	45.7
10 : 90	49.5	66.6	52.1	56.5
30 : 70	51.4	69.0	53.8	58.6
40 : 60	51.9	69.5	54.1	59.2
50 : 50	53.2	71.1	55.2	60.6
80 : 20	55.5	73.9	57.2	63.0
90 : 10	55.9	74.4	57.5	63.6
100 : 0	56.5	74.9	57.9	64.4

Fig. 15


γ, dynes cm^{-1}
80
70
60
50
40
30
0
50
100
% Styrene
Equtn
Data
⊙ } Owens & Wendt
△
O & W
X } Wu
⊡
Wu
Wu
O & W

various times, would be directly comparable. This was achieved by recording the water contact angle of polyethylene before and after each series of contact angle determinations. Provided the results obtained were within ± 2° of the initial determination for the water contact angle on that polyethylene sample the results were accepted for the series.

4.4. The use of Formamide as a wetting liquid.

In deriving Equation 18 Owens and Wendt did not limit its applicability to just the two liquids water and diiodomethane. In order to test the generality of the method a third liquid, formamide was introduced. Three non-hydrogel homopolymers, polyethylene, poly(methyl methacrylate) and poly(ethylene terephthalate) were used, along with a series of hydrophilic - hydrophobic copolymers. Table 10 shows the contact angles obtained with each of the samples investigated, along with the surface free energy estimate obtained when the diiodomethane and the formamide contact angles were used. in Equation 18.

As can be seen by comparing Table10 with Table 11 the results are very similar to those produced when water and diiodomethane are used as the wetting liquids. This shows that the method is probably a general one and that the assumptions made in arriving at Equation 18 are valid.

4.5. Time dependence of contact angle.

All the contact angles recorded were advancing contact angles and as such the time dependence of the contact angle is removed since the drop is increasing in size during the experiment and the equilibrium between the drop and the surface it is wetting is a dynamic one. However there is the possibility that as the

TABLE 10

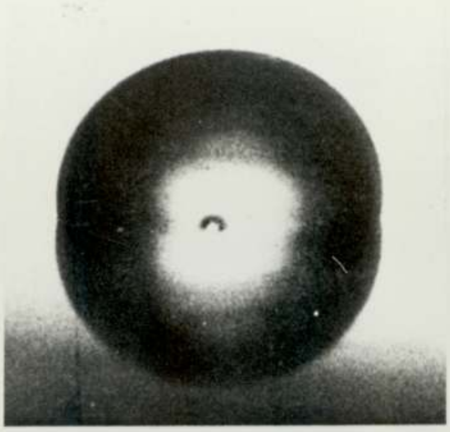
	Diiodo-methane	Formamide	γ^d	γ^p	γ
Polyethylene	50	73	34.9	0.0	34.9
Poly(methyl methacrylate)	40	59	38.2	1.5	39.7
Poly(ethylene terephthalate)	20	44	45.0	3.3	48.3
HPA : Styrene					
10 90	45	40	30.7	14.7	45.4
20 80	47	50	31.4	8.5	39.9
30 70	38	59	39.5	1.1	40.6
50 50	42	63	37.9	0.7	38.6
70 30	35	70	44.6	0.5	45.1

materials are hydrophilic, water, when it is used as a wetting liquid, will be absorbed into the material and this will adversely affect the contact angle. To test for this a static contact angle experiment was devised in which a drop of water was placed on the surface of a hydrogel sample and the drop was photographed at various times. The results of this test are given in Plate 1 and show that over a fairly long period, when compared with the time taken to get an actual measurement of a contact angle, what water uptake there is does not affect the contact angle significantly.

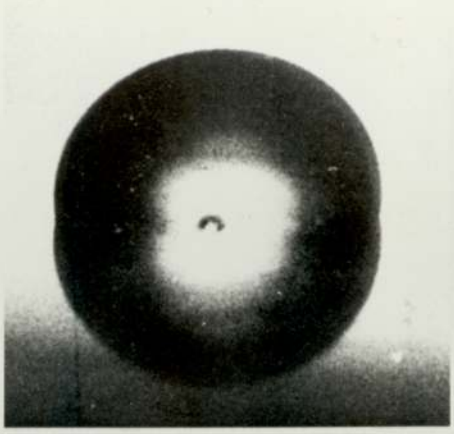
4.6. Results and Discussion.

The homopolymers produced from the vinyl monomers have been extensively studied, especially in respect of their surface free energies. However, there is no reported investigation of the surface properties of dehydrated polymers produced from more hydrophilic monomers. Surface studies of the polymers produced from these hydrophilic monomers are of increasing importance and are relevant in two fields; firstly in moulding where the surface largely determines the amount of mould adhesion seen and secondly, in biocompatibility where the surface constitution is of great importance in determining the amount of rejection the body exerts on the polymer implant.

As the type of polymers described here are sufficiently hydrophilic to absorb water and form hydrogels, it was expected that the surface properties would be somewhat different from those shown by the more conventional polymers. This was not the case, however, and it was found that hydrogel polymers came within the fairly narrow range of surface energies exhibited by the more polar of the conventional polymers, such as poly(methyl methacrylate), 42 d.cm^{-1}



0 min



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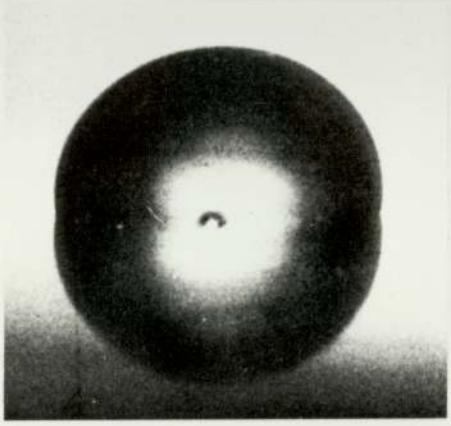

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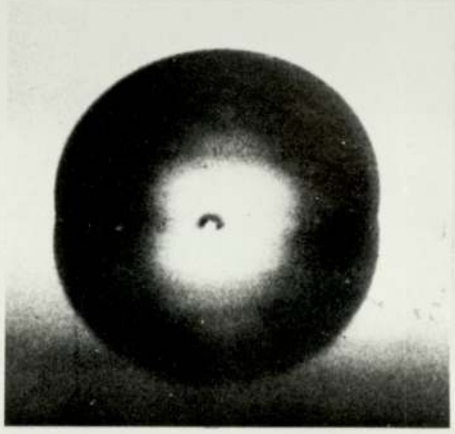

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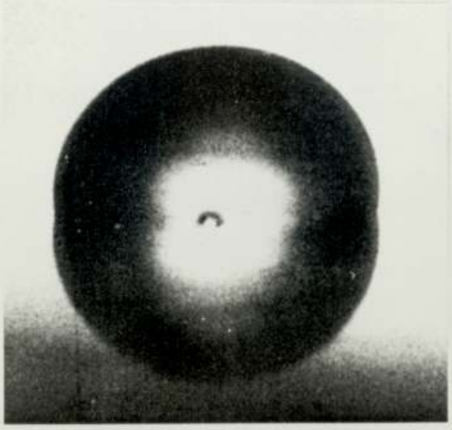
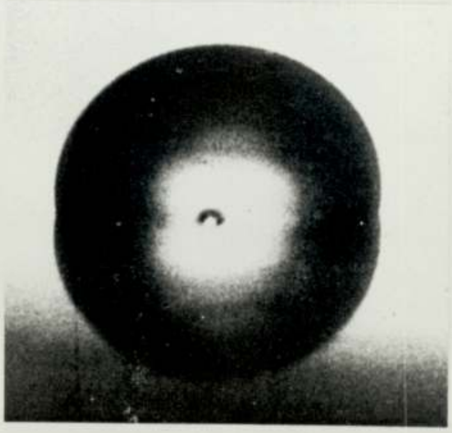


15 min



30 min

PLATE 1

and the nylons, 46-48 dynes cm^{-1}. Within this range it was found that there were variations due to the different amounts of hydrophilicity displayed by the monomers although all the values lay within the range given above.

The contact angle quoted for any liquid on any surface is an average of at least six results which all agreed to within ± 2°. When the contact angle results were put in the equation of Owens and Wendt and the simultaneous equations solved, estimates for the components of the surface free energy were produced. Table 11 lists the water and diiodomethane contact angles for the non-hydrogel homopolymers investigated in this project, along with the calculated components of the surface free energy.

TABLE 11

	Water	Diiodomethane	γ	γ^d	γ^p
Polystyrene	85	35	42.1	40.2	1.9
Polyethylene	94	50	34.2	33.3	0.9
Poly(methyl methacrylate)	73	40	42.6	35.3	7.3
Poly(ethylene terephthalate)	60	20	53.3	41.6	11.7
Poly(tetrafluoroethylene)	108	77	19.1	18.6	0.5

The surface free energy estimates produced by solving the equation of Owens and Wendt (Equation 18) were plotted against the composition of the sample for all of the series investigated and all show interesting trends due to the unique nature of the hydrophilic monomers. With all polymers the surface structure is dictated by interactions which occur in the bulk. Values which are observed for surface free energy are functions of the amount of freedom the polymer chains have in taking up any preferred orientation under the constraints of such things as inter- and intramolecular bonding;

ease of packing of any side chains and the amount of crosslinking which has taken place.

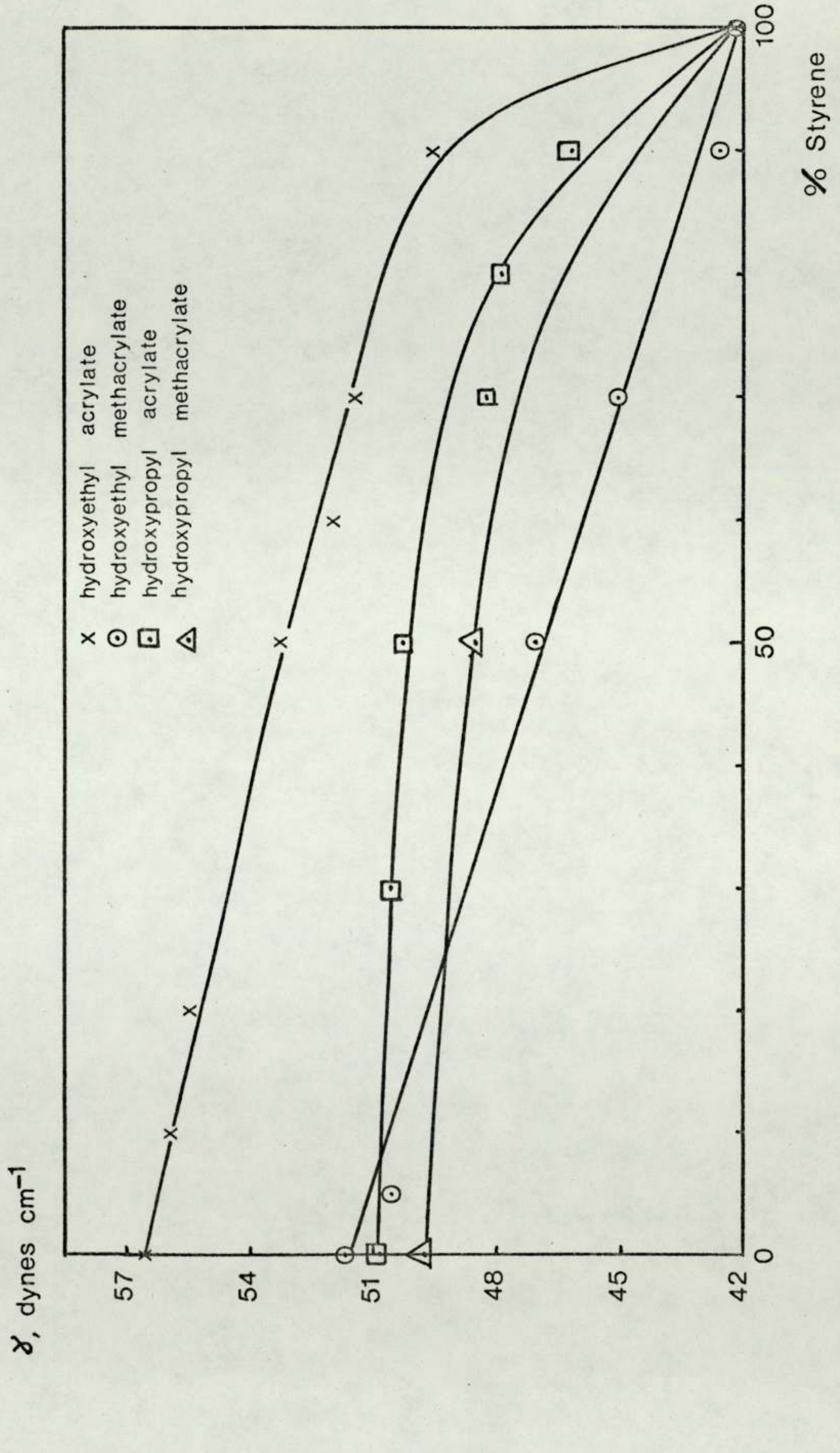
With the hydrophilic monomers there is the possibility of large amounts of both intra and intermolecular hydrogen bonding and this will tend to lead to the non-random presentation of groups at the surface. Fig. 16 shows a plot of surface free energy, γ , versus composition for copolymer samples of styrene and hydroxyalkyl acrylates or methacrylates. There is deviation away from linearity towards the more polar monomer and this suggests that with hydrophilic monomers the surface is not composed of randomly selected groups. With large amounts of hydrogen bonding it is to be expected that the surface free energy will be reduced because the amount of polar groups which are available to form the surface will be reduced by the bonding. With styrene-hydroxyalkyl acrylate or methacrylate copolymers, however, there would appear to be more polar groups at the surface than would be expected by adding together the surface energies of the two homopolymers in the correct proportions.

TABLE 12

Composition	Exptl. Surface Energy	Calculated Surface Energy
HEMA : Styrene 50 : 50	47.0	46.6
HEA : Styrene 50 : 50	53.2	49.3
30 : 70	51.41	46.4

Azrak[77] has shown that the material against which a sample is prepared has a large effect on the sample because it is capable

Fig.16


γ, dynes cm⁻¹
57
54
51
48
45
42
0
50
100
% Styrene
x hydroxyethyl acrylate
⊙ hydroxyethyl methacrylate
⊡ hydroxypropyl acrylate
△ hydroxypropyl methacrylate

of causing preferential orientation of certain groups towards the surface. A polar material will tend to increase the surface energy by the preferential adsorption of polar groups. Thus it would appear that, within the gross restraints laid down by the composition of the sample, the polar poly(ethylene terephthalate), (γ = 53 dynes cm^{-1}), is causing an increase in the number of polar groups at the surface with a concomitant increase in the surface energy.

If it were just the poly(ethylene terephthalate) film which was accounting for the increase in the polar component of the hydrophilic - hydrophobic copolymers, then samples of commercially available polymers which had been polymerised against poly(ethylene terephthalate) would show a higher surface polarity than would samples which had been purchased. Samples of both styrene and methyl methacrylate were polymerised against poly(ethylene terephthalate) film and showed similar surface energy results to those obtained with commercially polymerised samples.

TABLE 13

	Surface Energy	
Sample	Commercial	This project
Poly(methyl methacrylate)	40.8	42.6
Poly(ethylene terephthalate)	52.9	53.3

Additionally if the poly(ethylene terephthalate) film did have a major contribution to play in dictating the surface of the sample then once an equilibrium surface had been set up, consisting of mainly polar groups, this would remain constant as more of the more polar monomer was added to the copolymer. This is not seen to happen and the surface energy of the samples continues to increase with increasing amount of the more polar monomer.

The poly(ethylene terephthalate) film is therefore probably only exerting a fairly small effect on the surface composition of the sample and the magnitude of this effect can be estimated by looking at the decrease in surface energy seen following the first hydration-dehydration cycle. The surface energy of several different HEA - styrene copolymers were found before the initial hydration and the values obtained were somewhat higher than were subsequently found.

TABLE 14.

Sample. HEA : Styrene	SURFACE FREE ENERGY. (dynes cm^{-1}) Before hydration.	After hydration.
90 : 10	60.1	55.9
80 : 20	59.9	55.5
50 : 50	59.1	53.2

It is probable that this loss of energy (5 dynes cm^{-1}) is due to the polar groups, held at the surface by the effect of the poly(ethylene terephthalate) film, relaxing and reorientating into the bulk under the plasticising influence of the absorbed water.

If the effect of the poly(ethylene terephthalate) film is small and the effect of any hydrogen bonding would be of an opposite sense to that seen; there must be another effect which is causing the observed increase in surface energy above that expected. It is probable that this effect is some kind of packing restraint imposed on the hydrophilic monomer by the styrene molecule during polymerisation. The difficulty of packing the phenyl group and the hydroxyl containing side chain which occurs on the acrylate and methacrylate monomers could lead to the exclusion of the side chain which would then be relatively free to form a surface of polar hydroxyl groups. The amount of hydroxyl groups which were available would be controlled by the gross restraints of the composition; so there would never be sufficient to produce the same surface energy as was observed for the hydrophilic homopolymer.

By comparing the surface energies obtained for the homopolymers of the hydrophilic monomers, Table 15, it is clear that in going from acrylate to methacrylate and from hydroxyethyl to hydroxypropyl there is a drop in the surface energy.

TABLE 15

Sample	Surface Free Energy γ_d	γ_p	γ
Poly(Hydroxyethyl Acrylate)	37.4	19.1	56.5
Poly(Hydroxyethyl Methacrylate)	31.4	20.2	51.6
Poly(Hydroxypropyl Acrylate)	31.8	19.0	50.8
Poly(Hydroxypropyl Methacrylate)	33.1	16.6	49.7

In going from acrylate to methacrylate the only change in composition is the inclusion of a methyl group pendant to the backbone. This serves to restrict the rotation of the backbone and in so doing tends to prevent the polar carbonyl group from being so closely positioned to the surface of the sample as is the case with the acrylate homopolymer. This effect is similar to that seen with the water contents and Tg's of acrylates as compared to methacrylates or the hydrolytic stability of acrylamide as compared to methacrylamide. In going from hydroxyethyl to hydroxypropyl the sidechain has been extended by a single methylene group. This will have little effect on the ease with which the hydroxyl group may be placed at the surface but will serve to further shield the carbonyl group and prevent this from adding to the polar component at the surface.

A curve is also seen in the composition versus surface energy graph for other hydrophilic - hydrophobic copolymers, such as HEMA- methyl methacrylate (Fig. 17). The 50:50 copolymer (49.2 dynes cm^{-1}) has an increased surface energy when compared to the value given for the average of the two homopolymers (47.6 dynes cm^{-1}) and this is for the same reason as before, viz. steric effects, although the overall effect is less because of the size difference between the phenyl group and the methacrylate.

In systems composed of two hydrophilic monomers the situation is often more complex than was found with hydrophilic - hydrophobic copolymers. This is because the second hydrophilic monomer is often either acrylic or methacrylic acid and this shows a much higher tendency to intermolecularly hydrogen bond than did the hydroxyalkyl acrylates or methacrylates. Fig. 18 is the composition versus surface energy graph for HEMA copolymerised with both acrylic and methacrylic acid.

It is clear that the value obtained for the surface energy of acrylic acid, 50.9 dynes cm^{-1}, is much lower than might have

Fig.17

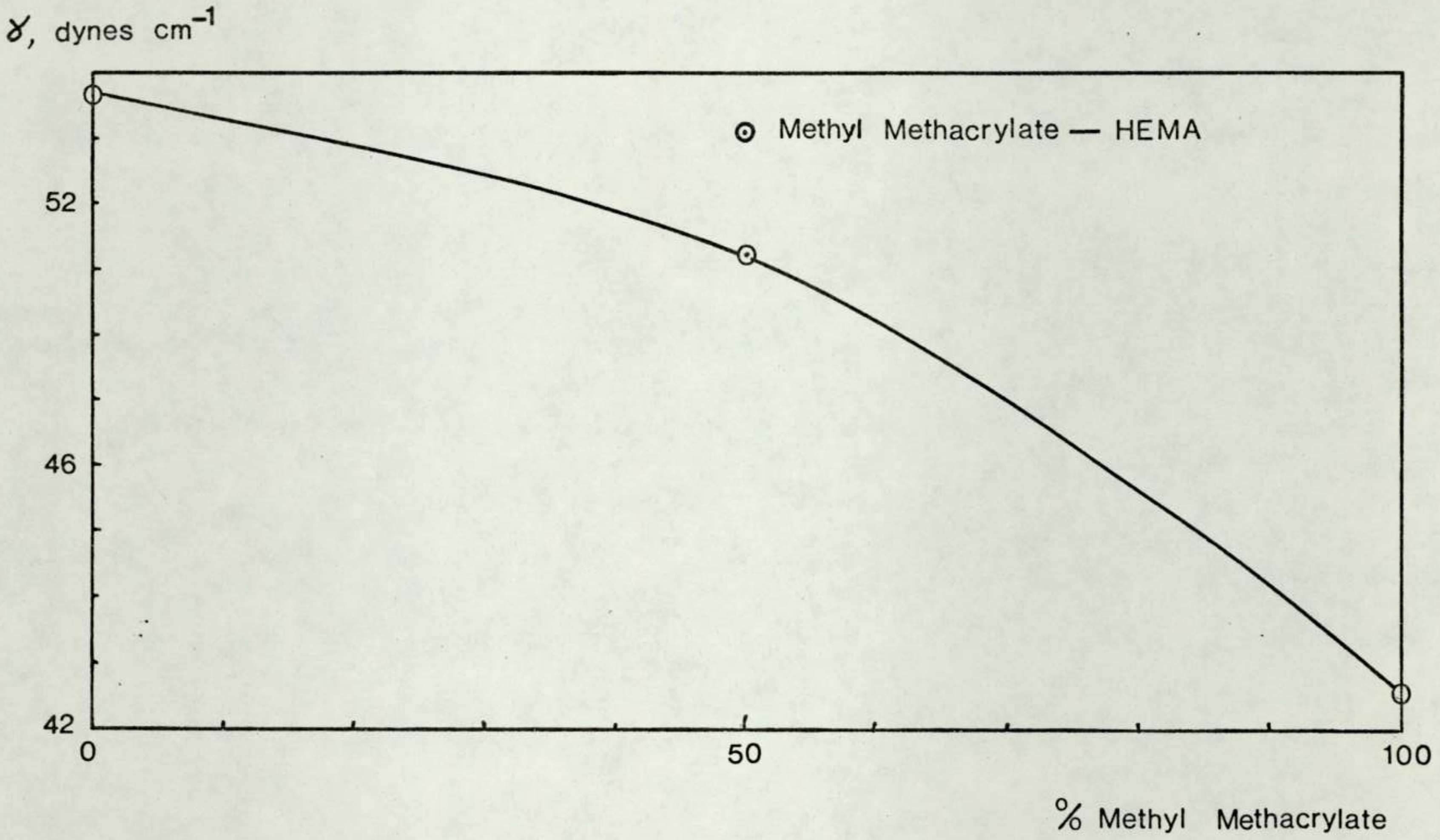
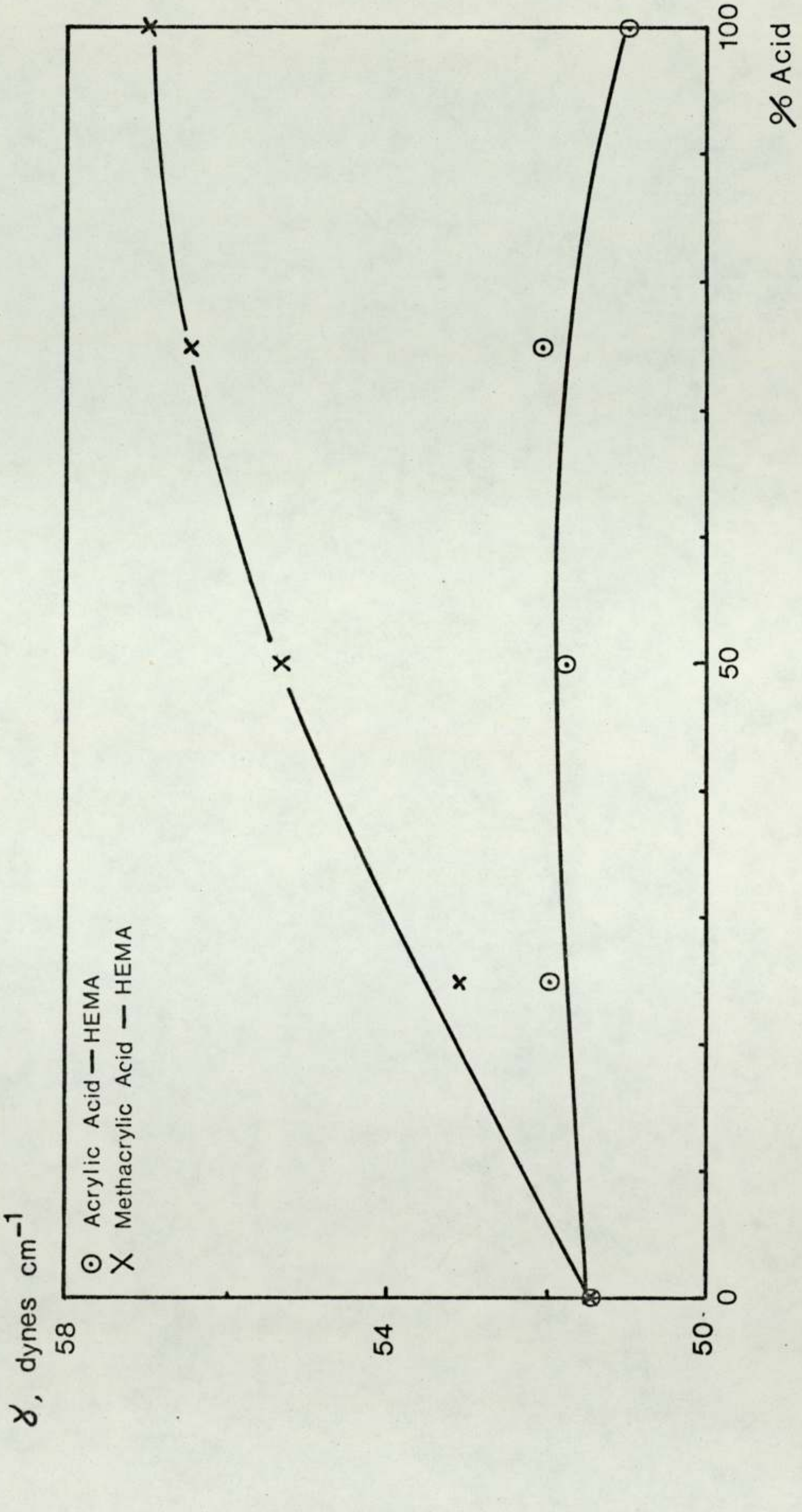

γ, dynes cm^{-1}
52
46
42
0
50
100
% Methyl Methacrylate
Methyl Methacrylate — HEMA

Fig.18



γ, dynes cm^{-1}
58
54
50
0
50
100
% Acid
⊙ Acrylic Acid — HEMA
X Methacrylic Acid — HEMA

been expected especially when compared to the values obtained with methacrylic acid, 57 dynes cm^{-1}, and with HEMA, 51.7 dynes cm^{-1}. It might have been predicted that both acrylic and methacrylic acid would show substantial amounts of hydrogen bonding because of the carboxyl group. This is not the case, however, as the surface energy results indicate.

With methacrylic acid there are low levels of hydrogen bonding, due to the methyl group which serves to restrict access to the carbonyl group by the carboxyl hydrogen of other molecules. It is this lack of hydrogen bonding which allows methacrylic acid to exhibit the high value of surface energy, 57 dynes cm^{-1}, which it does. The curve in the composition versus surface energy graph indicates that there is non-random presentation of the groups at the surface but in this case the cause is not exclusively a steric one. Methacrylic acid - HEMA copolymers exhibit trends which are between those shown by hydrophobic - hydrophilic copolymers in which steric effects predominate in dictating the surface energy and acrylic acid copolymers in which the effect of the intramolecular hydrogen bonding shown by the acrylic acid predominates. With methacrylic acid it is probable that the excess surface polarity is caused by a combination of factors: firstly by steric factors which prevent the packing of all of the hydroxyl groups in the methacrylate side chain with a subsequent increase in the surface polarity and second by some complexing which can occur between the two monomers and which serves to place excess polar groups at the surface.

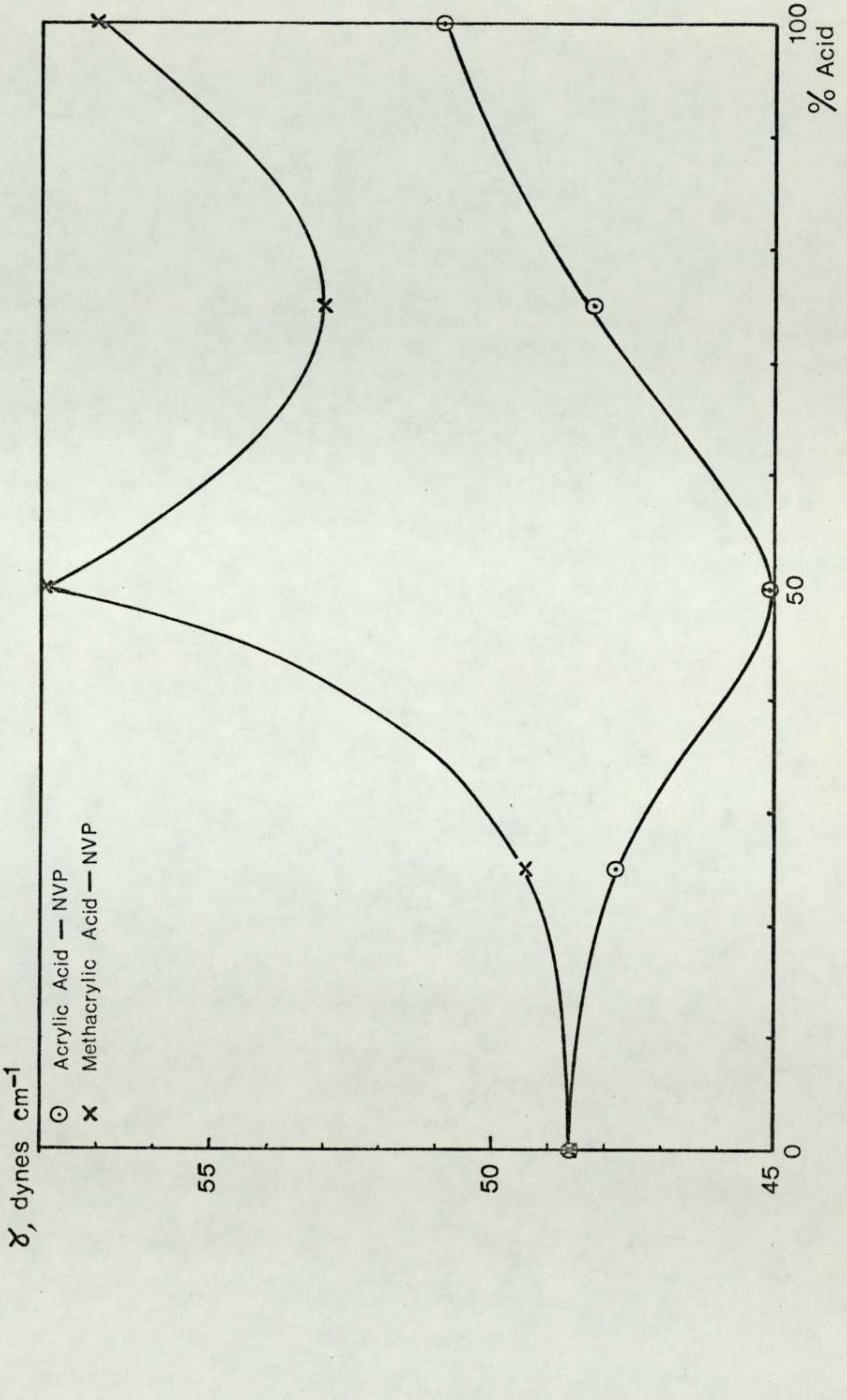
In acrylic acid there is no methyl group to prevent the hydrogen bonding from occurring and this is reflected in the low value obtained for surface energy, 50.9 dynes cm^{-1}. By comparing with the values obtained for surface energy in the case of hydroxyethyl acrylate, 56.6 dynes cm^{-1}, and hydroxyethyl methacrylate, 51.7 dynes cm^{-1}, it is clear that there is a substantial drop in surface energy resulting from high levels of hydrogen bonding.

When small amounts of HEMA are added to the copolymer this does little to reduce the amount of hydrogen bonding shown by the acrylic acid and so has little effect on the overall surface energy. Once enough HEMA has been added to the copolymer to produce an equilibrium surface then the surface energy remains relatively constant even when all of the acrylic acid has been removed.

When the HEMA in the copolymers with acrylic and methacrylic acid is replaced by N-vinyl pyrrolidone a further effect is introduced, that of complexing between the acid and the N-vinyl pyrrolidone. Fig. 19 shows the composition versus surface energy graphs for the copolymers produced.

With the copolymers of methacrylic acid (57 dynes cm^{-1}) and N-vinyl pyrrolidone (48.6 dynes cm^{-1}) the addition of N-vinyl pyrrolidone causes an increase in the amount of complexing which occurs until the maximum amount of complexing is reached and this will coincide with the maximum value obtained for the surface energy (57.9 dynes cm^{-1}). This is because the complexing is of such a type that it tends to present extra polar groups to the surface of the sample. When this maximum energy point is reached addition of more N-vinyl pyrrolidone only serves to dilute the surface by the addition of extra dispersive groups and the observed surface energy decreases until the value for N-vinyl pyrrolidone homopolymer is reached. The point of maximum surface energy also coincides with the point of

Fig. 19


γ, dynes cm⁻¹
⊙ Acrylic Acid — NVP
× Methacrylic Acid — NVP
55
50
45
0
50
100
% Acid

minimum water content and it is probable that the complexing is serving to exclude water from the polymer.

With copolymers prepared from acrylic acid the effect of the strong intramolecular hydrogen bonding is seen. Due to this bonding the amount of complexing is likely to be much less and so the upward curve with composition is less likely. What is observed is a downward trend in surface energy because what polar groups are left free of hydrogen bonding will be complexed by the N-vinyl pyrrolidone until at a minimum point (45 dynes cm^{-1}) the sample becomes increasingly pure poly(N-vinyl pyrrolidone) and the surface energy will increase again.

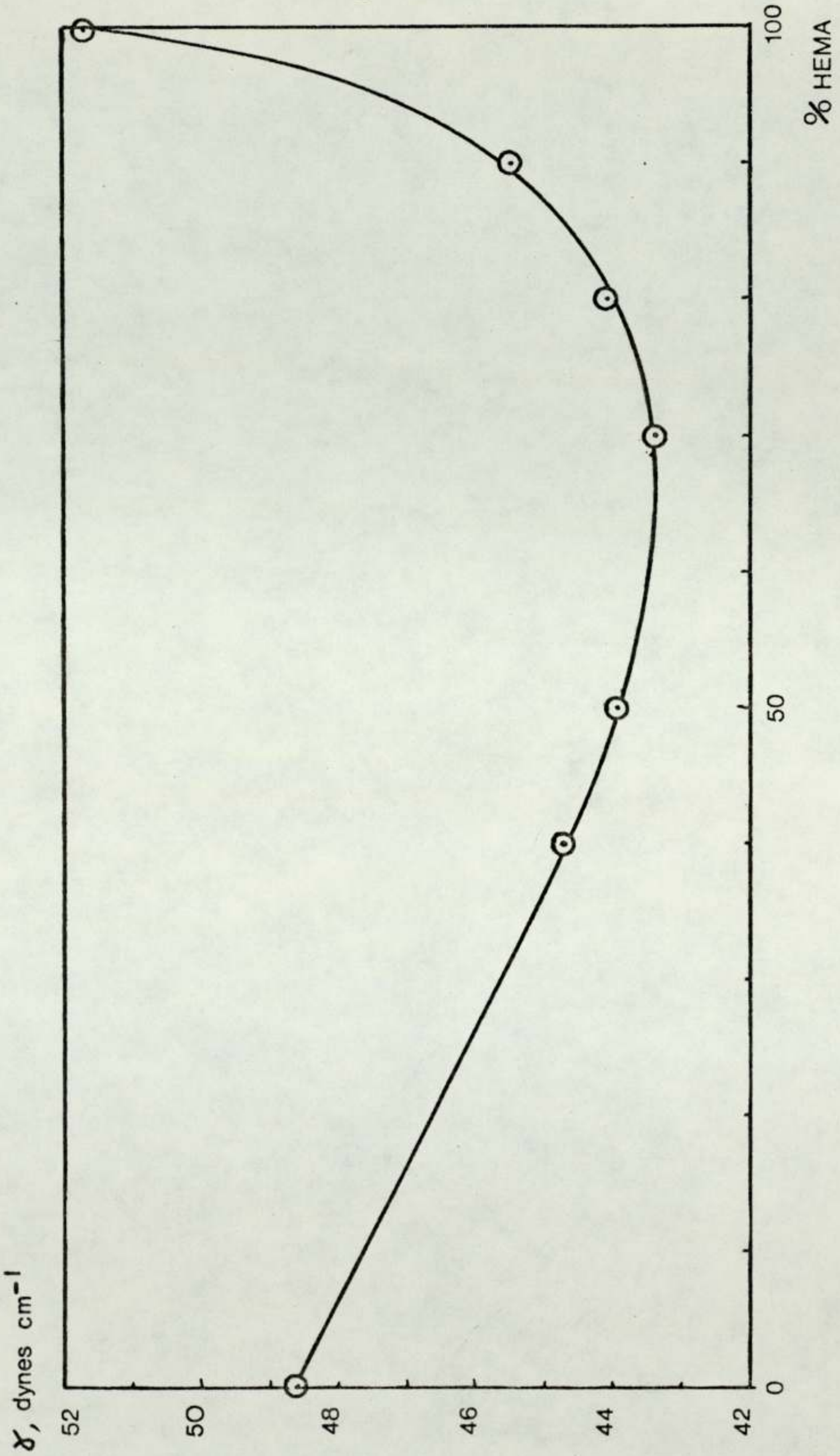
As was previously pointed out with HEMA there is very little hydrogen bonding and so copolymers with N-vinyl pyrrolidone ought to show only the effect of complexing and not the effect of complexing and hydrogen bonding as was observed with the acrylic acid copolymers. Given below, Table 16, are the water and diiodomethane contact angles, along with the surface free energy estimates produced.

TABLE 16.

Sample HEMA:NVP	Contact Angle Water	Contact Angle Diiodo-methane	Surface Free Energy γ_d	Surface Free Energy γ_p	Surface Free Energy γ
0 : 100	64.0	32.0	37.62	11.02	48.6
40 : 60	80.0	30.0	41.61	3.11	44.72
50 : 50	78.0	33.0	39.79	4.12	43.92
70 : 30	80.0	34.0	39.95	3.41	43.37
80 : 20	73.0	36.0	37.34	6.71	44.05
90 : 10	73.0	32.0	39.29	6.19	45.48
100 : 0	53.0	41.0	31.4	20.3	51.7

Fig. 20 shows the composition versus surface energy graph for copolymers of HEMA, 51.7 dynes cm^{-1}, and N-vinyl pyrrolidone, 48.6 dynes cm^{-1}. As can be seen this displays a minimum (43.3 dynes cm^{-1}) which is probably due to the complexing between the two species causing the surface to be composed of less and less polar material until the ideal molar proportions occur at which point the curve will start to increase towards the homopolymer as more and more polar groups are placed at the surface. It is clear from Table 16 that the amount of polar component to the total surface energy is small for all of the copolymers studied and this would tend to support the idea that the complexing is tending to produce specific orientation of groups at the surface in such a way as to render the surface as non-polar as possible.

Fig 20



EXPERIMENTAL TECHNIQUES
FOR
HYDRATED SURFACES.

5.1. Introduction.

The polymers used were prepared as described in a previous chapter. All the samples were left to hydrate for at least 3 weeks during which time the water in which they were hydrating was changed at frequent intervals to ensure that water soluble materials were completely removed from the hydrogel membrane. All the membranes were cleaned with strong soap solution followed by copious washing with distilled water to remove any trace of the surfactant material and were then stored in closed bottles under distilled water, which was changed at intervals of about two months. All the membranes were visually inspected for signs of bacterial contamination at these water changes and any showing signs of growth of colonies of bacteria were rewashed before being placed in fresh distilled water.

5.2. Sessile Drop Technique.

The sessile drop technique was investigated for use on hydrated surfaces as well as dehydrated. Several workers[78,79] have used sessile drop methods on hydrated surfaces but all suffer from the same serious shortcoming, viz. the film of water which must be removed from the surface of the sample before a drop of water can be applied. Failure to remove this film of water results in an apparent zero contact angle as the drop of water and the film of water on the sample's surface spontaneously coalesce. Removal of the water film without damage to the surface of the sample is the biggest problem which has to be overcome in this method, that and preventing the water in the bulk of the sample from re-establishing the equilibrium at the surface.

Although it is possible to partially overcome these difficulties and to obtain reproducable results, the difficulties lie in interpreting them in terms of the surface constitution of the sample which the drop was wetting.

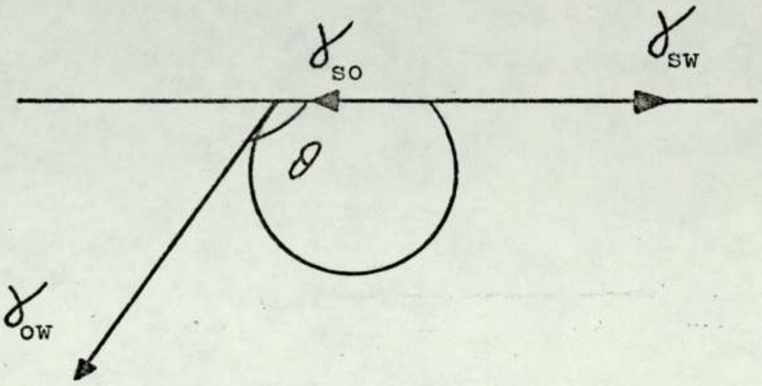
5.3. Captive Bubble Method.[80]

In an effort to overcome these failings it is possible to go to the captive bubble method. In this technique a sample of hydrogel is placed under water and a bubble of air is blown onto the surface from below. The contact angle is measured at the air - water interface through the aqueous phase. The largest source of error in this method, once the difficulty of keeping the bubble on the surface has been overcome, is in ensuring that the air bubble is in contact with the actual surface of the material under test and is not just resting on a monolayer of water which it has failed to displace from the surface of the sample. Thus it is difficult to equate the actual contact angle produced with the surface constitution of the sample. Additionally there is the problem of compression of the drop which can occur if the drop is not kept fairly small in size.

5.4. Hamilton's Method.[53]

One way of overcoming the problem of using water as a sessile drop liquid on a sample which is fully hydrated is to place the sample under water, as in the captive bubble method. However by using a water immiscible liquid to form the sessile drop instead of air, one can extract more information than one can from the captive bubble method. Hamilton found that both n-octane and water had the same dispersive component to their surface free energies, 21.8 dynes cm^{-1}, and that because of this the dispersive component of the surface free energy of the sample cancelled out in the mathematics of the system. This leaves only the polar component of the sample as an unknown and so this can now be evaluated.

Consider a sample, S held under water and wetted by a drop of n-octane:



where:-

γ_{ow} = free energy of the octane - water interface.
γ_{sw} = free energy of the solid - water interface.
γ_{so} = free energy of the solid - octane interface.

Youngs equation holds at the point of contact of the three phases:-

$$\text{Cos}\,\theta \cdot \gamma_{ow} = \gamma_{sw} - \gamma_{so} \qquad - \; 27$$

but

$$\gamma_{so} = \gamma_{o} + \gamma_{s} - 2\sqrt{\gamma_{o}^{d} \cdot \gamma_{s}^{d}} \qquad - \; 28$$

and

$$\gamma_{sw} = \gamma_{s} + \gamma_{w} - 2\sqrt{\gamma_{w}^{d} \cdot \gamma_{s}^{d}} - 2\sqrt{\gamma_{w}^{p} \cdot \gamma_{s}^{p}} \qquad - \; 29$$

Therefore subing 28 and 29 into 27 gives:-

$$\cos\theta\cdot\gamma_{ow} = \gamma_s + \gamma_w - 2\sqrt{\gamma_w^d\cdot\gamma_s^d} - 2\sqrt{\gamma_w^p\cdot\gamma_s^p} - \gamma_o - \gamma_s + 2\sqrt{\gamma_o^d\cdot\gamma_s^d} \quad - 30$$

as

$$\gamma_w^d \equiv \gamma_o^d$$

then

$$2\sqrt{\gamma_w^d\cdot\gamma_s^d} \equiv 2\sqrt{\gamma_o^d\cdot\gamma_s^d}$$

and so

$$\cos\theta\cdot\gamma_{ow} = \gamma_w - \gamma_o - 2\sqrt{\gamma_w^p\cdot\gamma_s^p} \quad - 31$$

Provided that γ_w and γ_o are known then a measurement of the contact angle, θ, will yield a value for the polar component of the surface free energy of the sample. However even the actual value of the contact angle is useful in ranking surfaces in order of increasing polar component. It can be shown that provided the sample has no polar component then the minimum value reached by the contact angle will be 52°. Table 17 shows the values obtained for the non-hydrogel polymers investigated in this project, also shown are the literature values, where these are available.

TABLE 17

Sample	This work	Hamilton's values
Poly(tetrafluoroethylene)	52	53
Polyethylene	52	53
Polystyrene	55	55
Poly(ethylene terephthalate)	103	-
Poly(methyl methacrylate)	78	-

As can be seen polyethylene and polytetrafluoroethylene both give values of 52°, as would be expected, whilst polystyrene has a value of 55°, thus showing a small amount of polar character caused by the asymmetry imparted to the backbone by the benzene ring. Poly(methyl methacrylate), 78°, and poly(ethylene terephthalate), 103°, have much higher values for their contact angles due to the much higher polar components in their structures.

In order to speed up the processing of the results, Equation 31 was converted to a computer program (Appendix 2 Table 5). The values ascribed to γ_w and γ_o , 51.6 and 21.8 dynes cm^{-1} respectively, were those used by Hamilton. However recently El-Shimi and Goddard[81] have stated that the value used by Hamilton for water saturated with n-octane is incorrect and that the value remains very close to the value for pure water, 72.8. They claim that independent confirmation of this comes from the adsorption data of octane on water published by Ottewill et al.[82]. No attempt has been made to confirm these findings and elucidate a value for the surface tension of n-octane saturated water, instead two graphs were produced of contact angle versus calculated polar component of the surface free energy for the samples. One used the value ascribed to the surface tension of the saturated water by Hamilton, 51.6 dynes cm^{-1}, and the other used the value of water said to be correct by El-Shimi et al., both graphs are given in Fig.21 . Using these graphs it was possible to convert the contact angle measurements into values for polar component.

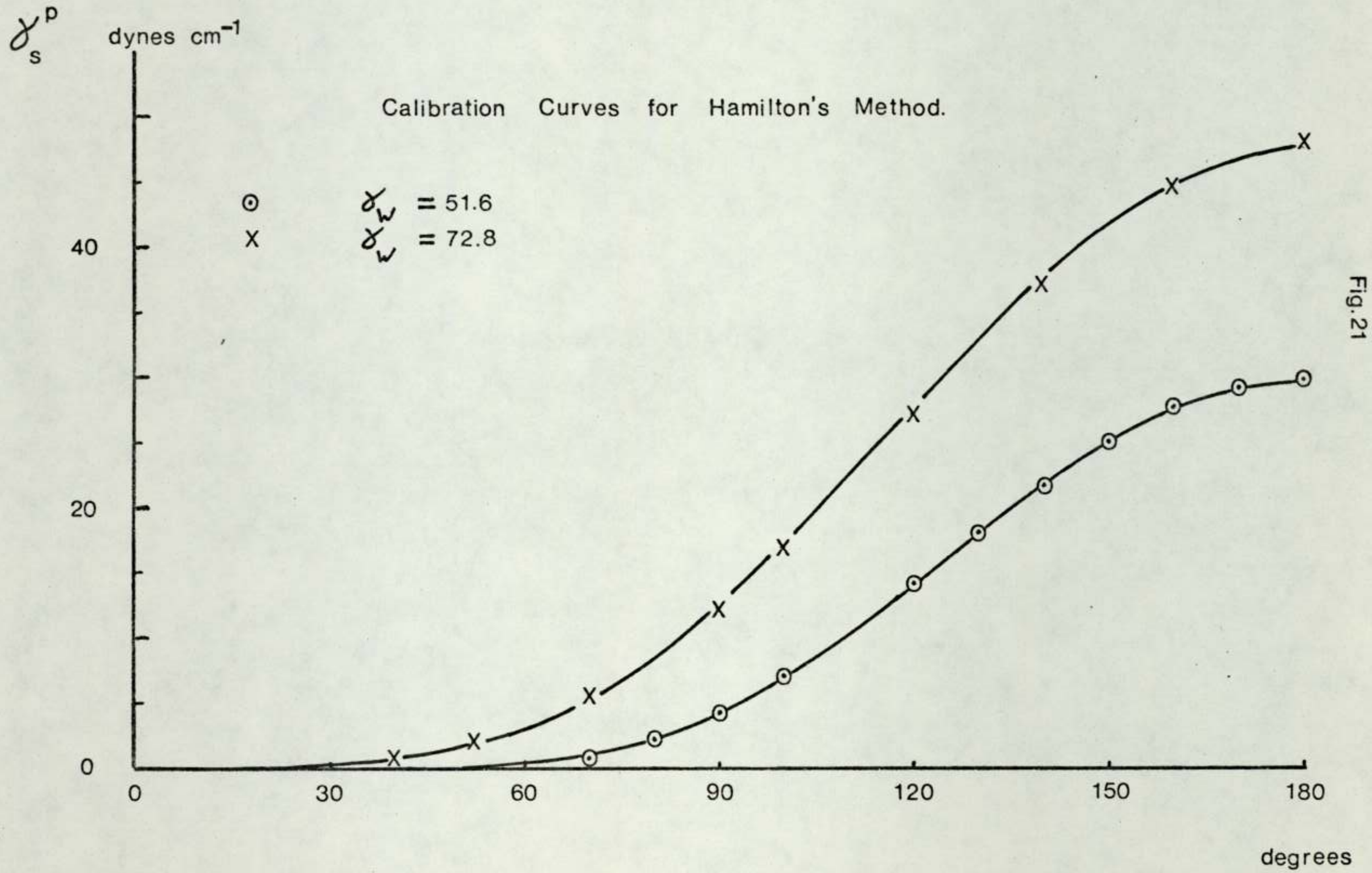


Fig.21

Calibration Curves for Hamilton's Method.

5.5. Results and Discussion.

All of the hydrogel copolymers prepared during this project were investigated by Hamilton's technique which enables the polar component to be isolated and given below are a typical set of results for the hydrophilic-hydrophobic copolymers.

TABLE 18

SAMPLE HPA : Styrene	Hamilton Contact Angle	Polar Component
100 : 0	148	24.6
90 : 10	145	24.0
70 : 30	140	22.3
60 : 40	145	24.0
20 : 80	110	10.5
0 : 100	55	0.5

It is clear that the inclusion of a relatively small amount of hydrophilic monomer increases the polar component, e.g.

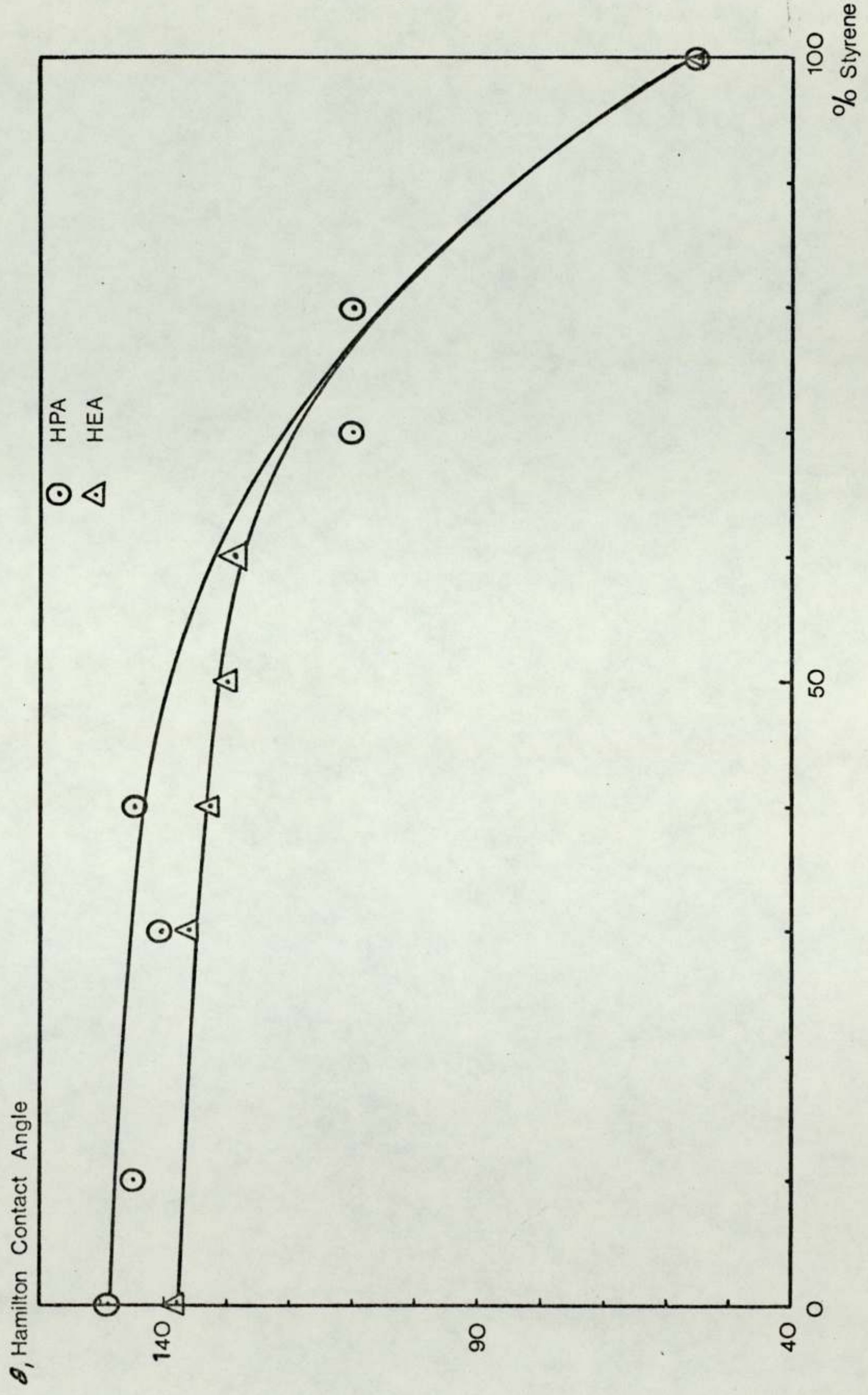
polystyrene 0.5 dynes cm^{-1} (55^{o})

and poly(styrene-co-HPA) (80:20) 10.5 dynes cm^{-1} (110^{o})

an increase of 10 dynes cm^{-1} in the polar component.

Fig. 22 is a comparison of the hydrophilic-hydrophobic copolymers produced in this project and in which the contact angle is plotted against the composition of the sample. This shows that the trends found in the sessile drop investigation have been repeated. All of the graphs show deviation from linearity in the form of curvature towards the more polar component, however the plateau area which occurs towards the more hydrophilic end of the composition

Fig. 22

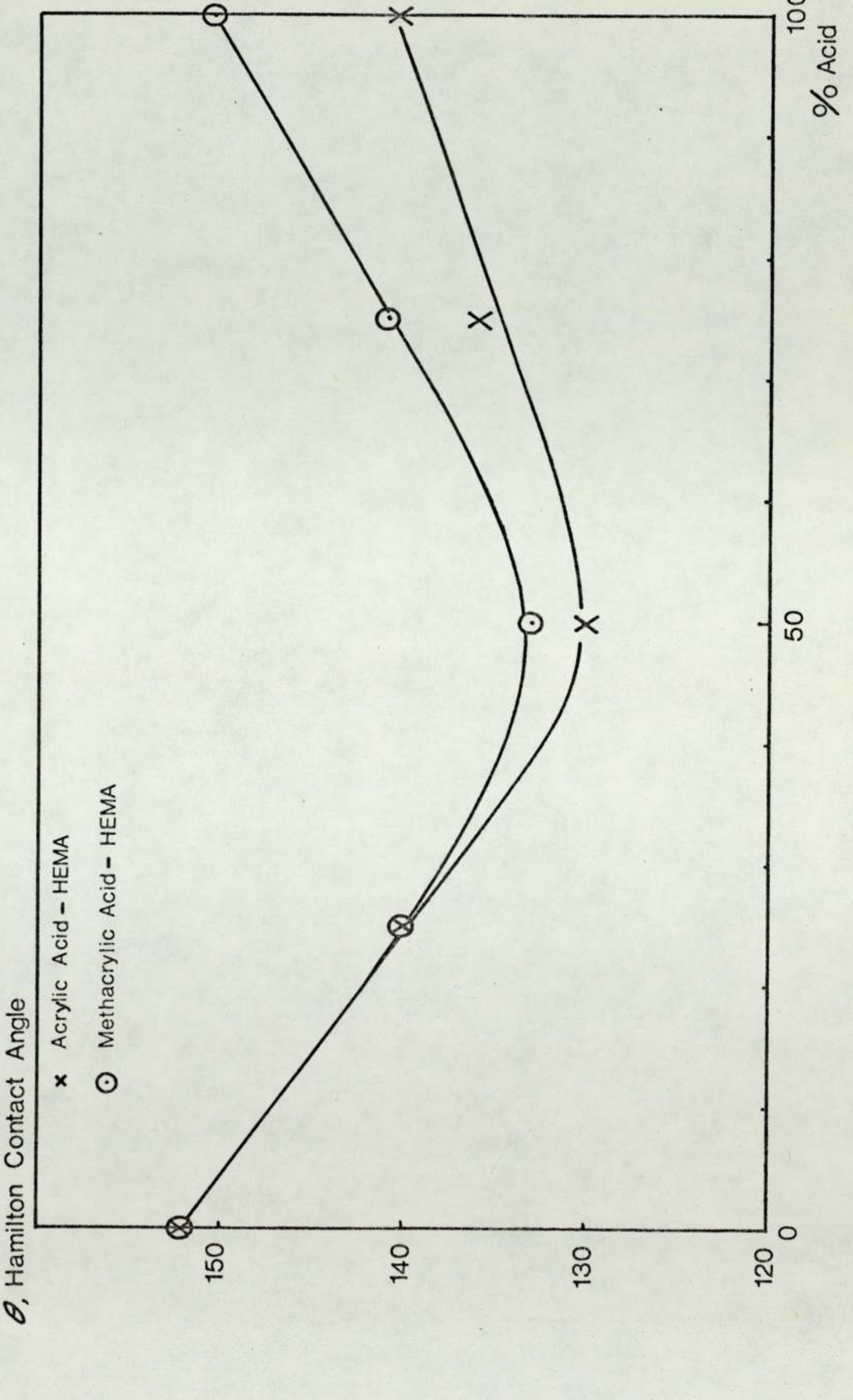


curve is longer than was the case in the sessile drop investigation. Since Hamilton's method only finds the polar component and this shows a rapid rise with only small amounts of the hydrophilic monomer it is to be expected that the plateau will be somewhat longer in this method.

The reasons for the rapid increase in polar component are the same as those described in Chapter 4 in relation to hydrophilic-hydrophobic copolymers; steric factors are causing the exclusion from the bulk of the polar side chains which are present in the hydrophilic monomers. Although this steric effect is the major cause of the rapid rise in polar component seen, the samples used in Hamilton's technique are hydrated and the water in the sample does have some effect on the value of the surface energy. The water which occurs in the sample is associated with the bulk and is acting as a plasticiser. This allows the polymer chains more freedom of rotation which allows more of the polar groups to orientate towards the surface of the sample. The effect which the water has on the surface energy of the sample can be seen by the difference in energy shown by samples of poly(styrene-co-HPA) (70:30) in the two different techniques. In the sessile drop method (dehydrated) the sample has a polar component of 15.4 dynes cm^{-1} whilst in the Hamilton method this has risen to 22 dynes cm^{-1}. This clearly shows the effect of the water in allowing relaxation of the chains to occur.

With the hydrated hydrophilic-hydrophilic copolymers produced from HEMA and acrylic or methacrylic acid the overall trends seen parallel those shown by the polar components of the dehydrated materials. Fig. 23 shows the graphs obtained when

Fig. 23


θ, Hamilton Contact Angle
× Acrylic Acid - HEMA
⊙ Methacrylic Acid - HEMA
150
140
130
120
0
50
100
% Acid

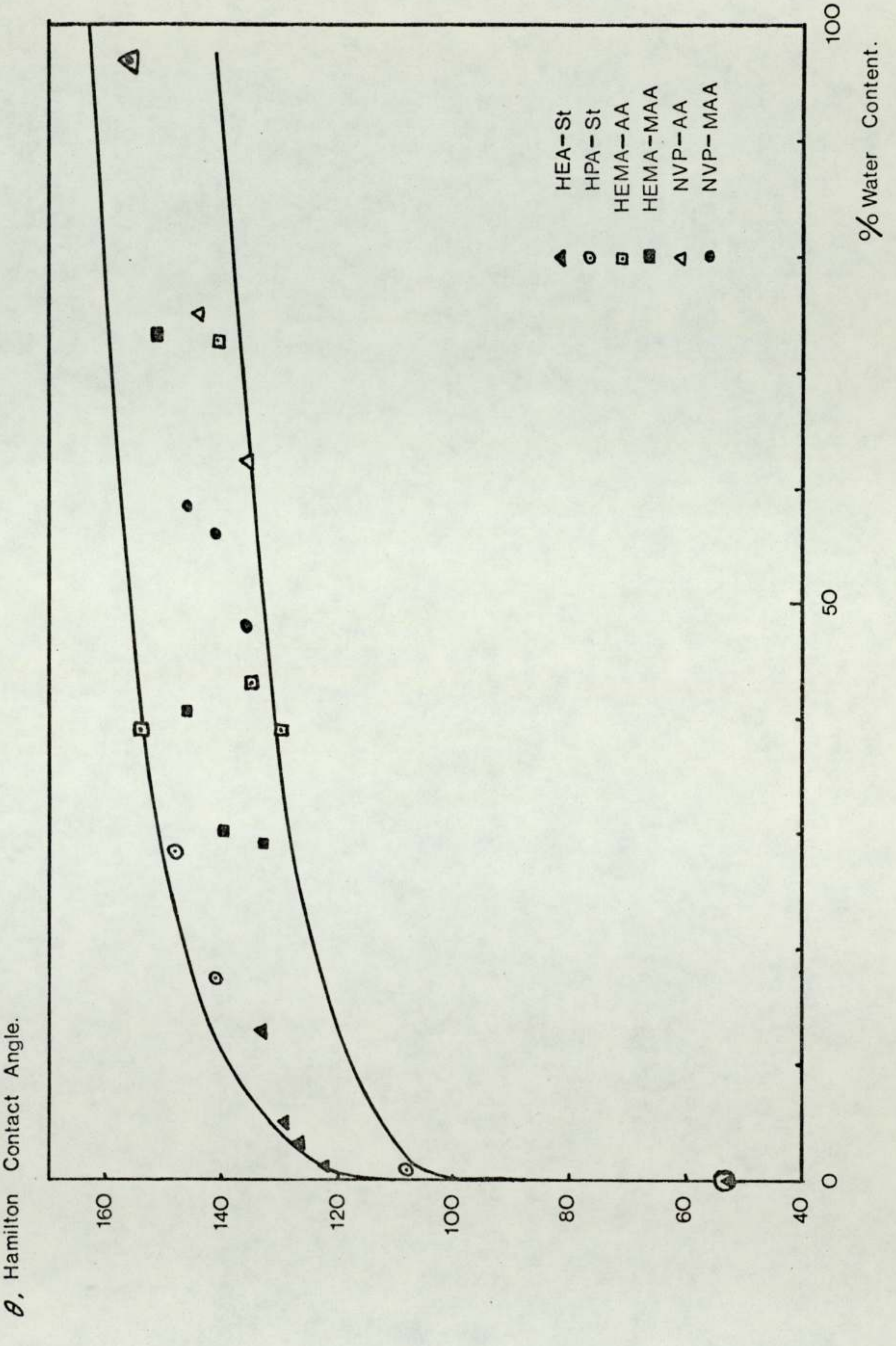
the contact angle is plotted against the composition and Table 19 is a comparison of the polar components, obtained by the sessile drop method on dehydrated samples, with the polar components obtained by Hamilton's method on hydrated samples.

TABLE 19

Sample.	Polar Comp. of Surface Free Energy Sessile Drop	 Hamilton	Water Content %
HEMA : Methacrylic Acid			
0 : 100	23.6	25.5	73.5
25 : 75	21.5	22.5	40.5
50 : 50	20.1	19.5	28.5
75 : 25	15.9	22.0	30.0
100 : 0	20.2	26.0	38.0
HEMA : Acrylic Acid			
0 : 100	13.13	22.5	73.0
25 : 75	16.3	21.0	43.5
50 : 50	15.4	18.5	38.0
75 : 25	14.4	22.0	37.5
100 : 0	20.2	26.0	38.0

An important conclusion can be made from a plot of Hamilton contact angle versus water content for all compositions, Fig. 24. Although various families have characteristically high or low values relative to a mean for a given water content, these values fall within a fairly narrow rectilinear band. More significantly a virtual plateau is reached at about 15 per cent water content. The obvious implication of this is that water is not making a direct contribution to the polar component of the surface

Fig. 24


θ, Hamilton Contact Angle.
160
140
120
100
80
60
40
0
50
100
% Water Content.
▲ HEA–St
⊙ HPA–St
⊡ HEMA–AA
■ HEMA–MAA
△ NVP–AA
● NVP–MAA

free energy as a result of its concentration (or mole fraction) but in terms of some secondary effect that it produces. Thus relatively small amounts of water have a dramatic effect between 0-15 per cent when much larger amounts in the region 15-90 per cent have a relatively small effect. This appears to offer clear support for the suggestion that the primary role of water in modifying the polar component of the surface energy is in its role in permitting chain rotation.

Similarly the copolymers of HEMA and methacrylic acid show very similar polar components in both investigations, approximately 20 dynes cm^{-1}, which would seem to indicate that the water is having little effect on the proportion of the surface which is occupied by polar groups. With the copolymers of acrylic acid there is an increase in polar component found in going from sessile drop to Hamilton technique (i.e. from dehydrated to hydrated). The largest increase was shown by acrylic acid which has a polar component of 13 dynes cm^{-1} by the sessile drop method but shows a value of 22.5 dynes cm^{-1} by Hamilton's method. The reason is that the intrachain hydrogen bonding, which gave the low value in the sessile drop method, is reduced by the action of the water present in the sample used for the Hamilton method. Thus individual chains are much freer to rotate and to take-up a more random orientation which will increase the number of polar groups at the surface. Similar effects, due to the decrease in hydrogen bonding are seen across the whole range of copolymer compositions, e.g. the 50:50 copolymer increases from 15.4 to 18.5 dynes cm^{-1} and the 75:25 HEMA: acrylic acid copolymer increases from 14.4 to 22 dynes cm^{-1}.

The effect which the composition has on the water content of hydrogels is being studied in depth by P.J. Skelly[83] and lies outside the scope of this project. However it is clear that the same bulk factors which are causing the changes in surface energy seen across a series of compositions are also affecting the water contents found for the same series of compositions. From the results of water content measurements presented in Table 19 it is clear that surface polarity and water content follow similar trends and these results would appear to support the premise that the same bulk factors are tending to control both the water content and the surface properties.

With copolymers of N-vinyl pyrrolidone and acrylic acid the values obtained for the polar component are much higher in the case of the Hamilton method than they are with the sessile drop technique. Table 20 shows the results obtained together with the water contents of the copolymers.

TABLE 20

Acrylic Acid : NVP		Polar comp. of surface free energy Sessile drop	Hamilton	Water content
100	0	13.1	22.5	73
75	25	0.0	22.0	-
50	50	3.8	20.5	62
25	75	1.9	24.0	75
0	100	11.0	27.0	97

The dramatic increase in polar component is related to the effect the water has on the hydrogen bonding. The water is acting as a plasticiser and reduces the amount of interchain bonding to a level below that which occurs in the dehydrated state. This allows increased rotation of the chains to occur which permits a higher proportion of the polar groups to appear at the surface. The large increases seen in going from dehydrated to hydrated are of the order of 22 dynes cm^{-1}, e.g. 75:25 acrylic acid:NVP copolymer shows an increase in polar component of from 0 to 22 dynes cm^{-1} whilst the 25:75 copolymer has an increase of 22.1 dynes cm^{-1}. Even with these large increases in polar component the trends shown across the copolymer range are still the same as those seen previously, probably because of the strong complexing which is occurring between the two species.

Copolymers of methacrylic acid and N-vinyl pyrrolidone show a trend with the Hamilton technique that is different from that revealed by the sessile drop method. The sessile drop method produces a curve which has a dramatic increase in surface energy at the 50:50 copolymer ($\gamma = 58$; $\gamma^{P} = 21.3$), probably due to some form of complexing between the two monomers. The value of polar component given by the Hamilton method is of the same order, 20.5 dynes cm^{-1}, but the copolymer samples on either side of this midpoint have polar component values which are much in excess of the values obtained in the sessile drop method, Table 21.

TABLE 21

	Polar comp. of surface free energy		
Methacrylic acid : NVP	Sessile drop	Hamilton	Water content
100 : 0	23.6	25.5	73.5
75 : 25	14.5	24.0	58.5
50 : 50	21.3	20.5	48.0
25 : 75	9.8	22.5	56.5
0 : 100	11.0	27.0	97

To this abnormal effect seen in the polar component of the 50:50 copolymer can be added two parallel effects,

i) Water content

ii) Mechanical properties

The mechanical properties are better, i.e. higher rigidity, in the case of the 50:50 copolymer than would be predicted on the basis of of an extrapolation of the water content-rigidity modulus relationship. It would seem that these effects are related either to the optimisation of the complex between the acrylic acid and the N-vinyl pyrrolidone or because of the lack of free water in the copolymer.

5.6. Conclusions.

The results obtained by Hamilton's method show the general trends revealed by the sessile drop method, although the actual values of the polar component are higher with Hamilton's method because of the influence of the water on the possible orientations allowed the polymer chains. Holly and Refojo [79] have recently tried to explain differences in advancing and receding contact angles of water on hydrated poly(HEMA) as being due to molecular reorientations in the polymer chain caused by the water present in the sample. They used two methods of finding the contact angle; sessile drop on a hydrated surface and the captive bubble method. Both techniques have inherent difficulties which have been previously pointed out in this chapter. Holly and Refojo [79] wipe the surface of the sample to remove the film of water but then allow the sample to stand so that the film of water can become re-established. Any contact angle performed under these conditions is likely to be affected by a high degree of irreproducibility and the difference between the advancing and receding angle is less likely to be because of molecular rearrangement than because of the inherently bad method selected. Additionally some of the glass plates, against which the samples were prepared, had been silicon treated. Although the samples were washed thoroughly with water some of the silicon coating will have remained as a surface contaminate because of the insolubility of silicon based release agents in water. The degree of contamination will vary from sample to sample and this will serve to increase the amount of variation found in the measured contact angles.

Hamilton's method would, however, appear to be the only way of arriving at an estimate of the surface energy of a hydrated gel and even this method only permits the elucidation of one component of the surface energy. Clearly it might be possible to use the value found for the polar component to predict the total surface energy of a hydrated gel assuming that the dispersive component is about the same order in the hydrated state as in the dehydrated state. If this assumption is to be made then the value of the dehydrated surface energy might as well be taken as a whole to be the energy of a hydrated gel surface.

The value obtained by Hamilton's method has proved useful in ranking samples according to the amount of polarity shown by their surfaces, which seems to correlate with the amount of adhesion shown by mucous and platelets[83]. Thus Hamilton's method might have some application in determining the likely biocompatibility of a sample but unless it is possible to find a non-miscible liquid which has the same polar component as water, which will enable the dispersive component of the surface free energy of the sample to be found, Hamilton's method appears to have limited usefulness in determining the surface energy of hydrated hydrogels.

THE
RELATIONSHIP OF THE SURFACE PROPERTIES
OF DEHYDRATED HYDROPHILIC
POLYMERS
TO THOSE IN THE MELT AND
HYDRATED STATE.

6.1. Introduction.

It is very difficult and expensive to evaluate the surface tension of conventional polymers because they exhibit both high melting points and high viscosities in the melt state. It was expected that hydrogel polymers would be even more difficult to evaluate because of their unique nature, however the melt surface tension is important in determining the amount of mould adhesion seen and so evaluation of the melt surface tension is of great importance.

It has been shown by Wu[69] that with conventional polymers such as polystyrene and poly(methyl methacrylate) there is a small temperature coefficient of surface tension and that all of the coefficients lie within a close band of values. Because of the small value of the temperature coefficient it is possible to consider the surface energy obtained in the solid state as being very close to the surface tension exhibited by the melt. Since it has been shown that the hydrogel polymers have surface energies of the same order as conventional polymers it is a fairly good assumption that the temperature coefficients will also be of a similar order and that it is possible, to a first approximation, to consider the value of the solid state surface energy as being the same as the value for the melt surface tension.

In considering the change from dehydrated to hydrated the position is not as clear. The addition of a second phase, water, to the polymer matrix makes for more complications especially as the water is known not to exist in hydrogels in a single state but in several states. It is fairly easy to find the total water content of a hydrogel but it is much more difficult to ascribe values to the different states of the water. Even when the water is assumed to exist in but two states, free and bound, the problem of finding quantitatively the amount of each requires expensive equipment.

Initial work, previously reported in this project, has attempted to clear the position with respect to the polar and dispersive components of dehydrated and hydrated cross-linked hydrophilic polymers.

6.2. Inverted Hamilton method and its application to dehydrated and hydrated polymers.

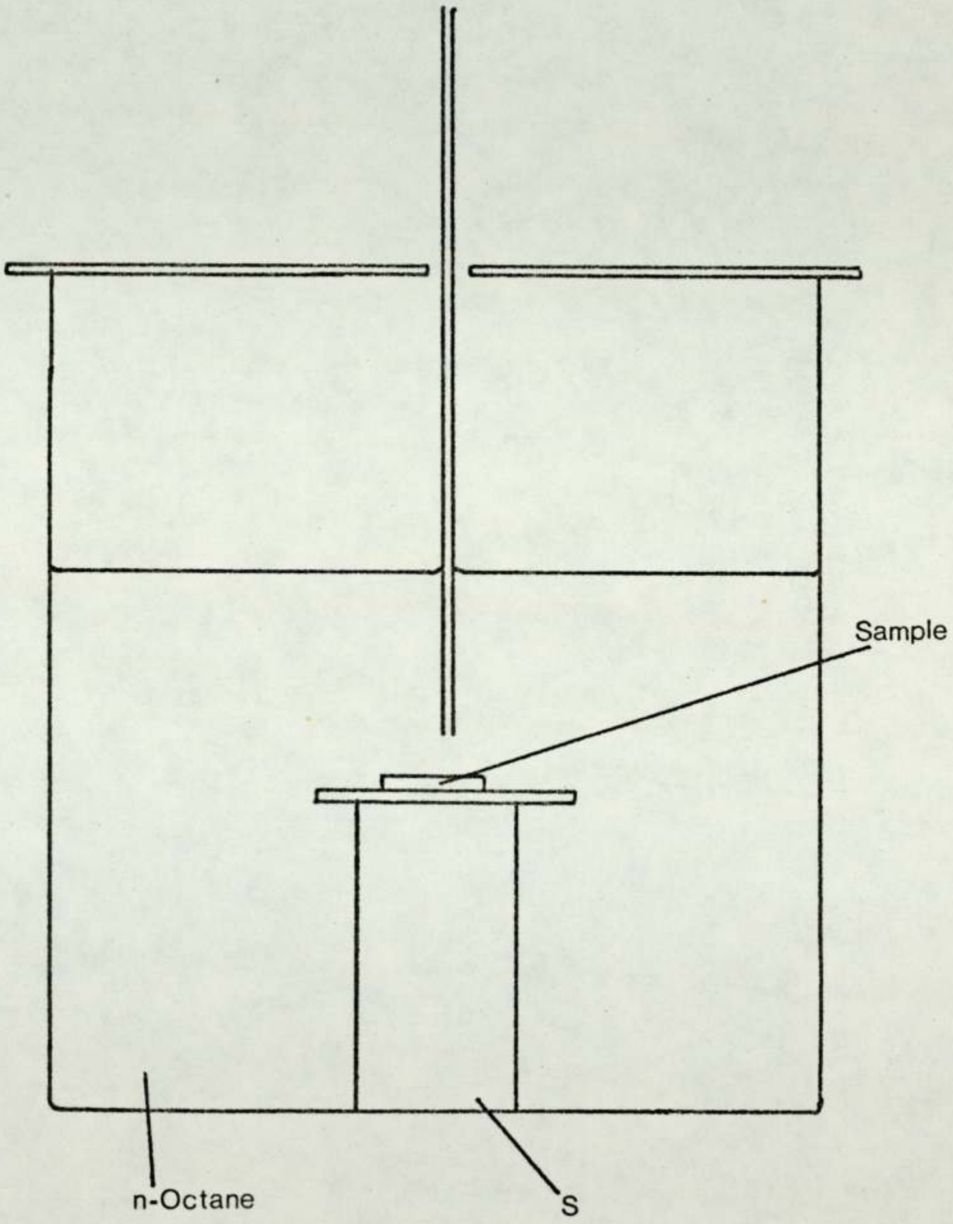
6.2.1. Introduction.

Following on the work of Hamilton in which the polar and dispersive components of a hydrated sample's surface free energy were separated such that a contact angle measurement gives information on one of the two components alone, a method was devised by which one of the two components of the surface free energy of a dehydrated sample might be evaluated. The method is based on that of Hamilton, except that the sessile drop forming liquid is water and the samples are under n-octane.

6.2.2. Experimental.

The experimental set-up is shown in Fig. 25 . The sample was placed on a stainless steel support, S , which in turn was under n-octane. A cover, perforated by a small hole was placed on the top of the optical cell. A G25 needle attached, as before, to a Prior micromanipulator and an Agla microsyringe, operated by a micrometer, was passed through and positioned below the surface of the n-octane and nearly in contact with the surface of the sample. The tip of the needle had been removed so that the drop formed

Fig. 25



would be symmetrical. An image was formed as before and a photographic record of each experiment was produced for later analysis.

The mathematics of the system are similar to that for the Hamilton method, except that the Young equation is now:-

$$\mathrm{Cos}\,\theta . \gamma_{wo} = \gamma_{so} - \gamma_{sw} \qquad - 32$$

substituting equations 28 and 29 gives the result that for this technique:-

$$\mathrm{Cos}\,\theta . \gamma_{wo} = \gamma_{o} - \gamma_{w} + 2\sqrt{\gamma^{p}_{w} . \gamma^{p}_{s}} \qquad - 33$$

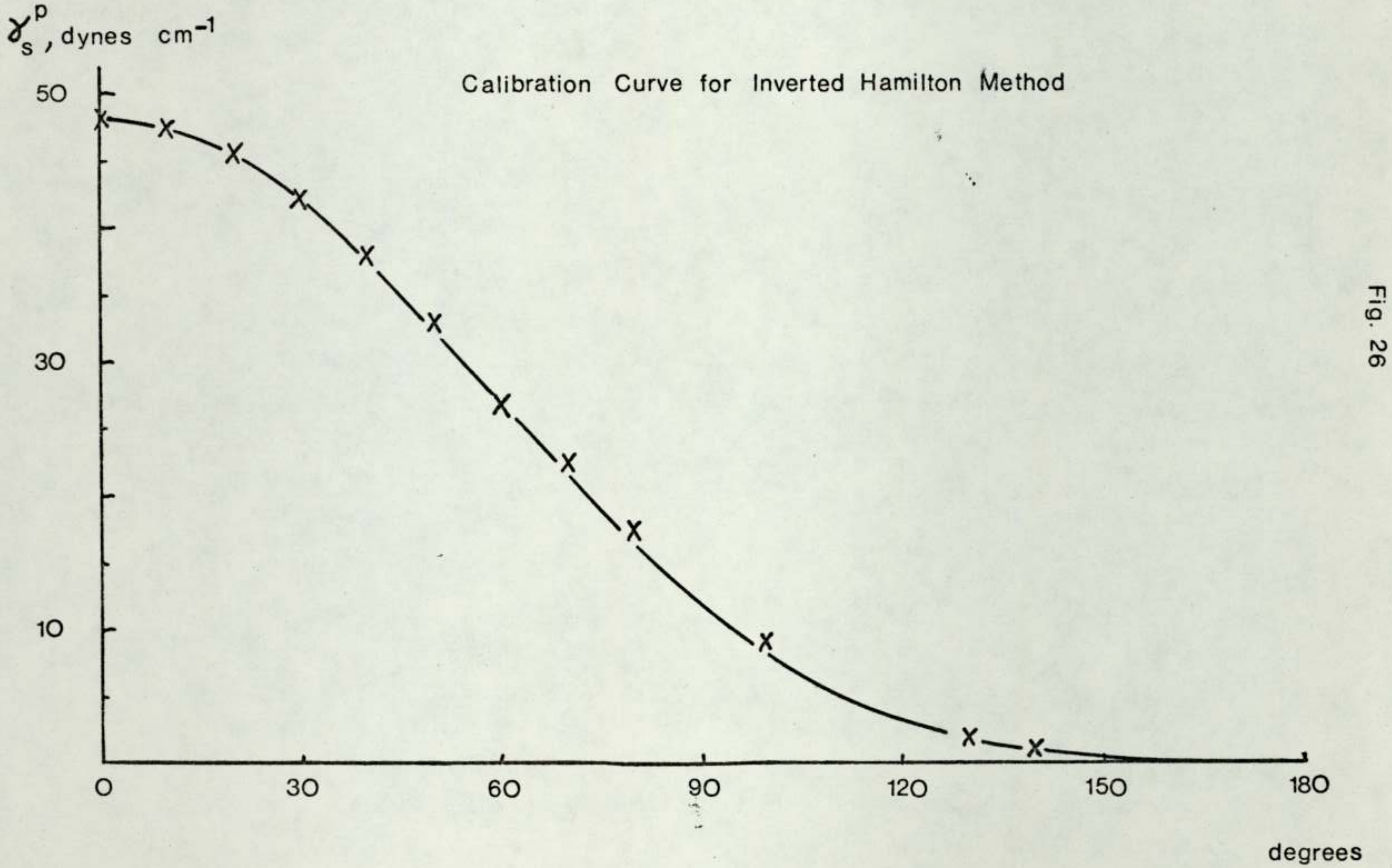
Equation 33 has been reduced to a computer program, (Appendix 2, Table 6) which evaluated γ^{p}_{s} for various values of θ, Fig. 26.

6.2.3. Results and discussion.

The samples which were in the hydrated state all showed a zero contact angle which ought to have indicated a surface free energy of about 48 dynes cm^{-1}. In this case however it was not the high value of the polar component of the surface energy which gave the very low contact angle but the water which was present in the samples. The presence of water in the samples was expected to give problems, as it had in attempting to use the sessile drop technique, however in the case of the Inverted Hamilton method these difficulties were increased by the additional problem that the n-octane used was being absorbed into the sample's aqueous phase and was reducing the surface tension of the water so that the added drop of water was trying to form a sessile drop on a very low surface energy material.

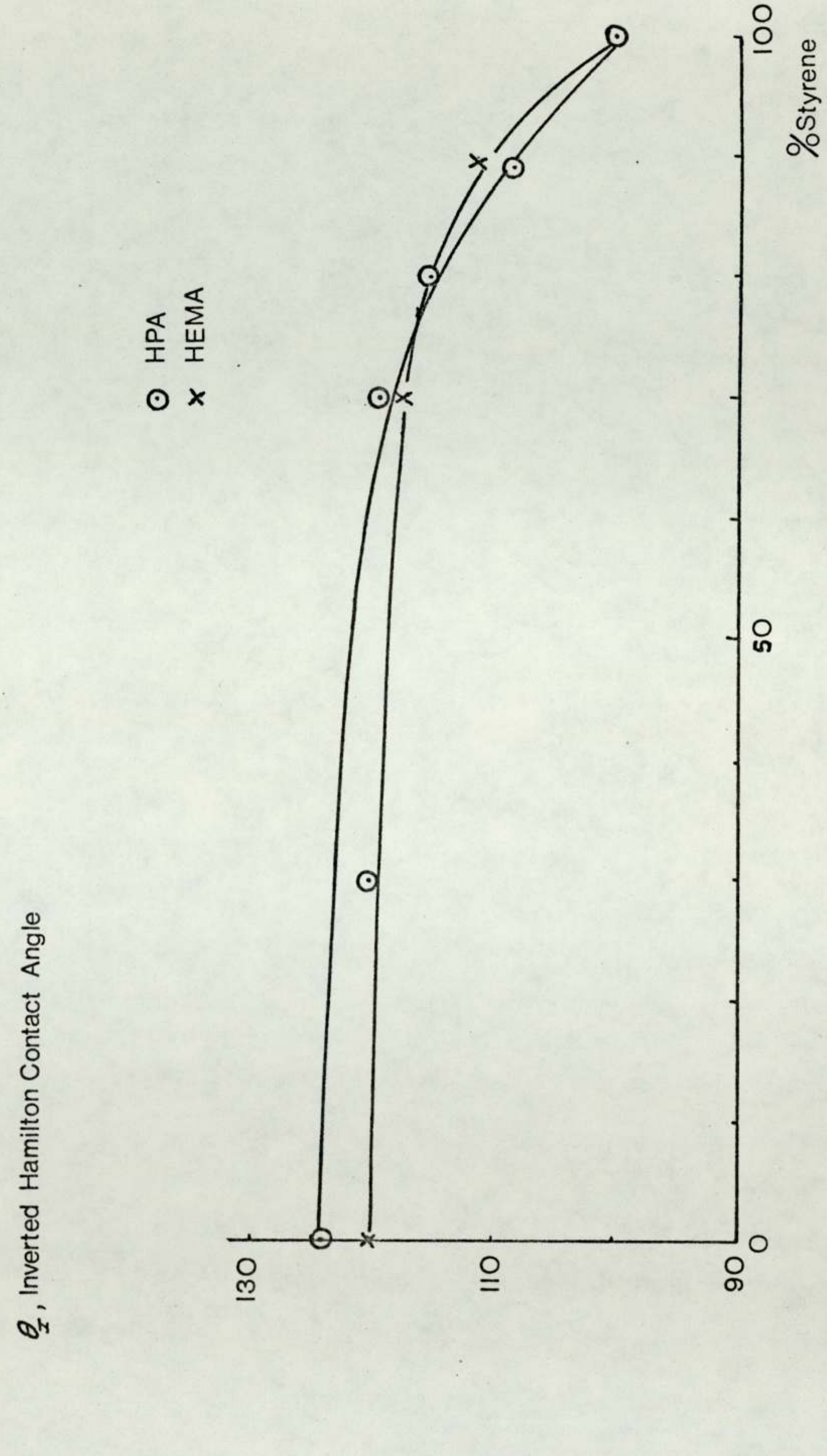
With the dehydrated samples the situation was somewhat improved and a contact angle could be recorded for the samples tested. With the hydrophilic-hydrophobic copolymers (Fig. 27) the

Fig. 26



Calibration Curve for Inverted Hamilton Method

Fig. 27


θ_I, Inverted Hamilton Contact Angle
⊙ HPA
× HEMA
130
110
90
0
50
100
%Styrene

values recorded for the contact angle all lay within a fairly narrow range of values, 125° to 100°, which corresponded to values of from 2 to 9 dynes cm^{-1} for the polar component of the surface energy for dehydrated samples. These values compare with values of from 7 to 21 dynes cm^{-1} for dehydrated samples as found by the sessile drop method.

Investigation of hydrophilic-hydrophilic copolymers show that although it is possible to see the same factors at work as were seen with the sessile drop investigation, i.e. hydrogen bonding and complexing, the values obtained were much lower than had been obtained previously for polar components. All of the copolymers had polar components which were in the range 2 to 9 dynes cm^{-1} and with the exception of the acrylic acid—N-vinyl pyrrolidone copolymers this was much less than the polar components found by the sessile drop method which were in the range 13 to 21 dynes cm^{-1}. The values for the acrylic acid—N-vinyl pyrrolidone copolymers were of a similar order to those produced by the sessile drop method. It is probable that the similarity in results seen is fortuitous; in the sessile drop investigation the reasons for the low value of polar component seen are because of the high degree of hydrogen bonding and complexing which occurs. In the Inverted Hamilton method it is probable that this effect is being masked by whatever is causing the low values seen throughout the range of samples investigated.

It is clear from the low values found that there are other factors influencing the polar component when it is found by the Inverted Hamilton method. When a sample of HPA:styrene (20:80) had a conventional sessile drop placed on its surface and the contact angle recorded, it was found that this was within experimental error of the result given in the sessile drop investigation (60°). Careful addition of n-octane did not cause any change in the contact angle, however when the drop was increased in volume the base of the drop remained constant and the contact angle increased in value until it reached the value found in the Inverted Hamilton investigation (118°) at which point the drop increased in size and the angle remained constant.

This would appear to be a clear indication that there is some absorption of the n-octane onto the surface of the sample and that this is the cause of the low values for the polar components found.

Although the use of the Inverted Hamilton method would appear to be a way of finding the polar component of dehydrated hydrophilic polymers directly, the problem of absorption of the n-octane appears to mean that the method will give constant answers which are much lower than the polar component found by the sessile drop method. This reduces the usefulness of the Inverted Hamilton method as a means of finding the polar component of the surface energy of dehydrated samples.

6.3. Predictive Work on Hydrated Hydrophilic Polymers.

In view of the difficulties of finding the total surface free energy of hydrated hydrophilic polymers an attempt was made to use bulk properties to predict the surface energy, assuming that the system could be said to be composed of two components, a polymer matrix and an aqueous phase.

Following the work described in Chapter 3 in which the surface properties of hydrophilic polymers were predicted from bulk parameters, the best method was used to predict the surface properties of a hydrated sample. By comparing the predicted results from Chapter 3 with the experimentally determined results in Chapter 4 it was clear that the parachor gave the best correlation when dealing with dehydrated samples.

It was fairly easy to ascribe values of the parachor to the repeat unit in the polymer chain and to extend this to a copolymer by assuming molar additivity of the parachors of the repeat units. The problem lay in assigning parachor values to the water which formed the second phase. In hydrated hydrophilic polymers the simplified view can be taken that water exists in two forms; (a) that which is bound to the polymer chain and (b) that which is free and forms the aqueous phase. The amounts of bound and free water can be quantitively determined by use of a Differential Scanning Calorimeter[84]. Using this information it is possible to calculate the number of moles of water which are bound to each mole of hydrophilic monomer. Once the number of moles of water bound to each mole of hydrophilic monomer are known it is possible to ascribe a new parachor value to that repeat unit. Having given a parachor value to the free water it is possible to use the molar additivity principle to find a value for the surface energy of a hydrated hydrophilic polymer. The concept can be extended to hydrophilic - hydrophobic copolymers, where the water will only be bound to the hydrophilic repeat units, and the summation of the parachors needs three terms; one for the bound hydrophilic polymer repeat units; one for the free water and one for the hydrophobic polymer repeat units.

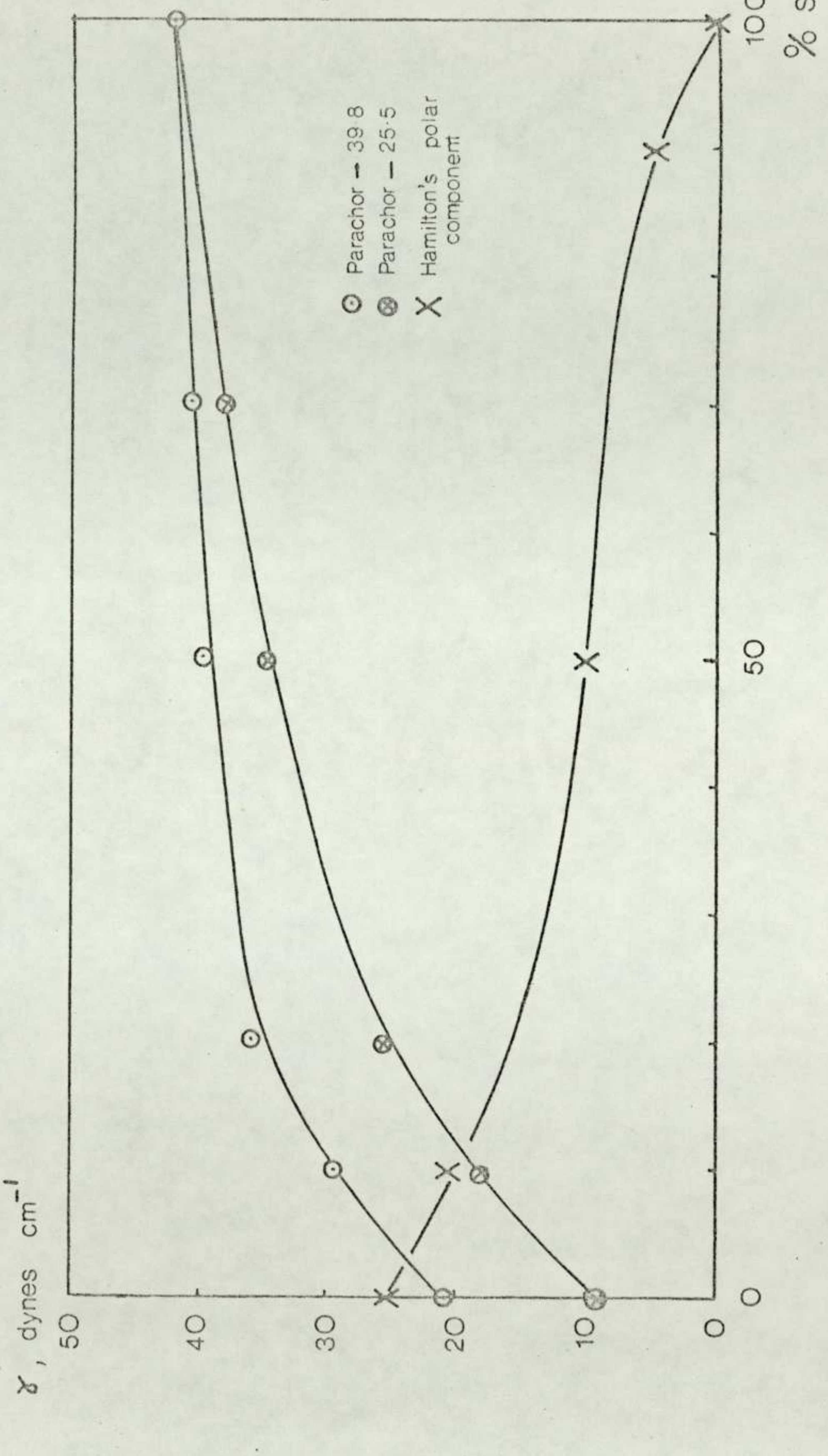
In order to simplify the calculation a computer program was written which was able to predict the hydrated surface energy from the amount of polymer and the quantity of bound and free water which occurs in the gel. (Appendix 3)

Because of the difficulties of finding values for bound and free water in a large number of polymer samples it has only been possible to find the surface energies for a range of hydrated samples of poly(styrene-co-HEMA).

Depending on the value ascribed to the parachor for water samples of poly(HEMA) can have predicted surface energies within the range 9 - 21 dynes cm^{-1}. By slowly increasing the amount of hydrophobic styrene in the copolymers the value of the surface energy rises to the value which was predicted by the parachor technique for polystyrene, 40 dynes cm^{-1}. Andrade[8] has said that the probable values of surface energy for hydrated hydrophilic polymers are in the range 3-10 dynes cm^{-1}, although he gives no indication as to how he arrived at this conclusion, so the results predicted by the parachor technique using experimental values of bound and free water are of the same order as he predicts. Thus it would appear that the use of the parachor makes it possible to predict the surface energy of a hydrated hydrophilic polymer from the amount of bound and free water which the polymer contains in the hydrated state.

An interesting comparison can be made between the calculated total surface energy of a hydrated hydrophilic polymer and the polar component as obtained by Hamilton's method. The comparison for samples of poly(HEMA-co-styrene) is given in Fig. 28 . It is clear that the calculation method is giving answers which are consistently higher than the polar component found by Hamilton's

Fig. 28


γ, dynes cm^{-1}
50
40
30
20
10
0
0
50
100
% Styrene
Parachor → 39·8
Parachor — 25·5
Hamilton's polar component

method. This difference is to be expected since the theoretical method is attempting to predict the total surface free energy of a hydrated hydrophilic polymer sample whereas the Hamilton Method only determines the polar component. Had there been no difference then the theoretical model used in the calculation would have been shown to be deficient in some respect and a new model would have had to be devised.

6.4. Surface Energy and Bioadhesion.

One of the important and new areas of applied polymer science in which surface properties are of paramount importance is that of the biocompatibility of these materials. The correlation of surface energy with biological interactions can be summarised into the following two areas:

a) the interaction of blood with foreign surfaces;

b) interaction of isolated cells with foreign surfaces.

When blood comes into contact with foreign surfaces there are specific adsorptive interactions which can initiate such events as thrombus formation and blood coagulation. Two well known processes may occur; a) the adsorption of proteins leading to coagulation; b) the adhesion of platelets, firstly to the implant surface and then to each other. The surface energy of the implant is involved in a number of ways: in the adsorption of proteins, in the initial adhesion of platelets and in the control of the adhesional life of the thrombus which is formed. The lifetime, and therefore size, of the thrombus should go down with decreasing surface energy of the implant material because of the poorer adhesional qualities displayed by low surface energy solids. Lyman et al.[44] have studied the relationship between the critical surface tension of some homopolymers and blood-coagulation time. They report an inverse relationship which seems to support what would be predicted from theory.

There seems to be general agreement that adhesion of isolated cells, from a variety of tissues, can be directly correlated with the surface energy of the implant material. Although the correlations with surface constitution seem promising, they only hold for serum-free media; recent work has shown that this simple relationship disappears in the presence of proteins adsorbed on the solids. Such interference can be understood since it has been well and frequently demonstrated that an adsorbed monolayer will completely change the wetting and adhesive characteristics of a surface.

The foregoing applies to laboratory simulations of biological systems. Since the presence of proteins plays a major role in even such model systems, in real biological systems, where there are numerous proteins, the difficulties are compounded. Thus if consideration of surface energies are to be useful, it will only be in the sense that they define properties which may affect adhesion of cells and proteins. The problems are also compounded by the difficulty of ascribing a value to the wettability of biological tissue, e.g. various workers have used essentially the same experiments to arrive at opposing views on the wettability of vascular endothelium.[85,86]

It is possible experimentally to determine the degree of interaction which blood has with a surface by conducting a series of blood clotting experiments. The technique consists, essentially, of placing a sample of polymer in contact with circulating stream of blood. The sample is observed until signs of thrombus formation appear at which point the experiment is terminated. This allows a blood clotting time to be found for each experimental polymer surface and permits a ranking to be arrived at in terms of the increasing thrombogeneity of each surface. The major problem associated with this technique is that the blood comes into contact with an air interface at some point in the experiment. This tends to upset the balance between the clotting and non-clotting factors in blood and will tend to produce a high degree of scatter and irreproducible in any results obtained. However, as in vivo screening of large numbers of samples is both expensive and impracticable a blood clotting test is the best method currently available.

With hydrogels the aqueous phase tends to impart a higher degree of biocompatibility to the sample than would be predicted from the surface energy. It is probable that there is an exchange between the water in the hydrogel and the surrounding tissue and that this imparts improved biocompatibility to the implant. That tissue and blood compatibility are not necessarily equal is discussed in Chapter 8 together with modification to the surface which will tend to improve both the above types of compatibility.

It has recently been found possible to correlate the Hamilton contact angle, which is a measure of the polarity of the hydrated surface, and the blood clotting time. Initial results[83] would seem to indicate that there are two families of hydrogels one of which has much shorter clotting times than the other. Some very long clotting times, of the order of 100 mins., are given by some samples which have a high surface polarity, i.e. large

Hamilton contact angle. However there is some doubt that these long times are an accurate representation of the biocompatibility of the surface. It is possible that because of air-blood interface which occurs at one point during the test certain clotting factors are adsorbed onto the sample and that these inhibit the clotting mechanism. What is clear, however, is that Hamilton's method can give an indication of the likely blood clotting time of a surface and hence of the biocompatibility.

6.5. Discussion.

Two main areas have been investigated in attempting to determine the surface energies of hydrophilic polymers:-

a) Prediction of surface energies from bulk parameters.

b) Determination of surface energies from wetting experiments.

The various approaches are now reviewed.

For the predictive work two different methods were used, the Parachor approach and the Cohesive Energy Density, CED, approach. These two methods use different bulk parameters to predict the surface energy. In the case of the Parachor approach it is the Parachor values of Quayle which are used whilst in the CED approach it is Small's force constants used in conjunction with the cohesive energy work of Hildebrand and Scott. The experimental methods used in this project were all variations on the classical contact angle wetting experiments in which a liquid forms a sessile drop on a solid surface and the angle of contact is used as a measure of the wettability of that surface. The methods considered were those of Owens and Wendt and of Wu which both use two wetting liquids, water and diiodomethane, to give two contact angles on a surface. These two contact angles are inserted into two simultaneous equations the solution of which is the surface energy of the sample under investigation. The methods differ in the way they analyse the results, i.e. Wu uses a harmonic mean equation whilst Owens and Wendt use a geometric mean equation, and in the values ascribed to the components of the surface energy of the two wetting liquids. For reasons previously discussed the majority of the experimental results were processed by means of the Owens and Wendt equation.

The surface tension of the liquids used in the above experimental methods were determined by means of a wetting balance and were found to be in good agreement with literature values. Although the purity of the wetting liquids had been monitored by GLC, direct surface tension measurement was used as the final control of purity. This was because even very small amounts of surface active material can affect the surface tension greatly and these low concentrations might have escaped detection by other techniques. Since good agreement was found between the literature and the experimental values for the surface tension of the wetting liquids, the literature values of the polar and dispersive components of the surface tension of the wetting liquids were used in the equation of Owens and Wendt. These literature values had previously been obtained by other workers to a high degree of accuracy and the errors which would have been introduced by determining them using the experimental value for the surface tension exceeds the errors introduced by assuming the experimental and literature value for surface tension were equal and using the literature values for the polar and dispersive components.

An alternative method of determining the surface tension of the wetting liquids, viz. a capillary rise technique, could have been substituted but this would also have been subject to the same problem of giving a value to the polar and dispersive components of the surface tension which had been experimentally determined. Additionally the capillary rise method has disadvantages when compared to the wetting balance method. Firstly the angle of contact between the glass wall of the capillary and the experimental liquid must be accurately known and secondly there are problems associated with surface contaminants on the inside wall of the capillary tube. It is difficult to ensure that the bore of the tube has a clean wall and that this is free from surface active contaminants. The use of chromic acid to remove these materials can cause problems since it is well known that chromate ions are left adsorbed onto the glass wall and these will have an effect on the value obtained for the surface tension.

The principal disadvantage of Owens and Wendt's method of using a sessile drop contact angle is overcome by Hamilton's method. This alternative technique uses a second liquid, immiscible with the sessile drop forming liquid, under which the sessile drop is formed. This is an alternative method of determining the surface energy of a sample and, if the dispersive components of the two liquids are equal, as is the case in Hamilton's method, this permits the polar component of the surface energy to be determined independently of the dispersive component.

The Hamilton method uses n-octane as the wetting liquid and the experiment is conducted with the sample placed under water. This means that the method is useful for hydrophilic polymers in the hydrated state since this allows one component, the polar, to be found without the sample suffering any dehydration at the surface. The disadvantage is that the total surface energy of the hydrated sample remains unknown. An 'Inverted' Hamilton technique was devised to permit the polar component of the surface energy of a dehydrated sample to be found so that this could be compared with the values found by the sessile drop in air method of Owens and Wendt. In this technique the sessile drop is water and the sample is placed under n-octane. The method suffers from the same drawback as the Hamilton method in that it is impossible to find either the total or the dispersive component of the surface energy by the method. In addition, as was previously discussed, there appears to be some adsorption of the n-octane onto the samples which produces ambiguous results.

All of the experimental methods used photographic means to record the sessile drops which were enlarged by the projection system used in the experimental set-up. This means that when the negatives were enlarged a many-times life size sessile drop was produced and this tended to improve on the accuracy of the contact angle measurement.

Using the equation of Owens and Wendt together with experimentally determined contact angles means that it is possible to evaluate the surface energy of a solid in terms of the solids polar and dispersive components. The method of Hamilton only gives information on the polar component of the surface energy and because the experiments are conducted with the sample under water the method does not lend itself to the study of dehydrated samples but is useful for hydrophilic polymers in the hydrated state. By using the Inverted Hamilton method it was hoped that it might be possible to determine the polar component of the surface energy in isolation. However, as was previously pointed out the technique is not as powerful as was first hoped because there appears to be some adsorption of the n-octane onto the surface of the sample which produces a low answer for the polar component.

It is not possible to separate the polar and dispersive components of the surface energy by means of a predictive approach. Both of the methods selected only give the magnitude of the surface energy in terms of the total for that surface. As was discussed in Chapter 3 the two methods selected, CED and parachor produce answers which are dissimilar for identical polymers. The two different methods can be correlated with different experimental methods for non-hydrophilic polymers. The CED approach has been shown to correlate with Zismans critical surface tension whilst the parachor has been shown to be in close agreement with the melt surface tensions which were experimentally determined for a range of non-hydrophilic polymers.

For hydrophilic polymers the CED approach produces values which are lower than those produced by the parachor method. By comparing the values for the parachor technique with those found experimentally by the contact angle method on dehydrated surfaces it is clear that there is good agreement between the two methods. In addition the CED method is close to the values found experimentally for the dispersive component of the surface energy. This tends to support the premise given in Chapter 3 that the CED method and the critical surface tension method can be said to be approximately the same as the dispersive component of the total surface energy. The reason is that both the CED and the critical surface tension method use parameters and interactions which are purely dispersive in nature and so the answer produced will tend to be biased towards the dispersive component at the expense of the polar component. Because of the way the parachors were found for the elemental units used in determining the surface energy this method will tend to produce a more balanced overall picture and so the final surface energy results produced will contain more polar character and will be a better reflection of the experimentally determined results. Assuming that the comparison can be made between hydrophilic and non-hydrophilic polymers then it is likely that as the parachor results reflect the melt surface energy results the wetting experiments results will also be a close reflection of the melt surface energy. Thus it is likely that wetting experiments can be used to predict the values of the melt surface energy without having to determine these experimentally for a whole range of polymers.

Having reviewed the techniques available for both calculating and determining experimentally the surface energy of samples, an attempt can now be made to relate the results obtained with the different techniques over the range of samples which have been studied and to assess the extent to which the surface properties of this group of materials are unique or unusual in relation to the generality of polymeric materials.

The polymers studied in this project can be grouped under two general headings related to the nature of the monomers used in this project - namely, hydrophilic-hydrophobic and hydrophilic-hydrophilic. These general groups can be further subdivided with respect to the amount of polarity shown by the individual monomers. For example both styrene and methyl methacrylate are hydrophobic monomers but they differ in the amounts of polarity shown by the surfaces of the homopolymers. Polystyrene has a polar component of 1.9 dynes cm^{-1} whilst poly(methyl methacrylate) has a polar component of 7.3 dynes cm^{-1}. The difference is attributable to that between the ester group, which imparts the polarity to the surface of poly(methyl methacrylate), and the phenyl group which is virtually non-polar.

Similarly there are differences between the polarity of the individual hydrophilic monomers, although none show the very low surface polarity displayed by polystyrene. With the hydrophilic monomers, however, a second factor, that of hydrogen bonding, must also be considered as this can have a large effect on the polar component of the surface energy exhibited by the dehydrated solid surface. It is for this reason that hydrophilic polymers, such as poly(acrylic acid), have a lower polar component of the surface energy than for example poly(HEMA), not because the polymers of the latter type have an inherently more polar surface but because of the inter- and intrachain hydrogen bonding which occurs with the former. This hydrogen bonding will reduce the concentration of polar groups at the surface and hence the surface polarity.

This hydrogen bonding tendency is also a factor in controlling the water content of the polymers. For example, as has been indicated, poly(acrylic acid) has a lower polar component of the surface energy in the dehydrated state, 13.13 dynes cm^{-1}, than does poly(HEMA) because of the large amounts of hydrogen bonding that occurs in the former polymer. The water content of poly(acrylic acid) is much higher than poly(HEMA), 73% as compared to 38%. This is a consequence of the greater hydrophilicity of the carboxyl group.

It might be expected that poly(methacrylic acid) would display the same high degree of hydrogen bonding seen with poly(acrylic acid). This is not the case, however, and poly(methacrylic acid) has a much reduced level of hydrogen bonding and this is reflected in the high polar component of the surface energy, 23.6 dynes cm^{-1}. The reason for the low level of hydrogen bonding is the restricted rotation imposed on the polymer chains by the methyl group. This prevents the optimisation of the hydrogen bonding between chains and results in a higher concentration of polar groups at the surface than is the case with poly(acrylic acid). However the water content of the polymer is about the same as that shown by poly(acrylic acid). This is because although the methacrylic acid monomer units do not interchain hydrogen bond very easily in the dehydrated polymer, the water is capable of increasing the rotation of the polymer chains and so help to optimise the amount of hydrogen bonding seen. This allows the same factors as were involved with poly(acrylic acid) to come into play and the water content rises to approximately the same value.

The arguments can be extended to the case when two different hydrophilic monomers are used. Minima are seen in the water contents with, for example copolymers composed of NVP/MAA and HEMA/MAA at the point were the concentrations of the different interacting species is approximately equal. Because restriction of rotational freedom in dehydrated polymers produces random orientation of groups at the surface there is no corresponding deviation observed in the surface energies of dehydrated polymers.

Thus although monomers may be grouped as either hydrophobic or hydrophilic there are differences within each of those groups in respect of the polarity shown by the monomers. In addition with the hydrophilic monomers the variation in polarity must be considered alongside variations in hydrogen bonding. For example both poly(HEMA) and poly(methacrylic acid) show approximately the same surface polarity in the dehydrated state (21 dynes cm^{-1}) but they have vastly different water contents (38% compared to 73%). Whilst poly(acrylic acid) has the same water content as poly(methacrylic acid) but displays a much reduced surface polarity, due, in the main, to hydrogen bonding preventing polar groups from being placed at the surface.

TABLE 22

	γ_d	γ_p	γ_t	H_2O content, %
Polystyrene	40.2	1.9	42.1	>1
Poly(methyl methacrylate)	35.25	7.31	42.56	>5
Poly(ethylene terephthalate)	41.6	11.7	53.3	>1
Poly(HEMA)	31.42	20.24	51.66	38
Poly(HEA)	37.43	19.12	56.55	60
Poly(HPMA)	33.12	16.58	49.70	23
Poly(HPA)	31.8	19.0	50.50	51
Poly(acrylic acid)	37.81	13.13	50.95	73
Poly(methacrylic acid)	33.40	23.6	57.01	73
Poly(N-vinylpyrrolidone)	37.62	11.02	48.64	97

It is not only the various degrees of polarity which this range of monomers show which can have an effect on the surface energy of the polymers. The ease with which the side chains attached to the backbone of the polymer chains may be packed can have a large effect on the surface energy. This can be seen by considering the hydrophilic-hydrophobic copolymers of hydroxyalkyl acrylates or methacrylates with styrene (Fig. 16). The 50:50 copolymers all have dehydrated surface energies greater than the 50:50 copolymer of HEMA and styrene.

TABLE 23.

	γ_d	γ_p	γ_t
Hydroxyethyl acrylate	33.29	19.91	53.20
Hydroxyethyl methacrylate	32.11	14.91	47.03
Hydroxypropyl acrylate	31.19	19.08	50.27
Hydroxypropyl methacrylate	34.70	13.80	48.51

This is probably a function of the ease with which the hydroxyethyl side chain may be packed along with the phenyl groups, relative to the ease with which hydroxypropyl groups may be packed. It is to be expected that it would be more difficult to pack a hydroxypropyl chain rather than a hydroxyethyl side chain and this difficulty is manifested by the increase in surface energy.

In addition the hydroxypropyl side chains are not exclusively n-propyl chains. There are two isomers which occur, one is the straight, 3-hydroxy isomer and the other is the 2-hydroxy isomer. This means that the latter side chain has a greater bulk factor and so is harder to pack than the 3-hydroxy isomer. Additionally this means that the 2-hydroxy isomer combines both a polar hydroxyl group and a hydrophobic methyl group at the end of the side chain. It is this which accounts for the increase in dispersive component seen over that found in the case of poly(HEMA-co-styrene).

An interesting comparison can be drawn with the copolymers of methyl methacrylate and HEMA in which because the two monomers have side chains which are of similar size there is little problem with packing. Because of this the copolymers have much less deviation from straight line behaviour than is the case with the copolymers of hydroxypropyl methacrylate and styrene in which the side chains are structurally dissimilar.

It is clear from the foregoing arguments that the water plays an important in determining the surface energy of a hydrated sample. However it is very difficult to determine experimentally the actual surface energy of a hydrated hydrophilic polymer (hydrogel). Wetting experiments using a sessile drop technique are not very successful because of the problems associated with the film of water which exists at the surface of a hydrogel sample. This film must first be removed in order to obtain contact between the sessile drop and the actual surface of the sample. There must, however, be no disturbance of the water which is held in the polymer matrix, for, if there is, then the sessile drop is only impingeing on the polymer and not on the polymer-water complex.

It was hoped that the problems encountered with trying to remove the surface water would be overcome by changing to the Hamilton method. This technique does not need the surface layer of water to be removed and so proved more reliable with hydrated samples than had the sessile drop technique. The one major problem inherent in the method is that it is not possible to evaluate both of the components of the surface energy. Only the polar component can be found using Hamilton's method and this leaves both the total and dispersive values still unknown for a hydrated sample.

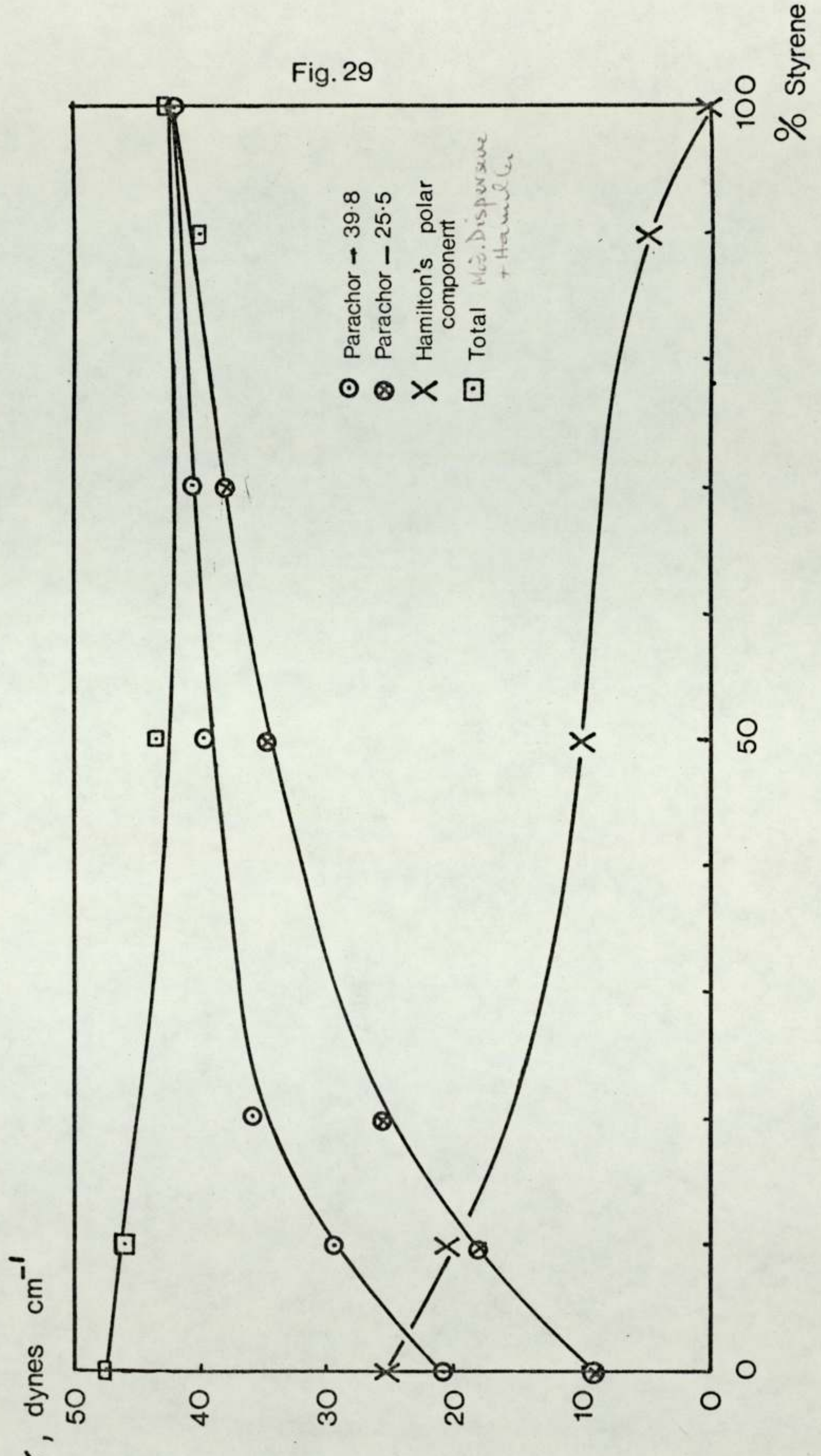
An attempt was made to estimate the total surface energy of a hydrated sample by a modification of the parachor method. The values produced were greater than those obtained experimentally by Hamilton's method on a hydrated sample and this is to be expected as Hamilton's method is only giving one component, the polar. It is difficult to obtain experimental values for the dispersive component of the surface energy of a hydrated sample. However values of dispersive components are available from wetting experiments on dehydrated samples and these values were combined with Hamilton's polar component values to obtain an estimate of the total surface energy of a hydrated sample. The values of the dispersive component were first modified to take account of the amount of swell each sample exhibits before being added to the Hamilton values for the polar component, Table 24 and Fig. 29.

It is clearfrom Fig.29 that the total surface energy predicted in this manner is relatively unaffected across the composition range. There is, however, increasing deviation away from the predicted surface energy as the HEMA content increases. The method used in the predictive technique, the parachor, has produced values for the dehydrated surface energies which are very close to the values obtained experimentally. Thus it is to be expected that the values obtained by the predictive method would be fairly close to the actual total surface energy of a hydrated sample. If this is the case, then the dispersive component must play a less prominent part in determining the surface energies of the hydrated samples as the water content increases. The use of the technique

TABLE 24

Sample HEMA : STYRENE	Hamilton Polar Comp. γ_p	Disp. Comp. of Surface Energy of Dehydrated γ_d	Linear Swell	Modified Disp. Comp. γ_d^m	Total γ $(\gamma_d^m + \gamma_p)$	Predicted Total γ^p
100 : 0	25.5	31.42	1.19	22.18	47.68	21.00
90 : 10	20.5	31.71	1.11	25.74	46.24	29.39
50 : 50	9.5	32.11	1.02	30.863	40.363	39.97
30 : 70	-	32.76	1.01	32.11	-	40.80
10 : 90	5.0	35.25	1.005	34.90	39.90	-
0 : 100	0.0	40.21	1.00	40.21	40.21	40.63

Fig. 29


γ, dynes cm⁻¹
50
40
30
20
10
0
0
50
100
% Styrene
Parachor → 39·8
Parachor — 25·5
Hamilton's polar component
Total McG. Dispersive + Hamilton

of adding Hamilton's polar component to the modified dehydrated dispersive component seems to be less useful as the water content rises and in the case of high water content gels, greater than 20%, the use of the polar component alone comes close to approximating the total surface energy of the hydrated sample. A further value for the parachor may be obtained by substituting the surface tension of water, 72.8 dynes cm^{-1}, into Mcleod's equation, Equation 21. This value of the parachor, 52.57 gives values for the hydrated sample which indicates the upper limit of the surface tension.

It is possible that the dispersive component is not very important in determining the applicability of a particular sample for an application. Recent work has shown that the Hamilton method produces values for the polar component which can be directly correlated to the basic biomedical parameter of blood clotting time. Thus it would seem probable that with high water content gels the surface is predominantly polar in character and the dispersive forces have a subordinant role in determining interactions at the sample's surface.

The surface energy investigations reported here and in previous chapters has permitted an initial overview of the interrelation between composition and the surface energy. The practical implications of these surface energy determinations with respect to such applications as biocompatibility and mould release are discussed in the following chapters.

MELT PROCESSABILITY
OF
HYDROPHILIC POLYMERS.

7.1 Introduction

It was initially assumed that hydrogels, because of their uniquely hydrophilic nature, would be difficult to process. In view of it having been found that the surface properties are of a similar order to conventional polar polymers, it should be possible to melt process these polymers by similar techniques to those used for conventional polymers such as polystyrene, poly(methyl methacrylate) and the nylons.

There would be a number of advantages in being able to melt process hydrophilic polymers since this would enable film and tube to be extruded for use in biomedical applications and thick sheets of polymer to be prepared for use in contact lens applications. Melt processing, however, does appear to present some problems with hydrophilic polymers the foremost of which is mould adhesion.

The interest in melt processing arose because the whole project on the surface studies of hydrophilic polymers was a SRC CASE award in which the co-operating body was Kelvin Lenses Ltd. who manufacture contact lenses by a melt process. They had highlighted several areas in which it was thought that a fundamental study of the surface properties would give useful information to enable the processing of hydrophilic polymers into contact lenses to be achieved. These areas are: fusion of polymer particles, void formation in the lenses, and mould adhesion. In this chapter the conclusions arising from the work carried out with the co-operating body are summarised in terms of the fundamental parameters which are believed to control them.

7.2 Mould adhesion.

7.2.1. Introduction.

Before a full understanding of mould adhesion is possible the wetting of materials by polymer melts must be understood. In the moulding process a melt is being asked to spread over the surface of the mould in such a way that the melt covers the surface and spreads but does not wet so completely as to form an adhesive bond between the material and the mould. The degree of spreading which a melt will allow is a function of the surface tension of the material in the melt state and the viscosity of the melt; additionally the adhesion depends on the interfacial tension between the melt and the mould material.

7.2.2. Surface Tension of the Melt.

Wu,[68,69] in a study of conventional polymers was able to determine values of both the melt surface tension and its temperature coefficient ($-d\gamma/dt$).The value of $-d\gamma/dt$ lies between 0.059 and 0.076 dynes. $cm^{-1}.deg^{-1}$. It is therefore probable that since it has been shown that the surface energies of hydrophilic polymers are of the same order as those of conventional polymers then the melt properties, or more specifically the temperature coefficient ($-d\gamma/dt$), will also be of the same order in hydrophilic polymers. If this is the case the melt surface tension will be of the same order as that shown by poly(methyl methacrylate), 32 dynes cm^{-1} at 140°C, and so it is to be expected that if the melt surface tension does play a role in determining mould adhesion in hydrophilic polymers its effect will be similar to that encountered with poly(methyl methacrylate).

7.2.3. Interfacial Properties of Polymers.

Wu[41] has looked at the problem of interfacial tension in polymer melts and how this is related to wettability. He studied the surface and interfacial tensions of a number of polymers and found that he could draw a number of conclusions about the role of these two parameters in determining which polymers did or did not spread.

Wu defined a spreading coefficient of phase 1 on phase 2 by:-

$$\lambda_{12} = \gamma_2 - \gamma_1 - \gamma_{12}$$

WHERE:- λ_{12} = Spreading coefficient of phase 1 on phase 2.
γ_1 = Surface energy of phase 1
γ_2 = Surface energy of phase 2
γ_{12} = Interfacial tension.

by using this and the converse expression of phase 2 spreading on phase 1 he was able to show that these expressions could be used to predict whether one phase will spread on the second. He found that the polymer having the lower surface energy might not necessarily spread on the polymer with higher surface tension. The controlling factor was whether the product of the spreading factors was greater or less than zero. When the product of the two spreading coefficients is greater than zero then neither phase will spread on the other.

He also found that a decisive role in wettability was played by the interfacial tension and that where the interfacial tension was greater than the difference between the two surface tensions the polymers will not spread on one another. Further, since the interfacial tension is largely a function of the polarity of the polymers then this will play a key role in determining the wettability of the two polymers.

A second approach to the problem of adhesion was made by Sell and Neumann[87] who considered the interface between two phases in contact. It is clear that for a good adhesive bond the interface which exists between the adhesive and the adherand must be reduced to a minimum. By considering two phases in contact Sell and Newmann were able to arrive at an equation which can be used to predict the value of the interfacial tension.

$$\gamma_{12} = \frac{(\sqrt{\gamma_1} - \sqrt{\gamma_2})^2}{1 - 0.015\sqrt{\gamma_1 . \gamma_2}}$$

From this equation it can be seen that when $\gamma_1 = \gamma_2$ the value for the interfacial tension is reduced to zero, i.e. there is a perfect bond between the two phases. In order to maximise the interfacial tension and hence obtain good mould release, the values of γ_1 and γ_2 must be as different as possible.

If instead of having two polymeric phases in contact, one of the phases is taken to be the metal forming the mould it might be thought possible to calculate whether a polymer melt would spread on the surface. If the necessary mathematics are carried out it is found that by Wu's criteria the melt ought to wet the mould metal completely. This complete and spontaneous wetting is found not to be the case with high energy samples which were investigated. Burns and Lau[88] found that there was an energy barrier to wetting when polystyrene was placed on glass (23 Kcal mol^{-1}) and as glass and pure metals have surface energies of the same order it is to be expected that the metals will display this effect. In addition it is extremely unlikely that any real mould would be formed of pure metal; there are almost certain to be areas of imperfection in the surface which will reduce the surface energy, as well as contamination which will also serve to reduce the energy, to such a level that wetting becomes very unlikely. With polymer melts there are also the restraints imposed by the viscosity of the system.

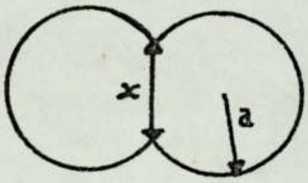
The consequence of this in terms of mould wetting and mould adhesion is that although some differences in behaviour are observed as between polymers having values of surface tension at the extreme ends of the range encountered with polymers, this factor will not be critical in governing mould adhesion phenomena.

7.2.4. Effect of Viscosity.

It is not only the interfacial tension which will in principle at any rate affect the degree of mould adhesion encountered. The viscosity of the melt will govern the amount of flow seen and this will serve to control the amount of wetting. Since good adhesion requires a high area of contact and the removal of air from between the adhesive and the substrate wetting will play an important role in determining the amount of adhesion seen.

There have been several investigations of the kinetics of wetting[89,90] and what it is which governs the flow of polymer melts. The rate of wetting has been followed by either the change in contact angle as the drop spreads $\mathrm{Cos}\,\theta/\mathrm{Cos}\,\theta_{\infty}$ or the change in the area covered by the polymeric drop measured as a change in the radius of the base, r/r_o. It is generally believed that wetting is achieved by capillary forces and retarded by the viscosity of the liquid. If capillary forces balanced by viscous resistance were the sole forces acting in the wetting process, then a characteristic scaling law would apply.[91]

Scaling laws[92] were derived to apply to the other important process in melt forming that of sintering together of particles. When two spheres are coalesced, the radius of the interface between the two spheres increases with time because of the action of surface tension and when this is resisted only by the viscous flow should satisfy the Frenkel law[93].



$$(x/a)^2 = 3\gamma t / 2\eta a$$

where a is the initial radius of the polymer spheres.

By considering both the effect of sintering and of the spreading of drops on various surfaces, Schonhorn[94] has been able to demonstrate that the rate of wetting is a function of both the surface tension and the viscosity of the melt and that the latter is highly temperature dependant. By using this relationship Schonhorn has shown that one can superimpose the kinetics of wetting data, i.e. $\cos\theta / \cos\theta_\infty$ and r/r_0 vs time for all polymer-substrate pairs, drop sizes and temperatures by only shifting horizontally on the time scale of a log-log plot.

The difficulty in using the above relationship to find out information on hydrophilic melts is that it is hard to find experimental data on the viscosity of the melts which would enable the kinetics of wetting to be determined from the master curves produced by Schonhorn.

Initial experiments have shown that the viscosity of hydrophilic polymer melts is of the same order as that found for poly(methyl methacrylate) melts, i.e. 9000 poise at 240°C. The viscometer used, however, was not sufficiently powerful (in terms of torque) to allow a thorough investigation to take place. Recently work has been carried out on a Weisenberg Rheogoniometer, a type of oscillating viscometer, which is much more powerful and allows the viscosity of hydrophilic polymer melts to be determined.

The available results suggest however that to all intents and purposes at the low shear rates used in commercial production of contact lenses, the viscosity of the melt will have little effect on the mould adhesion.

7.2.5. Effect of Mould Material.

In adhesion theory the substrate plays an important part in determining the amount of adhesion. All adhesives must bond to the surface of the substrate with forces of adhesion of about the same order of magnitude as the forces of cohesion in the bulk of the adhesive to obtain a maximum strength adhesive bond. In order to maximise the forces of adhesion the greatest surface area possible must be covered by the adhesive, which for most adhesives is a planar surface. This is because of the viscosity effects which prevent the adhesive from wetting the surface of a rough substrate sufficiently to remove all of the air from the imperfections.

In moulding, the polymer melt is forced into the mould cavity under pressure and this ensures that all of the air will be removed from below the spreading polymer melt. Any imperfections which occur will be filled and this will increase the surface area of contact and hence will increase the adhesive bond. In addition these imperfections which occur will provide mechanical keys and these will also serve to increase the adhesive bond. In order to reduce these two effects the mould ought to be as smooth as possible.

In contact lens applications the smoothness of the mould will also control the optical quality of the lens and so smooth mould surfaces will be required on two accounts. Provided that the metal mould is smooth there ought to be no problem with either quality or mould release.

7.2.6. Mould Adhesion: Conclusions.

There are a number of conclusions which can be drawn from the foregoing about the effect on mould adhesion of hydrophilic polymers.

i) There is no reason why hydrophilic polymers should be any more likely to adhere to a mould than should hydrophobic polymers. The unique nature of hydrophilic polymers does not extend to surface properties which are of the same order as all other polymers and so the degree of mould adhesion seen ought to be the same.

ii) The viscosity, which controls the wetting, is of the same order as was found in poly(methyl methacrylate) and so the effect of the viscosity ought to be the same in both cases. As there is little problem with poly(methyl methacrylate) then hydrophilic polymers should present little difficulty.

iii) Provided the mould is produced from good quality steel and is finished to a high standard the mould material should play little part in determining the adhesion. Microscopic imperfections can have their effect reduced by the application of a mould release agent, provided this does not interfere with the surface of the finished article.

7.3. Fusion.

It would be an advantage to be able to produce contact lenses directly from powder but this requires the fusion of particles into a homogenous whole. It was found that with hydrophilic polymers this presented some difficulties which it was believed was the fault of the surface properties in some way. It was thought that because of the unique nature of hydrophilic polymers the surface properties would be somewhat different from conventional polymers and that this would have some effect on the fusion of the particles. It has been shown that the surface properties are not unique and ought to have the same effect on the fusion of particles of hydrophilic polymer as on the fusion of particles of conventional polymer. As was previously stated the fusion of polymer particles ought to obey a scaling law in which the surface tension and the viscosity appear as terms. It was found that poly(methyl methacrylate) obeyed a modified version of the Frenkel law but that sintering of particles into a whole ought to proceed fairly easily.[95]

$$\left(x/a^{3/5}\right)^{n} = K(T)\,t$$

where n varies from 5 at T=127°C to 0.5 at 207°C.

The problem of fusion of hydrophilic polymers is not so much a function of the surface properties or the viscosity of the melt as the molecular structure of the polymer itself. It is very difficult to produce linear hydrophilic polymers because of problems with disproportionation which occurs when trying to prepare pure hydroxyalkyl acrylates or methacrylates. This introduces branches into the polymer which serves to restrict the fusion of the particles.

Although pressure does not directly enter into the scaling laws any increase in pressure will serve to increase the ease of fusion of two particles because this will help the surface tension to overcome the resistance of the viscosity. Initial attempts to fuse hydrophilic polymer particles under the low pressures encountered in the mould used to make contact lenses failed (Plate 2) because of the increased resistance to fusion imposed on the polymer by the branches. As pressure was increased it was found that the polymer particles could be fused at a critical pressure for any temperature. The higher the temperature the lower the pressure needed to ensure complete fusion, Plate 3.

Too high a temperature would have activated the latent cross-links in the polymer before the fusion - flow process had occurred in the mould so this placed a restriction on the pressure which was needed. Too low a mould temperature would have needed a high pressure to ensure fusion of the particles and this would have been impracticable with the moulds used to produce contact lenses. These two limits set an optimum range of pressures and temperatures at which fusion occurs. These are from 3.0 psi at 110° to 1.1 psi at 150° and under these conditions complete fusion occurs but cross-links are kept to a minimum.

PLATE 2

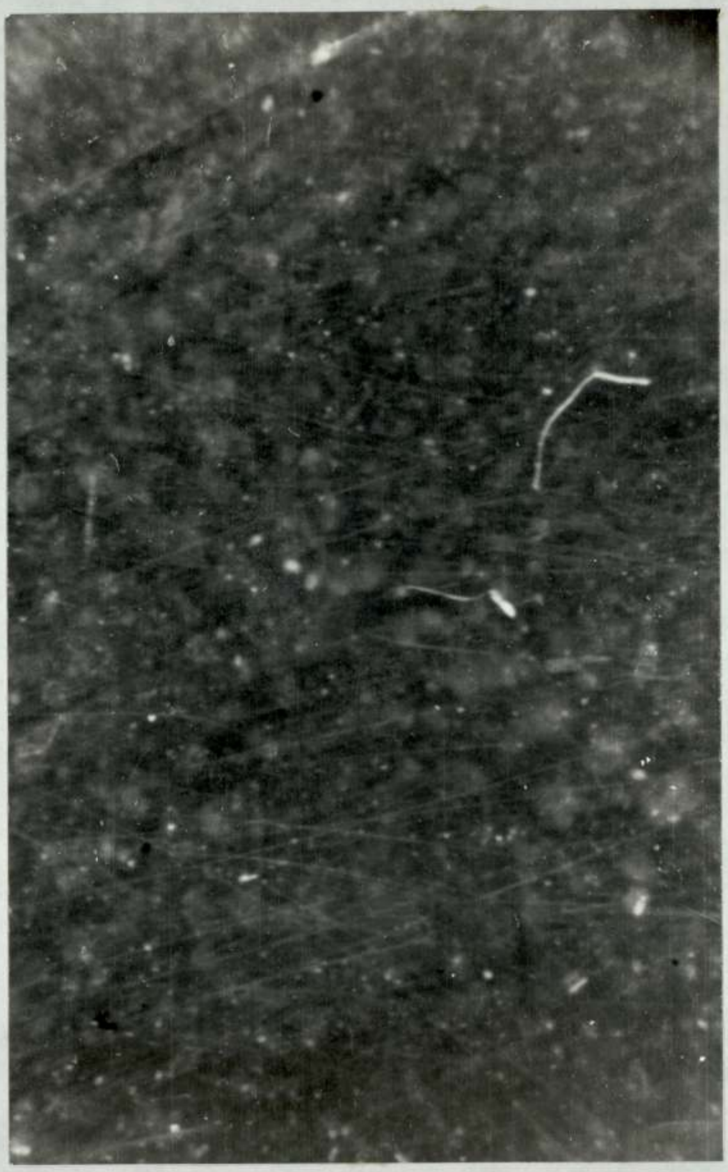


PLATE 3

7.4. Void Formation.

Attempts to mould lenses, even from fully fused sheets produced lenses which had voids, Plate 4. It was at first thought that the problem was caused by degradation of the material in the mould however investigation showed that the material was thermally stable up to a temperature in excess of that used in the moulding process.

In an attempt to reproduce the voids in moulded sheets of hydrophilic polymer an experimental set-up was built on a larger scale. Using this apparatus the voids were shown to be directly related to a reduction of the pressure in the mould. The cause of this pressure reduction could be either leakage of material from the mould which will reduce the quantity of material in the mould and so will produce voids or reduction of pressure on the mould cavity caused by some external force. The most probable cause of the voids seen in the commercial moulding of contact lenses is loss of material from the mould cavity. This loss of material occurs because the tools used to produce contact lenses from poly(methyl methacrylate) sheet are not fully positive, i.e. the cavity is not completely closed during the moulding cycle. This allows the hydrophilic material to escape from the tool under the increased pressure needed to produce contact lenses from hydrophilic material and this produces voids in the lens.

By including a gasket which converted the tools to a fully positive mould it was found that the problem of voiding was overcome and satisfactory articles could be produced which were void free.

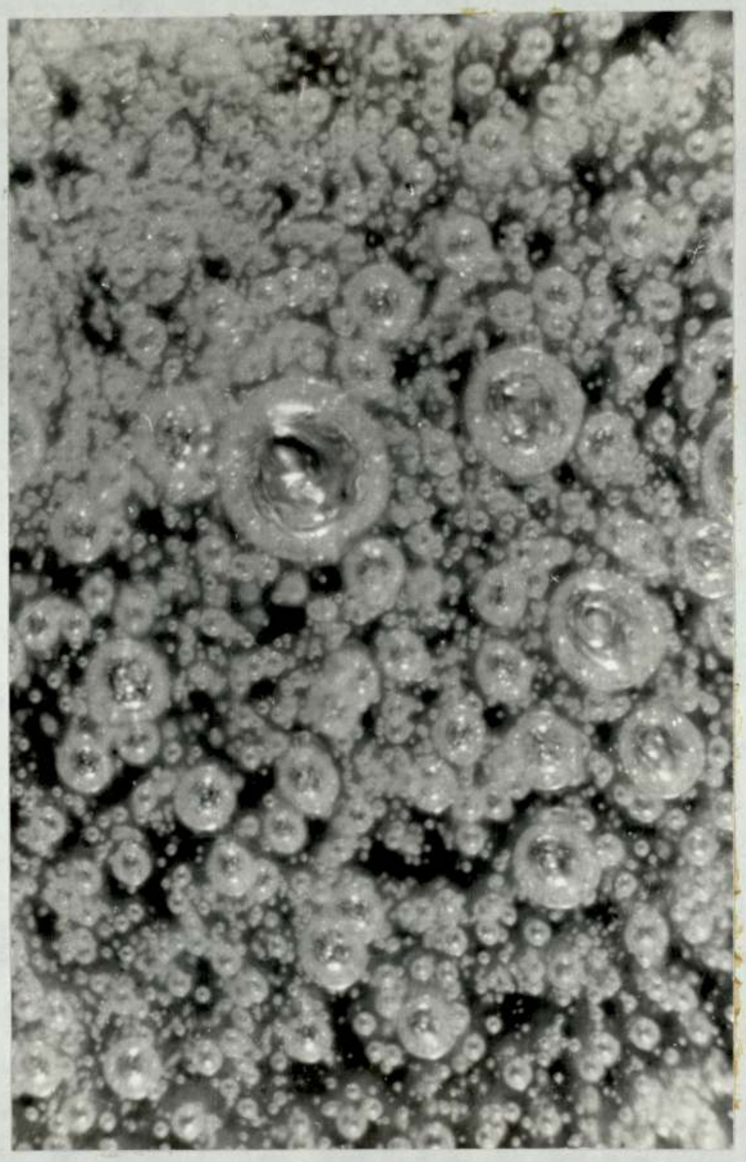


PLATE 4

7.5. Conclusion.

It has been shown that the hydrophilic polymers should present little problem in being melt processed both in terms of mould adhesion and in fusion of particles. In addition the voids which were present in early lens mouldings have been shown to be caused by a reduction of pressure in the mould cavity, either because of pressure reduction on the tool or because of leakage of material from the cavity which will reduce the internal pressure in the mould. A way of making the tools fully positive, by inclusion of a gasket, has been suggested which appears to prevent this voiding.

Mould adhesion should be no problem with the polymers processed but by lowering the moulding temperature and using fully fused sheets which had been produced by a different process the adhesion problem has been substantially reduced. Unfortunately the reduction of the temperature at which lenses are moulded has meant that the cross-linking reaction progresses at a very slow rate and this means unacceptably long times in the mould. Although some cross-links are needed to prevent the lens dissolving it is important that they are only introduced at the end of the moulding cycle and so an investigation which is outside the scope of the project, was initiated to investigate a range of possible cross-linking reactions.

STRUCTURE MODIFICATION.

8.1. Introduction.

Hydrophilic polymers have greater physiological compatibility than conventional hydrophobic polymers because of the water they absorb. The water present in the polymer, however, also causes a number of problems. Firstly, it is not possible to use conventional processing aids and lubricants with hydrophilic polymers because of the danger of these being leached out in use. One approach to obtaining mould release without the use of processing aids is to incorporate into the polymer a monomer which has a high surface to bulk activity and which will reduce the surface energy of the sample and thus reduce mould adhesion. This reduction in surface energy will help prevent adhesion of mucous and platelets. These aspects of surface behaviour have been discussed previously.

Secondly, one consequence of the water content is the enhancement of surface growth of colonies of bacteria. These cannot be killed with the range of conventional sterilising solutions as the anti-bacterial agent in those solutions is in many cases absorbed into the hydrophilic polymer and concentrated to toxic proportions. A potential solution to the difficulty is to copolymerise a monomer having anti-bacterial properties into the hydrophilic polymer chain. The bacteriocidal group should, in this approach, be given sufficient localised mobility to be effective within the gel and at its surface but unable to diffuse out of the gel and into the surrounding tissue area.

8.2. Polymers having anti-bacterial properties.

8.2.1. Introduction.

The need for effective sterilisation of biomedical materials, for example those used in contact lenses, is well known. For many years antiseptic solutions have been used to provide sterilisation of hard lenses[96]. The use of such solutions with contact lenses made from hydrophilic polymers is, however, undesirable since residues of the solution, left in the hydrophilic material, can be leached out and cause irritation to the eye. One anti-bacterial agent, thiomersal, has been recommended for use with hydrophilic contact lenses since although thiomersal diffuses into the bulk of the gel, it appears that it is not bound to sites on the polymer backbone and so the overall concentration in the lens remains fairly low. This means that the concentration in contact with the eye will be of the same order as with conventional solutions when these are used on hard lenses.

It has been shown that the build-up of conventional sterilisation solutions in hydrophilic contact lenses is considerable. A regime of boiling can be used but this is not a complete answer as boiling can cause proteins to denature and adhere strongly to the lens. This creates a potential for lens discomfort, poor vision and irritation. Furthermore, when the sterilised contact lens is removed from its case for insertion into the eye, recontamination with bacteria from the fingers is very likely.

In other fields of polymer technology it is well known that it is possible to polymerise a species into the bulk of the polymer to impart special properties, most notably resistance to UV or thermal degradation and it has been found possible to extend this to the polymerisation of anti-bacterial species. A convenient technique consists of reacting a known anti-bacterial agent with an ethylenically unsaturated molecule so that the double bond remains in the species. The resultant monomer can then be reacted into the bulk of the polymer film so that the anti-bacterial agent is bound into the polymer matrix.

There is a vast range of species which have been found to have some anti-bacterial action[97]. Amongst the most common are the substituted phenols such as 2,6-dibromo-3-hydroxyphenol, 2,6-dichloro-4-aminophenol and 2,4,6-triaminophenol. There are, however, many other molecules which possess anti-bacterial action to some lesser or greater extent. Amongst these are the cresols such as o-chlorocresol; the alcohols such as benzyl alcohol and chlorobutanol and various acid and amino derivatives such as chlorhexidine diacetate and benzalkonium chloride. In addition both thiomersal and cetrimide have found use as anti-bacterial agents in the more limited field of contact lens applications.

An ethylenically unsaturated group may be introduced into compounds having anti-bacterial action by reaction with an appropriate unsaturated compound, which may for example in the case of a phenolic compound, be an allyl halide or an allyl acid chloride. Preferably, however, the monomer having a substituent possessing anti-bacterial activity comprises an acrylate or methacrylate group and these may be introduced by reacting a compound having anti-bacterial properties with for example acryloyl or methacryloyl chloride.

8.2.2. Polymerisation of modified anti-bacterial agents.

To test the effectiveness of binding an anti-bacterial agent into a hydrophilic polymer a number of modified substituted phenols were prepared and polymerised into the bulk of a polymer rod. In a typical experiment 0.1 moles (2.68g) of 2,6-dibromo-4-hydroxyphenol was added to a lye of 0.1 moles (0.4g) of sodium hydroxide in 40ml of methanol. The methanol was removed and the solid was dried under vacuum. The dried solid was then suspended in dried benzene and 0.1 moles (0.9g) of acryloyl chloride were added whilst the temperature was maintained at under 5°C. Following complete addition of the acryloyl chloride the temperature was raised to 20°C for 1 hour, followed by 15 minutes at reflux. The sodium chloride was filtered off; the solvent was removed by rotary evaporation and the acrylic ester was recrystallised from aqueous ethanol. 0.42g of this monomer was added to the following purified and inhibitor free components;

Acrylamide	3.6g
Hydroxypropyl acrylate	13.0g
Ethyl acrylate	5.0g
Azobisisobutyronitrile	0.042g

The reactants were poured into lengths of polyethylene tubing sealed at one end. The system was then purged with nitrogen and sealed and the sealed tubes were placed in a water bath at 50°C for 72 hours and then postcured for 2 hours at 90°C in an oven.

Contact lenses were cut from this material and were stored in aqueous solution partially open to the atmosphere. These lenses show a markedly reduced tendency to sustain a surface growth of bacteria when compared to the unmodified polymer materials without the anti-bacterial substituent.

In view of the effectiveness of the bound anti-bacterial agent in preventing contamination by bacteria, a patent[98] was applied for, and was granted to cover the commercial exploitation of this work.

8.3. Polymers Modified by Fluorinated Additives.

8.3.1. Introduction.

Hydrophilic polymers cannot be processed with the aid of conventional processing aids as these would tend to be leached out of the polymer and into the living tissue containing the hydrated hydrophilic polymer (hydrogel) implant. Thus mould release must be a property of the base polymer and must not rely on external agents. We can identify two areas of importance in relation to the biocompatibility of polymers. One is tissue compatibility in which the exchange of fluid between the polymer and the surrounding tissue is thought to be a major factor affecting success. The second is compatibility with blood and certain other body fluids in a dynamic situation (e.g. blood vessels, kidney dialysis, ocular devices which interact with tear fluid such as contact lenses). Although hydrogels show extremely good compatibility in the former type of application (mechanical properties present the main problem in this area), in the second type the interdependence of high surface energy and adhesion results in a tendency for material to be deposited from the fluid and adhere to the hydrogel surface. Any low adhesive surface (low surface energy) will help to overcome this biocompatibility problem which in the field of contact lenses is that of build-up of proteinaceous material[99], oils[100] and calciferous deposits[101] on the lens surface. Having a low surface energy, however, does not necessarily make the material biocompatible in an absolute sense (i.e. in both respects referred to above) otherwise PTFE, with its low surface energy, would be one of the most biocompatible materials known, which it is not. The excellence of PTFE in biomedical applications is known but is limited to the second of the categories mentioned above, i.e. blood vessel replacement, where it is used because it possesses a surface which has low adhesion to other species not because it is biocompatible per se.

Any reduction in the surface energy of hydrogels, for example by the inclusion of a fluorinated additive, will help to increase this aspect of their biocompatibility by reducing surface adhesion, provided that the additive does not reduce the water content to any extent.

8.3.2. Wettability of Fluorinated Polymers.

The low intermolecular forces present in highly fluorinated organic compounds are widely recognised and account for the relatively low surface tension of fluorinated organic liquid compounds. In fluorine-containing polymeric substances, low intermolecular forces at the air/solid interface can also give rise to surfaces with extremely low surface free energy. As a result, fluorine-containing polymers are difficult to wet with organic or aqueous liquids and, in addition, these surfaces tend to have a nonadhesive character.

8.3.3. Effect of composition on wettability.

Shafrin and Zisman[102] emphasized the influence of surface structure on wetting behaviour in their "constitutive law of wetting". This law states that "the wettability of organic surfaces is determined by the nature and packing of the surface atoms or groups of atoms and is otherwise independent of the nature and packing of the underlying atoms and molecules". This law is based partly on Langmuir's "principle of independent surface action", which pointed out the extreme localisation of surface forces.[103] In arriving at this concept Zisman et al.[104] examined the wetting properties of a number of solid surfaces. It was found that high-energy surfaces could be coated with condensed monolayers of organic compounds and that the wettability was always a reflection of the outermost atoms of the monolayer regardless of the substrate. For example, a monolayer of perfluorolauric acid on platinum gave a critical surface tension value of 6 dynes cm^{-1}. This value represents the least wettable surface known and is a result of a highly allineated $-CF_2-$ chain terminated by $-CF_3$ at the air/solid interface. The importance of the terminal group can be appreciated by considering that a similar fluorinated acid terminated by $-CF_2H$ gave a critical surface tension value of 15 dynes cm^{-1}, which is more than twice the value of the $-CF_3$ terminated acid. Wettability studies were also conducted on a diverse range of polymeric materials and it is evident upon examination of the results that substitution of elements such as chlorine or hydrogen for fluorine in a polymer increases the wettability of the polymer. Recently it has been pointed out that the surface energy decrease which occurs in the order:

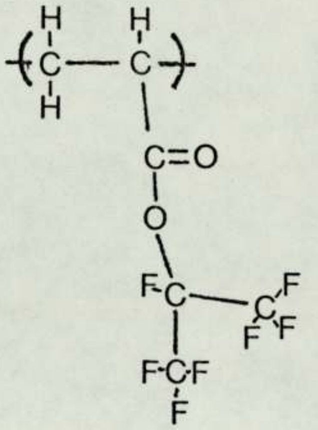
$$-CH_2- > -CH_3- > -CF_2- > -CF_3-$$

is primarily due to increasing group size. The larger volume occupied by CF_3, as compared to CF_2, results in fewer interactions per unit area and a lower surface energy.

8.3.4. Effect of pendant chain composition.

In dealing with polymers containing pendant groups, such as poly(fluoroalkyl acrylates), it might be anticipated that the wetting properties of these type of polymers would be influenced to some extent by the main chain composition and the amount of surface exposure of the main chain. However, the primary contribution to critical surface tension in polymers of this type is the side chain composition and the ability of the side-chains to align in some way.

By comparing the critical surface tension for the acrylate,



with those values obtained by Bernett and Zisman for monolayers of acids with similar terminal groups, Pittman[105] has been able to show that the value obtained for the acrylate, 14.1 dynes cm^{-1} is within the range found by Bernett et al., 13.3 to 15.2 dynes cm^{-1} for the acids studied. Thus the surface constitution of this polymer must be very similar to the branched acid monolayers.

A study of the poly(fluoroalkyl acrylates) in which hydrogen and chlorine had been substituted for fluorine on the fluoroalkyl side-chain showed that the substitution of hydrogen for fluorine increased the critical surface tension slightly and that substitution of chlorine for fluorine increased the critical surface tension by a larger amount. This paralleled the results found with substituted monolayers of acids.

8.3.5. Effect of side-chain length.

Hare, Shafrin and Zisman[106] have shown that with monolayers of perfluorinated acids the critical surface tension is affected by the length of the perfluorocarbon chain. In progressing from perfluorobutyric acid to perfluorolauric acid the critical surface tension value decreases from about 9 to 6 dynes cm^{-1}. This effect of decreasing critical surface tension with increasing perfluro chain length has been attributed to an increased efficiency in allining the chains so that the longer chained fluorocarbon acids present a higher concentration of $-CF_3$ groups at the air/solid interface.

It has been shown by Zisman et al.[107] that simply using a long-chain fatty acid with a terminal trifluoromethyl group did not result in low critical surface tension values. It was found that in order to achieve the low values associated with completely fluorinated acids, a long fluorinated chain terminated by $-CF_3$ was required. This behaviour has been explained in terms of the uncompensated dipole which exists at the junction $-CF_2-CH_2-$. With shorter fluoroalkyl units the dipole arising at the junction can increase the dipole at the terminal CF_3 and can also adversely affect chain allineation.

Pittman et al.[108] examined the relationship between wetting properties of fluorinated acid monolayers and fluoroalkyl acrylate polymer films. Table 25 gives a comparison of the critical surface tension values for fluorinated acid monolayers and fluoroalkyl acrylate polymers. It can be seen that the acid monolayers give lower values of critical surface tension than the acrylates with a comparable fluorocarbon side chain. This is not too surprising since chain allineation would be expected to occur with greater ease in a monolayer than with the fluorocarbon chain covalently attached to alternate carbon atoms along the polymer backbone.

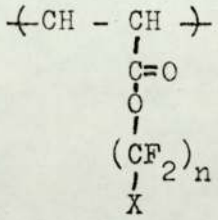
TABLE 25

Wetting Properties of Acid Monolayers versus Comparable Acrylate Films.*

Number of C atoms	Terminal group	γ_c (dynes cm^{-1})	
		Monolayer acid	Acrylate film
4	$-CF_3$	9.2	15.5
8	$-CF_3$	7.9	10.3
9	$-CF_2H$	-	13.0
11	$-CF_2H$	15.0	14.5

* Structure of acid monolayers:- $X(CF_2)_nCOOH$

Structure of acrylate film:-



$-\!(CH - CH(C(=O)-O-(CF_2)_n-X))\!-$

(X= F or H)

8.3.6. Modification of the surface properties with fluorine-containing additives.

Jarvis, Fox and Zisman[109] found that it was possible to produce fluorocarbon-like low-surface-energy polymers by the addition of small amounts of selected fluorocarbon additives to such non-fluorinated polymers as poly(methyl methacrylate) and polyacrylamide. Generally the amount of additive varied from approximately 0.2-1.0% and the method of addition to the polymer involved either addition to the monomer before polymerization or addition to a polymer with subsequent solvent evaporation. Dramatic changes in the wetting properties were demonstrated, for example, addition of 0.5% of tris(1,1—dihydropentadecafluorooctyl) tricarballylate to poly (methyl methacrylate) reduced the critical surface tension from 40 dynes cm^{-1} to 19 dynes cm^{-1}.

8.3.7. Modification of hydrophilic polymers.

It was thought that fluorinated additives would exhibit higher surface than bulk activity in hydrophilic polymers and would thus reduce the surface energy without significantly reducing the water content. Hydroxypropyl acrylate was polymerised with a range of fluorinated acrylates and methacrylates in an attempt to evaluate the extent of the surface activity which they would produce. In an attempt to accentuate any surface or bulk effects produced, the monomers were included at the maximum concentration that could be used commercially, 10 mole percent.

Because Hamilton's method only gives information on the polar component, the use of the sessile drop method on dehydrated samples was selected as the main technique to evaluate the surface energy. This method does not give information as to the value of the surface energy of hydrated samples but does allow the surfaces to be ranked in order relative to the effect which the fluorinated additive has on the surface energy. The water and diiodomethane contact angles are listed in Table 26 for each fluorinated monomer-HPA copolymer, along with the surface energy estimates produced.

When compared to the value for poly(hydroxypropyl acrylate), 50.8 dynes cm^{-1}, all of the copolymers have reduced surface energy although it is clear that the amount of polar component has been greatly reduced whilst the total surface energy has been only slightly reduced. It was found that the most effective monomer both in terms of reducing the total surface energy and the polar component was 1,1-dihydroperfluorobutyl methacrylate. When the side chain was reduced as in 2,2,2-trifluoroethyl methacrylate the value of the total surface free energy remained constant (46.4 dynes cm^{-1}) but the polar component was increased (7.7 dynes cm^{-1} from 0.14 dynes cm^{-1}). It is probable that the smaller side chain in 2,2,2-trifluoroethyl methacrylate is capable of being packed more easily and so less of the low energy fluorinated groups will be seen at the surface. With 1,1-dihydroperfluorobutyl methacrylate the longer side chain will be less easily packed and so more of the fluorinated groups will appear at the surface and this will reduce the surface energy.

When the terminal $-CF_3$ groups are replaced by a $-CF_2H$ group in the side chain the total surface energy increases. 1,1,3-trihydroperfluoropropyl methacrylate has only a slight increase in total surface energy over that shown by 1,1-dihydroperfluorobutyl methacrylate although the polar component is much larger, 4.9 dynes cm^{-1}. When the sidechain length is increased by the inclusion of more $-CF_2-$ groups the total surface energy increases even though the

TABLE 26

Fluorinated Monomer*	Contact Angles.		Surface energy (dynes cm^{-1})		
	Water	Diiodomethane	γ_d	γ_p	γ
1,1,3-Trihydroperfluoropropyl methacrylate	75	28	41.47	4.86	46.33
1,1,5-Trihydroperfluoropentyl methacrylate	81	13	47.66	1.90	49.57
1,1,7-Trihydroperfluoroheptyl methacrylate	85	15	48.08	1.01	49.09
1,1-Dihydroperfluorobutyl methacrylate	94	30	44.56	0.14	44.70
2,2,2-Trifluoroethyl methacrylate	70	32	38.72	7.67	46.40
Hexafluoroisopropyl methacrylate	69	30	39.43	7.93	47.37
Hexafluoroisopropyl acrylate	74	19	44.59	4.55	49.15

HPA
50.8

* Composition of samples:- HPA: Fluorinated Monomer (90:10)

polar component does not show a very large increase and the actual value is less than that shown by 1,1,3-trihydroperfluoropropyl methacrylate. It is probable that the small value of polar component shown by the longer side chain monomers is because of the shielding, caused by the unpacked side chains, of the backbone. The higher total surface free energy is because of the terminal $-CF_2H$ groups on the side chain.

With hexafluoroisopropyl methacrylate the branching of the side chain has little effect on the total surface energy (47.4 dynes cm^{-1}), although the polar component is slightly higher, 7.9 dynes cm^{-1}, than might be expected. This is probable due to the chains being able to pack the side chain in some regular way which allows more polar groups at the surface. As would be expected when the methacrylate monomer is changed to the acrylate, with the same side chain, the total surface energy increases (49.2 dynes cm^{-1}). However, the polar component is smaller (4.55 dynes cm^{-1}) than was the case with the methacrylate (7.9 dynes cm^{-1}). This is probable because without the methyl group on the methacrylate the packing of the chains is better and the side chain on the acrylate will be excluded which will reduce the surface energy.

Pittman[105] has pointed out that the surface energy in a particular polymer is not necessarily dependent on the total fluorine content but rather on the arrangement of the fluorine atoms. For example, poly(tetrafluoroethylene) with an overall 76% fluorine is more wettable than poly(perfluoroisopropyl acrylate), which has a 55% fluorine content. So although fluorine content might be a useful parameter in deciding which monomer is best at reducing the surface energy the arrangement of the fluorine atoms in the side chain has a greater bearing on the actual value of the surface energy. This can be seen by considering the case of 1,1-dihydroperfluorobutyl methacrylate which has a fluorine content of 50% and 1,1,3-trihydroperfluoropropyl methacrylate with a fluorine content of 38% both of which have lower surface energies when polymerised with poly(hydroxypropyl acrylate) than does the higher fluorine content, 57%, 1,1,7-trihydroperfluoroheptyl methacrylate.

8.3.8. Hamilton's technique applied to the modified hydrophilic polymers.

To observe the effect of hydration on the polar component of the surface energy, hydrated samples of the fluorinated monomer: HPA copolymers were investigated by Hamilton's method, Table 27 . It is clear that the water is acting as a plasticiser and is allowing a greater proportion of the polar groups to appear at the surface. This is increasing the value of the polar component although the values follow the same gross trends as were previously seen in the dehydrated method results.

By comparing the results of the Hamilton method with the equillibrium water contents it is clear that although the HPA copolymers with 1,1,5-trihydroperfluoropentyl methacrylate; 1,1,7-trihydroperfluoroheptyl methacrylate and 1,1-dihydroheptafluorobutyl methacrylate have similar polar components of the surface free energies (21 dynes cm^{-1}) the water contents are significantly different. The 1,1-dihydroperfluorobutyl methacrylate has a much higher water content for the same polar component and so this monomer is showing a much higher surface to bulk activity than are the other monomers. A similar effect can be seen with 2,2,2-trifluoroethyl methacrylate which has a similar water content to

TABLE 27

Fluorinated Monomer*	Hamilton Contact Angle, θ	Derived Polar Component, γ_p^D	Water Content %
1,1,3-Trihydroperfluoropropyl methacrylate	136	21	31.3
1,1,5-Trihydroperfluoropentyl methacrylate	135	21	21.9
1,1,7-Trihydroperfluoroheptyl methacrylate	133	20	20.5
1,1-Dihydroperfluorobutyl methacrylate	137	21	31
2,2,2-Trifluoroethyl methacrylate	142	23	30
Hexafluoroisopropyl methacrylate	137	21	21.1
Hexafluoroisopropyl acrylate	141	23	27.9

* Composition of samples:- HPA: Fluorinated Monomer (90:10)

1,1- dihydroperfluorobutyl methacrylate but an appreciably higher polar component of the surface energy.

	Water content(%)	θ	γ_p^D
1,1-dihydroperfluorobutyl methacrylate	31	137	21
2,2,2-trifluoroethyl methacrylate	30	142	23

This supports the dehydrated sample results in which 1,1-dihydroperfluorobutyl methacrylate showed a much greater reduction in surface energy than any of the other monomers.

8.3.9. Conclusion.

The inclusion of samll amounts of highly fluorinated monomers to hydrophilic polymers reduces the surface energy of those polymers, although the actual value depends on the type of additive. It has been shown that certain structures tend to reduce the value of the surface energy more than do others and that the actual percentage fluorine which the additive contains is of less importance than the structure of the additive.

It has been shown that the surface energy of a number of other highly fluorinated acrylates and methacrylates are much lower than the species used in this project. This shows that it might be possible to reduce the surface energy still further by using, for example 1,1-dihydroperfluorooctyl acrylate as an additive. It would appear, however, that it might be better to use the methacrylate rather than the acrylate of any additive chosen since this will reduce the surface energy by a greater extent than would the acrylate.

8.4. The surface properties of Poly α-esters: the effect of the pentafluorophenyl group on the surface free energy.

8.4.1. Introduction.

The opportunity arose to use the techniques discussed in this thesis to investigate the effect of pendant pentafluorophenyl groups on the surface properties of poly α-esters.[110] This was felt to be of relevance for two reasons:-

a) It gave an opportunity to investigate the value of the technique in a study in a system unrelated to the polymers previously investigated, (i.e. Poly α-esters are heterochain polymers)

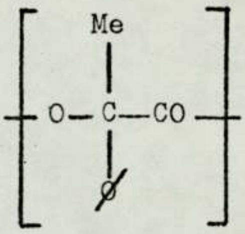
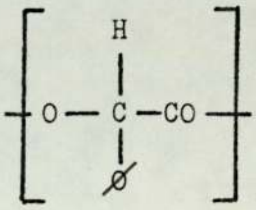
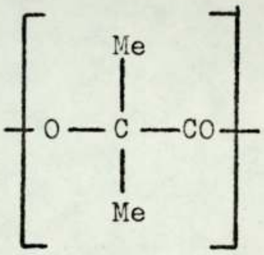
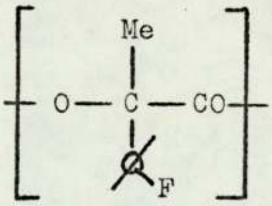
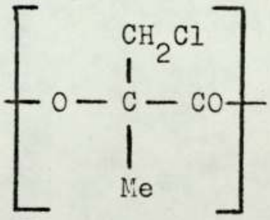
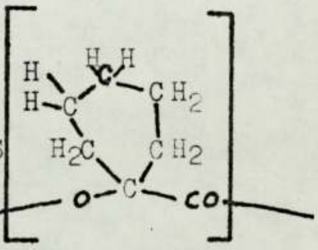
b) No published work on the surface properties of the pendant pentafluorophenyl group in relation to the phenyl group is known to the author.

Although surface properties of fluoro-aliphatic compounds are profoundly different from those of aliphatic compounds the surface properties of fluoroaromatic compounds are not greatly different from those of aromatic compounds, (i.e. hexafluorobenzene relatively similar to benzene). The properties are predominantly those associated with aromaticity and fluorine substitution shows no overriding effect.

8.4.2. Surface Properties.

The surface free energies of the polymers were examined by the sessile drop contact angle technique involving diiodomethane and water thereby enabling the separate polar and dispersive components of the surface free energy of the substrate to be determined. The polymers available for examination are listed in Table 28 and the results are shown in Table 29 together with values of the reference

TABLE 28

Name of parent acid.	Abbreviation	Repeat Unit
Poly(atrolactic acid)	PolyAAAC	 $\left[-O-\overset{Me}{\underset{\phi}{C}}-CO-\right]$
Poly(mandelic acid)	PolyMAAC	 $\left[-O-\overset{H}{\underset{\phi}{C}}-CO-\right]$
Poly(α-hydroxyisobutyric) acid	PolyDMAS	 $\left[-O-\overset{Me}{\underset{Me}{C}}-CO-\right]$
Poly(pentafluorophenyl) atrolactic acid	PolyPFAAC	 $\left[-O-\overset{Me}{\underset{\phi_F}{C}}-CO-\right]$
Poly(α-hydroxy-β-chloro) isobutyric acid	PolyMCDMAS	 $\left[-O-\overset{CH_2Cl}{\underset{Me}{C}}-CO-\right]$
Poly(1-hydroxycyclohexane-) 1-carboxylic acid	PolyC'hex AS	

Note:- The abbreviations are derived from the precursors from which the polymers were prepared.

TABLE 29

Results for poly α-ester surface free energies: dispersive free energy (γ_d), polar free energy (γ_p) and total surface free energy (γ)

Polymer	Contact Angle		Surface Free Energy (dynes cm^{-1})		
	Water	Diiodomethane	γ_d	γ_p	γ
Poly MAAC	82	19	46.29	1.84	48.13
Poly AAAC	86	21	46.50	0.98	47.49
Poly PFAAC	88	35	40.82	1.20	42.02
Poly DMAS	83	20	46.18	1.62	47.81
Poly MCDMAS	70	38	35.9	8.0	43.9
Poly C' hex AS	85	23	45.57	1.26	46.84
P. E.	94	50	33.3	0.93	34.23
P.T.F.E.	108	77	18.6	0.5	19.1
P.E.T.	60	20	41.5	11.8	53.3
P.M.M.A.	73	40	35.25	7.3	42.55

polymers, poly(ethylene) (P.E.), poly(tetrafluoroethylene) (P.T.F.E.), poly(ethyleneterephthalate) (P.E.T.) and poly(methyl methacrylate) (P.M.M.A.)

Although it is not possible to make direct comparison of the changing polar and dispersive contribution of surface free energies of polymers with changes in the gross chemical structure, some general trends can be clearly seen. Thus, in moving from P.E. to P.T.F.E. a considerable drop in the dispersive component (γ_d) coupled with a small decrease in the polar component (γ_p) is observed. Similarly the change in structure from P.E. to P.M.M.A. for example, results in a major increase in the polar component.

Turning now to the results obtained with the poly α-esters (which are incidentally the first surface study on polymers of this family), this shows some changes in the balance of polar and dispersive components with the three polymers, poly AAAC, poly C'hex AS and poly(α-hydroxy isobutyric acid) α-ester but a figure for the total surface free energy in each case that falls within the range 47.3 ± .65. Lying outside this range are poly MAAC (the only polymer having an α-hydrogen atom which will markedly reduce shielding of the backbone) which has a somewhat higher surface free energy of 48.13. At the other extreme the pentafluorophenyl substituted polymer and the monochloro substituted polymer show a decrease in surface free energy to 42.02 and 43.9 respectively.

A more detailed consideration of the polar and dispersive contribution to surface free energy is interesting and instructive. Thus the change from poly AAAC to poly PFAAC is accompanied by a distinct drop in the dispersive component (γ_d) and a slight rise in the polar component (γ_p). This is, of course, parallelled to the change observed on moving from P.E. to P.T.F.E. The magnitude of the overall change is however much smaller. This is consistent with the fact that surface and interfacial properties of aromatic and fluoroaromatic compounds are much more similar to each other than is the case with their aliphatic counterparts.

The highest polar contribution in all the poly α-ester studies is found in the case of poly MCDMAS which has a single chlorine atom pendant to the backbone. This is capable of being placed near the surface and will impart the observed high polarity. The next highest polar contribution is found in the case of poly MAAC having as it does one side of the chain shielded only by α-hydrogens. The next highest is found in the case of disubstituted but highly crystalline poly(α-hydroxy isobutyric acid) ($R^1 = R^2 = CH_3$) possessing as it does a helical structure. The fourth highest polar contribution is found with spirohexyl substituted polymer which has two α-methylene groups whose confirmation is constrained by the fact that they are held in a spiro system.

Thus the major contribution to the polarity of the surface, except in the case of the monochlorine substituted polymer, comes from the ester backbone itself. This again is quite consistent with the P.E., P.M.M.A. and P.E.T. results shown in the table. Such contributions are expected to be virtually the same, however, in the cases of poly AAAC and poly PFAAC.

SUMMARY
AND
SUGGESTIONS FOR FURTHER WORK.

9.1. Summary.

As has been stated the work was undertaken because of a CASE award. The object of the project was to study, a) the melt processability of hydrophilic polymers in the dehydrated state and b) the surface properties of the subsequently hydrated polymers in relation to the requirements for biomedical use. Initially there was little or no knowledge in this area and considerable effort went into compiling and correlating the relevant background information and literature before a programme of experimental work could begin. The literature search showed that the surface energy had a major part to play in determining the behaviour of the polymer in all the relevant areas of study. Thus the first stage of the project was to develop a range of experimental techniques to study the surface energy of hydrophilic polymers in the three relevant states, viz. hydrated, dehydrated and melt. Simultaneously with this effort, work was in hand to find a method of predicting the surface energy of the polymers studied from bulk parameters.

The studies associated with the dehydrated polymer were the most fundamental since this state is the easiest to study accurately. The sample is stable at room temperature; has no associated complicating factors such as water which occurs in the hydrated samples; and the method of examination, contact angle wetting measurement, is reproducible and does not show either a time or temperature dependence over the range used in the experimental work. Additionally the work on the dehydrated can, in principle, give information about both the melt and hydrated samples.

The best documented approach to surface energy measurement is the critical surface tension method of Zisman. He used the method of extrapolation to zero contact angle to give an indication of the surface energy of the substrate he was studying. His initial work was carried out using a range of wetting liquids which interacted with the sample through exclusively dispersive forces. The so called critical surface tension found by this method was found to correlate well with surface energy measurements for samples which had only dispersive forces acting at their surfaces but the fit was less good for samples which had both polar and dispersive forces operating at the surface of the samples. Additionally, studies have shown that the melt surface energies do not correlate very well with Zisman's critical surface tension. However, the critical surface tension method does give good correlation with the dispersive component of the surface energy. This is to be expected since Zisman's method of obtaining the results depends on the use of wetting liquids which can act only through dispersive forces and would thus be expected to give a value which is in good agreement with the dispersive component of the total surface energy. Thus it can be said that Zisman's critical surface tension (obtained with nonpolar and nonhydrogen bonding liquids) will give a good indication of the dispersive component of the surface energy of the sample.

The literature search produced two possible methods of predicting the total surface energy of a sample from bulk parameters. One, the CED (Cohesive Energy Density) method, used a modification of the cohesive energy density approach to the solubility of polymers coupled with the force constants of Small. This gave a value for the surface energy which was close to the values obtained by Zisman for the critical surface tension of comparable samples. It is not surprising that this should be the case since Small's force constants were derived by considering only dispersive forces and the whole equation is a function of only dispersive forces. The second method, the parachor, is based on the work of Macleod which was later modified by Sugden to apply to more complex molecular species. The parachor is derived from actual experimental data, obtained from molecules which have both polar and dispersive forces in their constitution. Thus the values obtained for the surface energy of experimental samples by using the parachor might be expected to have values more nearly equal to actual experimentally determined values for the surface energy. This is found to be the case and the parachor predicted surface energies show very good correlation with both melt surface tensions and the surface energies obtained from wetting experiments.

The main value of a predictive method which gives values close to actual experimental values for surface energy is that it is possible to use the predictive method as a means of screening large numbers of possible formulations. The best combination of monomers can be predicted without the need to produce a large number of samples for testing. Conversely a new monomer can have its possible effect on the surface energy predicted before it is included in a range of experimental samples. Thus a predictive method can complement the experimental methods and speed up the process of arriving at a structure which has the required surface energy.

The experimental method of Zisman was rejected because of the lack of wetting liquids which could be used on the plot to obtain the critical surface tension. Two methods were found, however, which gave a value for the surface energy of a sample from wetting measurements. The two methods were similar in that they used two wetting liquids to give two contact angles which were substituted into a modified Young equation, the solution of which was the surface energy of the sample. The method of Owens and Wendt differs from that of Wu in the equations used to obtain the surface energy estimates. Wu uses a harmonic mean term in the equation whilst Owens and Wendt favour the use of a geometric term. Additionally the values ascribed to the various components of the wetting liquids surface tensions are different in the two methods. The values obtained for the surface energy are thus different for the same sample. The bulk of the available literature supports the equation of Owens and Wendt and the values they use for the components of the surface tensions of the wetting liquids. The method of Wu is only supported by the work published by himself and his co-workers, although there does appear to be a sound theoretical background to the derivation of his equation. The values he uses for the wetting liquids surface tensions are much less supported by background data and have not been reported by other workers. All of the work reported in this thesis was processed by the method of Owens and Wendt and uses their data because of the greater background of support.

The ability to find the surface energy of a sample from a wetting experiment is a great advantage over having to conduct melt state studies and then extrapolating to lower temperatures. It is far easier to produce a sample for contact angle wetting experiments than it is to produce sufficient polymer to enable a melt study to be undertaken and this might be an important criterion with expensive monomers. In addition the method employed in this project does not need the range of wetting liquids which Zisman's method needs and also gives both the polar and dispersive components in a single experiment of two contact angle measurements.

Provided that a predictive method is available which gives values for the surface energy that are comparable with the results obtained by wetting experiments then a predictive method has a great advantage over a wetting experiment method. This is that the physical surface need not be produced before a value of the surface energy can be obtained. However, there is the difficulty of predicting the amount and effect of any complexing which might occur. The only way to find the effect of any complexing is to produce the surface and measure the energy which precludes the predictive method.

In extending the work to cover hydrated hydrophilic polymers (hydrogels), there are several problems. It is difficult to use the conventional sessile drop methods on hydrated surfaces because of the difficulty of preventing spontaneous spreading of the sessile drops over the surface layer of water. Careful removal of the surface film of water can be attempted and does enable sessile drops to be placed on the surface and contact angles to be obtained. However there is difficulty in ensuring that the drops are in contact with a representative area of the hydrogel and are not in contact with the polymer alone which would be equivalent to a sessile drop experiment carried out on a partially dehydrated sample. It was hoped that this particular disadvantage would be overcome by the use of Hamilton's method. This technique uses a sessile drop of n-octane placed on the hydrated surface which is held under water. The use of n-octane and water serves to remove the difficulty previously encountered in that the water forms a continuous phase and the n-octane drop impinges onto a surface which is composed of both water and polymer. Additionally the use of n-octane with water means that it is possible to find the polar component alone without finding either the dispersive component or the total surface energy. This is because both n-octane and water have the same value for the dispersive component of their respective surface tensions. These then cancel out in the mathematics of the system and leave the polar component as the only unknown in the equation. Although this might appear to be a great advantage it does mean that it is not possible to evaluate the total surface energy of a hydrated sample. The only way to overcome this problem is to change the two wetting liquids but this would mean that the equation now has two unknowns and so two sets of two wetting liquids must be employed to enable the surface energy of a hydrated sample to be found.

In an attempt to overcome this problem (i.e. the inability to find the total surface energy of a hydrated sample) two methods of predicting the value were investigated. The first method is purely predictive and uses the Parachor technique to estimate a value for the surface energy. The technique was modified to take account of the water which occurs and the values were found to be lower than those obtained by the same method on dehydrated samples but were of the same order as the values predicted for hydrogels by other workers.

The second method is not exclusively a predictive method but uses a combination of Hamilton's polar component and a modified value of the dispersive component obtained from the dehydrated studies. The value of the dispersive component is modified to accommodate the swell which the water imparts to the sample since the forces at the surface will be reduced by the water which is present. The sum of these two components ought to give some indication of the value of the surface energy of a hydrated hydrophilic polymer. The values obtained were higher than those obtained by the predictive method and were found to be fairly constant across the composition range for the samples investigated.

It seems fairly likely that the values obtained by the predictive method gives a fairly good reflection of the actual surface energy of a hydrogel. The results given by the summation method are apparently unaffected by changes in composition across the range and this seems unlikely. It is probable that the dispersive forces in hydrogels are modified to some extent in comparison with those in the dehydrated polymer by increased hydrophobic bonding consequent upon the greater freedom of chain rotation in the gel. This has not been taken into account by merely modifying the value of the dispersive component to take account of the swell. It would however, be very difficult to predict the level of any hydrophobic bonding which occurs in order that allowances could be made in the method to take this into account. The actual value of the surface energy of a hydrated sample is still unknown and undetermined by experiment and so the question of which value is correct is still open to debate although the predicted values do seem to be the best estimates at present.

Work was also carried out to modify the surface of the sample by incorporation of a monomer with high surface to bulk activity. It was hoped that the incorporation of such a monomer would reduce the surface energy, or more specifically would reduce the polar component of the surface energy without increasing the dispersive component by too large an amount, whilst leaving the overall water content unaffected. It was expected that monomers having highly fluorinated substituent groups would have this effect on the surface energy because these fluorinated groups, being very hydrophobic, would tend to be orientated away from the bulk, where the water occurs, and towards the surface. It was hoped that this would produce a surface which was highly dispersive in character but that the water content would be relatively unaffected and that the reduced surface energy would tend to lower the adhesion of such biological species as blood platelets and mucous to the surface. The difficulty arose, however, that with bioadhesion there was initially insufficient basic knowledge to predict the behaviour of the species which interact with the surface and hence it was difficult to produce a surface which had the required characteristics. As more surfaces were characterised with respect to their surface energies it became clearer the type of surface which was required to give the low bioadhesion. Although the work has progressed in this area much still needs to be done before a full understanding of the complex problems associated, not only with the hydrogel surface but also with the chemistry of the interacting species are fully understood.

It was hoped that the understanding of adhesion phenomena with respect to biological systems might also be of use in the continuing problem of melt processing because the problems involved are of a similar nature viz. the factors affecting bioadhesion will be the same as those affecting the adhesion of polymers to the mould. The work of Wu on non-hydrophilic polymers has shown that because the temperature coefficient was small the melt surface tension could be approximated by the surface energy of the solid. Since there appears to be so much similarity between the surface properties of the hydrophilic and the polar non-hydrophilic polymers, i.e. the surface energies of hydrophilic polymers are of the same order as those of polar non-hydrophilic polymers, it is perhaps reasonable to assume that these similarities extend to both mould adhesion properties and the melt surface tensions. Investigation of the problem of mould adhesion with respect to hydrophilic polymers showed that the problem was not a function of the base polymer but was because of the mould surface. This provided mechanical keys which prevented release and once very smooth moulds were used the problem was largely overcome.

Other problems associated with melt processing were also encountered. It had proved very difficult to fuse particles of hydrophilic polymers to produce homogeneous mouldings under the conditions used commercially and it was thought that this was a function of the value of the surface energy. Investigation, however, showed that in trying to fuse hydrophilic polymer particles other factors were at work. The hydrophilic polymers which were causing the problem tend to be slightly branched and this branching increases the melt viscosity sufficiently to prevent the fusion of the polymer particles under the conditions used commercially. By investigating the pressure-temperature profile the boundary condition for fusion-non-fusion was found for the hydrophilic polymers under investigation. Once this boundary had been found the fusion of particles into a whole could be accomplished.

A further difficulty encountered with moulding hydrophilic polymers was that of void formation within the mouldings. At first it was thought that this voiding was being caused by decomposition of the polymer but it was found that the polymers were stable up to temperatures above that at which moulding took place. It was found that the voids were a function of the moulding cycle and did not depend on the value of the surface energy of the polymer sample. The voids could be reproduced by reducing the pressure on the mould cavity. In practice this pressure reduction is more likely to occur because of leakage from the mould. By making the mould fully positive so that the leakage was reduced to a minimum it was found that void-free mouldings could be produced.

Thus investigation of surface properties has been of fundamental use in connection with moulding and mould release of melt processed hydrophilic polymers. Although it was necessary to consider other parameters, such as the viscosity of the melt, to enable a complete picture to be built-up.

9.2. Suggestions for further work.

There are several general areas of research which need to be explored, in particular with reference to some aspects of biocompatibility, i.e. blood clotting, deposition of mucous from tear fluid. This would involve, for instance, more efficient characterisation of hydrogels, in particular the resolution of the extent to which dispersive forces contribute to the total surface energy of a hydrated hydrophilic polymer, and the extent to which the presence of particular groups at the surface override any other contributions to the surface energy in governing bioadhesion phenomena. The approach described with respect to synthesis and characterisation should be developed along the lines indicated.

In addition specific aspects of the determination techniques need to be improved:-

a) An attempt should be made by means of ATR to determine the type of group which occurs at the surface. The results obtained could then be correlated with the surface energy measurements and conclusions drawn about the effect which different groups have on the surface energy.

b) A range of samples should be polymerised against other substrates of different surface energy, i.e. PTFE. This would help to clarify the position over the effect which the substrate has on the samples surface energy.

c) A set of samples should be moulded against a metal surface which can then be etched away to leave the surface exposed. This would give further information on the energy of the surface which is next to the mould surface. Etching away the metal is necessary as this will leave the surface layer intact which might not be the case if the metal and the sample were sheared apart.

d) The overall composition of the samples should be more thoroughly investigated with respect to the reactivity of each of the monomers involved.

e) An attempt should be made to isolate the dispersive component of the surface energy of a sample by means of a modified Hamilton technique. It would be very useful to be able to determine the dispersive component for both the hydrated and the dehydrated samples by an independent technique. This could then be compared with the results obtained by the method of Owens and Wendt and the polar component found by Hamilton's method. The difficulty is that the method needs two immiscible liquids which have exactly similar polar components and which do not adsorb onto the surface of the sample to any great extent.

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APPENDICES.

APPENDIX 1.

RESULTS

TABLE 1.

CALCULATED SURFACE FREE ENERGY.(dynes cm^{-1})

COMPOSITION.		CED	PARACHOR	
			Eqtn. 23	Eqtn. 24
HEMA	: STYRENE			
100	0	39.1	50.51	50.51
90	10	38.7	49.34	49.18
80	20	38.4	48.37	48.09
70	30	-	-	47.04
60	40	-	-	46.01
50	50	37.54	45.47	45.03
40	60	-	-	44.08
30	70	36.93	43.53	43.16
20	80	-	-	42.28
10	90	36.45	41.60	41.44
0	100	36.12	40.63	40.63
HEA	: STYRENE			
100	0	45.06	57.04	57.04
90	10	44.20	-	55.58
80	20	43.34	-	54.07
70	30	42.46	52.12	52.52
60	40	41.58	50.48	50.93
50	50	40.69	48.84	49.30
40	60	39.79	47.20	47.63
30	70	38.88	45.55	45.93
20	80	37.97	-	44.19
10	90	37.05	42.28	42.42
0	100	36.12	40.63	40.63
HPMA	: STYRENE			
100	0	39.47	43.46	43.46
90	10	39.09	43.18	42.90
80	20	38.72	42.90	42.40
70	30	38.36	42.62	41.95
60	40	38.01	42.34	41.56
50	50	37.67	42.06	41.22

COMPOSITION.		CALCULATED SURFACE FREE ENERGY.(dynes cm^{-1})		
		CED	PARACHOR	
			Eqtn. 23	Eqtn. 24
HPMA :	STYRENE			
40	60	37.34	41.78	40.95
30	70	37.01	41.50	40.75
20	80	36.70	41.22	40.62
10	90	36.40	40.94	40.58
0	100	36.12	40.63	40.63
HPA :	STYRENE			
100	0	34.86	35.9	35.9
90	10	-	36.85	36.65
80	20	34.99	37.26	36.90
70	30	35.07	37.67	37.19
60	40	35.17	38.08	37.53
50	50	35.28	38.49	37.90
40	60	-	38.90	38.33
30	70	35.56	39.31	38.81
20	80	35.72	39.72	39.35
10	90	35.91	40.13	39.96
0	100	36.12	40.64	40.64
HEMA :	Acrylic Acid			
100	0	39.1	50.51	50.51
90	10	39.58	49.62	50.57
80	20	40.10	48.93	50.69
70	30	40.64	48.24	50.66
60	40	41.20	47.55	50.45
50	50	41.78	46.86	50.03
40	60	42.39	46.17	49.37
30	70	43.03	45.48	48.42
20	80	43.70	44.79	47.16
10	90	44.44	44.10	45.51
0	100	45.23	43.51	43.51

CALCULATED SURFACE FREE ENERGY. (dynes cm^{-1})

COMPOSITION.		CED	PARACHOR	
			Eqtn. 23	Eqtn. 24
HEMA : Methacrylic Acid				
100	0	39.10	50.51	50.51
90	10	38.89	49.24	49.41
80	20	38.70	48.16	48.49
70	30	38.51	47.09	47.53
60	40	38.31	46.02	46.53
50	50	38.10	44.95	45.50
40	60	37.89	43.87	44.42
30	70	37.66	42.80	43.30
20	80	37.42	41.73	42.12
10	90	37.17	40.65	40.88
0	100	36.89	39.58	39.58
NVP : Acrylic Acid				
100	0	39.68	39.62	39.62
90	10	40.32	39.73	40.41
80	20	40.95	40.14	41.41
70	30	41.57	40.55	42.31
60	40	42.16	40.96	43.07
50	50	42.74	41.37	43.69
40	60	43.30	41.78	44.12
30	70	43.83	42.19	44.35
20	80	44.33	42.60	44.33
10	90	44.80	43.01	44.03
0	100	45.23	43.51	43.51
NVP : Methacrylic Acid				
100	0	39.68	39.62	39.62
90	10	39.53	39.35	39.50
80	20	39.35	39.37	39.66
70	30	39.15	39.40	39.78
60	40	38.92	39.42	39.87
50	50	38.67	39.45	39.93
40	60	38.38	39.48	39.95
30	70	38.07	39.50	39.92
20	80	37.71	39.53	39.86
10	90	37.33	39.55	39.75
0	100	36.89	39.58	39.58

TABLE 2

COMPOSITION		CONTACT ANGLE		SURFACE FREE ENERGY		
		WATER	DIIODOMETHANE	γ_d	γ_p	γ
HEMA : STYRENE						
100	0	53	41	31.42	20.24	51.66
90	10	55	41	31.71	18.81	50.53
50	50	61	42	32.11	14.91	47.03
30	70	65	42	32.76	12.30	45.07
10	90	73	40	35.25	7.31	42.56
0	100	85	35	40.21	1.94	42.15
HEA : STYRENE						
100	0	50	27	37.43	19.12	56.55
90	10	50	30	36.20	19.70	55.91
80	20	50	32	35.33	20.12	55.46
50	50	52	37	33.29	19.91	53.20
40	60	53	40	31.93	19.97	51.91
30	70	53	42	30.90	20.51	51.41
10	90	55	45	29.58	19.92	49.51
0	100	85	35	40.21	1.94	42.15
HPMA : STYRENE						
100	0	58	39	33.12	16.58	49.70
50	50	61	37	34.70	13.80	48.51
0	100	85	35	40.21	1.94	42.15
HPA : STYRENE						
100	0	54	41	31.80	19.00	50.80
70	30	58	35	35.19	15.35	50.54
50	50	55	42	31.19	19.08	50.27
30	70	61	38	34.20	14.01	48.21
20	80	57	47	28.77	19.05	47.83
10	90	61	45	30.48	15.66	46.14
0	100	85	35	40.21	1.94	42.15

		CONTACT ANGLE		SURFACE FREE ENERGY		
COMPOSITION		WATER	DIIODOMETHANE	γ_d	γ_p	γ
HEMA : Methacrylic Acid						
100	0	53	41	31.42	20.24	51.66
75	25	56	31	36.70	15.88	52.59
50	50	50	32	35.33	20.12	55.46
25	75	48	32	35.04	21.49	56.54
0	100	46	35	33.40	23.60	57.01
HEMA : Acrylic Acid						
100	0	53	41	31.42	20.24	51.66
75	25	58	30	37.47	14.40	51.87
50	50	57	32	36.42	15.41	51.84
25	75	56	33	35.80	16.27	52.08
0	100	60	30	37.81	13.13	50.95
NVP : Methacrylic Acid						
100	0	64	32	37.62	11.02	48.64
75	25	65	28	39.55	9.85	49.40
50	50	47	28	36.59	21.32	57.91
25	75	57	27	38.54	14.54	53.09
0	100	46	35	33.40	23.60	57.01
NVP : Acrylic Acid						
100	0	64	32	37.62	11.02	48.64
75	25	82	20	45.97	1.88	47.85
50	50	78	30	41.20	3.83	45.04
25	75	97	23	48.21	0.00	48.21
0	100	60	30	37.81	13.13	50.95
HEMA : NVP						
100	0	53	41	31.42	20.24	51.66
90	10	73	32	39.29	6.19	45.48
80	20	73	36	37.34	6.71	44.05
70	30	80	34	39.95	3.41	43.37
50	50	78	33	39.79	4.12	43.92
40	60	80	30	41.61	3.11	44.72
0	100	64	32	37.62	11.02	48.64

		CONTACT ANGLE		SURFACE FREE ENERGY		
COMPOSITION		WATER	DIIODOMETHANE	γ_d	γ_p	γ
HEMA : PMMA						
100	0	53	41	31.71	20.24	51.66
50	50	68	25	41.31	7.85	49.17
0	100	73	40	35.25	7.31	42.56
HEMA : p-Me STYRENE						
100	0	53	41	31.71	20.24	51.66
90	10	66	32	37.97	9.86	47.84
80	20	70	34	37.77	7.96	45.73
50	50	70	30	39.62	7.41	47.04
0	100	80	34	39.95	3.41	43.37

APPENDIX 2

COMPUTER PROGRAMS

<u>TABLE 1</u>

Equation 23.

```
10ASK(O) N
15FOR I=1,N;DO 20/50
16QUIT
20ASK(O) M
23SET T=0
25FOR J=1,M;DO 30/46
26GO 46
30ASK(O) A,B,P,E
35SET G=P*B/A
40SET H=G↑4
45SET T=T+H*E
46C CONT
50T !!!,%9.05,T
```

Equation 24.

```
 10ASK P,Q,R,S,T,U
 20SET X=100;S Y=0
 30SET A=((X*P)+(Y*Q))↑4
 40SET B=((X*R)+(Y*S))↑4
 50SET C=((X*T)+(Y*U))↑4
 60SET G=A*B/C
 65SET G=G/100000000
 70T !,                %6.04,G
 80SET X=X-10;S Y=Y+10
 90IF(X),100,30,30
100QUIT
```

TABLE 2

```
 4SET P=100;S N=0
 10ASK(O) M
 11IF(M),12,120,12
 12ASK(O) L,S,T,Y,X,Q,W
 20S Z=(P*M)+(N*L)
 25S NO=(P*S)+(N*T)
 26S D=((P*Q)+(N*W))/100
 30S V=((P*Y)+(N*X))/D
 40S C=FEXP(FLOG(.327)+1.85*(FLOG(Z)-FLOG(NO))+1.52*(FLOG(NO)-FLOG(V))
105T !,%8.05,C
106SET P=P-10;S N=N+10
107IF(P),4,20,20
120QUIT
```

TABLE 3

```
  3S N=2
  5S B(1,1)=21.8;S C(1,1)=72.8;S D(1,1)=51.0
  7S B(2,1)=49.5;S C(2,1)=50.8;S D(2,1)=1.3
  8T !," SAMPLE       CONTACT ANGLE             SURFACE FREE ENERGY",
  9T !,"              H2O       CH2I2          G D     G H    G TOTAL",
 10ASK(0) M
 11FOR J=1,M;DO 13/101
 12QUIT
 13FOR I=1,N;DO 19/35
 15GO 40
 19ASK(0) E(I)
 20ASK(0) Z(I)
 25S A(I,1)=1+FCOS(Z(I)*3.142/180)
 30S A(I,2)=(2/C(I,1))*FSQT(B(I,1))
 35S A(I,3)=(2/C(I,1))*FSQT(D(I,1))
 40S U=A(1,1)-(A(1,3)*A(2,1)/A(2,3))
 50S V=A(1,2)-(A(1,3)*A(2,2)/A(2,3))
 60S W=U/V
 70S H=W↑2
 80S X=(A(1,1)-A(1,2)*W)/A(1,3)
 85S G=X↑2
 90S Q=G+H
100T !,%4.00,E(1),":",%3.00,E(2)," ",%4.01,Z(1),"    ",%4.01,Z(2)
101T "        ",%4.02,H,"    ",%4.02,G,"      ",%4.02,Q
```

TABLE 4

```
  5SET X=72.8
  6SET W=50.8
  7SET U=22.1
  8SET V=50.8
  9SET T=44.1
 10SET S=6.7
 11ASK Z,Y
 15S A(1)=.25*X*(1+FCOS(Z*3.142/180))
 20S A(2)=.25*W*(1+FCOS(Y*3.142/180))
 30S B(1)=U;S B(2)=V;S C(1)=T;S C(2)=S
 40S A=B(2)+C(2)-A(2);S B=A(1)*B(1)*C(1)
 50S C=C(1)*(B(1)-A(1));S D=B(2)*(C(2)-A(2))
 60S E=A(2)*B(2)*C(2);S K=B(1)*(C(1)-A(1));S G=B(1)+C(1)-A(1)
 70S H=C(2)*(B(2)-A(2));S M=(H*G)-(A*C)
 80S N=(A*B)-(D*C)-(E*G)+(H*K);S O=(D*B)-(K*E)
 90IF(N↑2-(4*M*O)),160,110,110
110S L(1)=(FSQT((N↑2)-(4*M*O))-N)/2*M
130S P=(B-(C*L(1)))/(G*L(1)+K)
140S I=P+L(1)
150T !!!,"                SOUHENG WU METHOD                  "
155T !,"GAMMA TOTAL =",%4.02,I
160T !,"GAMMA D =",%4.02,L(1),!,"GAMMA P =",%4.02,P
```

<u>TABLE 5</u>

```
 10ASK Q
 15SET W=51.6
 16SET P=FSQT(51)
 20IF(Q),30,100,30
 30SET S=FCOS(Q*3.142/180)
 40SET GAMMA=(((48.3*S)-W+21.8)/(2*P))↑2
 50T !," POLAR COMPONENT = ",%6.04,GAMMA
 55T !
 60GO 10
100QUIT
```

<u>TABLE 6</u>

```
 10ASK Q
 20IF(Q),30,100,30
 30SET S=FCOS(Q*3.142/180)
 40SET T=((48.3*S)+51)/14.282
 45SET T=T↑2
 50T !!,"   POLAR COMPONENT =",%6.04,T
 55T !!
 60GO 10
100QUIT
```

APPENDIX 3

COMPUTER PROGRAM FOR
CALCULATING
THE
SURFACE ENERGY
OF A
HYDRATED HYDROPHILIC POLYMER.

The listing for the program to calculate the surface energy of a hydrated hydrogel is given below:-

```
  1ASK X,Y
  3ASK POL,B,V
  5SET MN=130;S MW=104;S MU=18
 10SET Q=0
 13IF(X),20,15,20
 15SET A(1)=0
 18GO 25
 20SET A(1)=(((X*MN)/(X*MN + Y*MW))*POL)/MN
 25IF (Y),30,32,30
 30SET A(2)=(((Y*MW)/(X*MN + Y*MW))*POL)/MW
 31GO 40
 32SET A(2)=0
 40SET C=(B+V)/MU
 42IF (A(1)),50,44,50
 44SET D(1)=0;S E(1)=0
 46GO 70
 50S D(1)=C/A(1)
 60SET E(1)=FITR((B/(B+V))*D(1))
 70SET G(1)=A(1)/(A(1)+A(2)+C)
 80SET G(2)=A(2)/(A(1)+A(2)+C)
 90SET H=(B/18)/(A(1)+A(2)+C)
100SET K=(V/18)/(A(1)+A(2)+C)
105IF(E(1)),110,106,110
106SET M=0
107GO120
110SET M=H/E(1)
120SET L=G(1)-M
130SET N=4
131SET M(4)=L
141SET M(1)=M;S M(2)=K
160SET M(3)=G(2)
161S MW(1)=(E(1)*18)+130
162S MW(2)=18;S MW(3)=104;S MW(4)=130
170FOR I=1,N;DO 177/200
175GO 220
177ASK H(I),D(I)
178COMMENT H=PARACHOR AND D=DENSITY.
179SET P=39.8
180SET H(1)=H(1)+P*E(1)
185SET G=H(I)*D(I)/MW(I)
190SET C(I)=G↑4
200SET Q=Q+C(I)*M(I)
220T !!!,%9.05,Q
*
```

Lines 1 and 3 ask for the basic data:-

X = Fraction of monomer X in copolymer.
Y = Fraction of monomer Y in copolymer.
POL = Percentage weight of polymer.
B = Percentage weight of bound water.
V = Percentage weight of free water.

Lines 5 and 10 input data required later in the execution of the program.

Lines 13 to 32 calculate the number of moles of monomers X and Y in the copolymer.

Line 40 finds the number of moles of water, C, which is then used in line 50 to find the number of moles of water per mole of comonomer X, D(1). From this information line 60 calculates the number of moles of water bound to each mole of monomer X.

Lines 70 to 100 calculate respectively:-

The mole fraction of comonomer X in the copolymer, G(1).
The mole fraction of comonomer Y in the copolymer, G(2).
The mole fraction of water bound to the polymer, H.
The mole fraction of free water, K.

Line 105 is to test whether E(1) = 0. If it does then line 110 is short cut and the value of 0 is given to M by line 106. If E(1) is positive then line 110 calculates the number of moles of water-bound comonomer X. Whatever the value of E(1) and hence M (the number of moles of water-bound comonomer Y) line 120 calculates the number of moles of water-free comonomer X. There is now sufficient data for the program to assign values to the parameters in a conventional parachor calculation. Lines 130 to 162 are sorting the data into order prior to inserting the values into lines 170 to 220 which are the normal parachor calculation steps.

The program as given in the listing is set-up to calculate values for copolymers of HEMA, X, and styrene, Y, using values for bound and free water found experimentally. Any deviation to a different copolymer system would require that lines 5,161 and 162 be altered. Additionally the program is set-up for using the value of 39.8 as the parachor for water (line 179) and this would have to be altered before different values were inputted to the program in the ASK line, line 177.

An example of data input and of the values obtained at each line.

Copolymer composition:- HEMA — 100 = X
Styrene — 0 = Y
Percentage weight of polymer — 61 = POL
Percentage weight of bound water — 16 = B
Percentage weight of free water — 23 = V

The above data is imput to the program and the values from each line are given:-

Line No.	Symbol	Value
20	A(1)	0.469
30	A(2)	0.0
40	C	2.167
50	D(1)	4.62
60	E(1)	2
70	G(1)	0.178
80	G(2)	0
90	H	0.377
100	K	0.485
110	M	0.168
120	L	0.01
130	N	4
140	M(1)	0.168
140	M(2)	0.485
160	M(3)	0
131	M(4)	0.01
161	MW(1)	166
162	MW(2)	18
"	MW(3)	104
"	MW(4)	130
179	P	39.8
190	C(1)	52.06
190	C(2)	23.9
190	C(3)	40.63
190	C(4)	50.31
220	Q	21.00

The output instruction of line 220 is such that the value for the hydrated surface energy, Q is given in the form:-

21.00749

Lines 1 and 3 ask for the basic data:-

X = Fraction of monomer X in copolymer.
Y = Fraction of monomer Y in copolymer.
POL = Percentage weight of polymer.
B = Percentage weight of bound water.
V = Percentage weight of free water.

Lines 5 and 10 input data required later in the execution of the program.

Lines 13 to 32 calculate the number of moles of monomers X and Y in the copolymer.

Line 40 finds the number of moles of water, C, which is then used in line 50 to find the number of moles of water per mole of comonomer X, D(1). From this information line 60 calculates the number of moles of water bound to each mole of monomer X.

Lines 70 to 100 calculate respectively:-

The mole fraction of comonomer X in the copolymer, G(1).
The mole fraction of comonomer Y in the copolymer, G(2).
The mole fraction of water bound to the polymer, H.
The mole fraction of free water, K.

Line 105 is to test whether E(1) = 0. If it does then line 110 is short cut and the value of 0 is given to M by line 106. If E(1) is positive then line 110 calculates the number of moles of water-bound comonomer X. Whatever the value of E(1) and hence M (the number of moles of water-bound comonomer Y) line 120 calculates the number of moles of water-free comonomer X. There is now sufficient data for the program to assign values to the parameters in a conventional parachor calculation. Lines 130 to 162 are sorting the data into order prior to inserting the values into lines 170 to 220 which are the normal parachor calculation steps.

The program as given in the listing is set-up to calculate values for copolymers of HEMA, X, and styrene, Y, using values for bound and free water found experimentally. Any deviation to a different copolymer system would require that lines 5,161 and 162 be altered. Additionally the program is set-up for using the value of 39.8 as the parachor for water (line 179) and this would have to be altered before different values were inputted to the program in the ASK line, line 177.

An example of data input and of the values obtained at each line.

Copolymer composition:- HEMA — 100 = X

Styrene — 0 = Y

Percentage weight of polymer — 61 = POL

Percentage weight of bound water —16 = B

Percentage weight of free water — 23 = V

The above data is imput to the program and the values from each line are given:-

Line No.	Symbol	Value
20	A(1)	0.469
30	A(2)	0.0
40	C	2.167
50	D(1)	4.62
60	E(1)	2
70	G(1)	0.178
80	G(2)	0
90	H	0.377
100	K	0.485
110	M	0.168
120	L	0.01
130	N	4
140	M(1)	0.168
140	M(2)	0.485
160	M(3)	0
131	M(4)	0.01
161	MW(1)	166
162	MW(2)	18
"	MW(3)	104
"	MW(4)	130
179	P	39.8
190	C(1)	52.06
190	C(2)	23.9
190	C(3)	40.63
190	C(4)	50.31
220	Q	21.00

The output instruction of line 220 is such that the value for the hydrated surface energy, Q is given in the form:-

```
21.00749
```