THE UNIVERSITY OF ASTON IN BIRMINGHAM

DEPARTMENT OF CHEMISTRY

A STUDY IN RADIOPAQUE POLYMERIC MATERIALS

by

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SUBMITTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

APRIL 1975

SUMMARY

The problems associated with x-ray-transparent denture base are defined and conventional approaches to their solution are assessed.

Consideration of elemental absorption parameters leads to the postulation that atoms such as zinc, and bromine, may be effective radiopacifiers over at least part of the clinical x-ray spectrum. These elements had hitherto been considered too light to be effective.

Investigation of copolymers of methylmethacrylate and p-bromostyrene revealed no deleterious effects arising from the aromatically brominated monomer (aliphatic bromination caused UV destabilisation). For effective x-ray absorption a higher level of bromination would be necessary, but the expense of suitable compounds made further study unjustifiable.

Incorporation of zinc atoms into the polymer was accomplished by copolymerisation of zinc acrylate with methylmethacrylate in solution. At high zinc levels this produced a powder copolymer convenient for addition to dental polymers in the dough moulding process. The resulting mouldings showed increasing brittleness at high loadings of copolymer. Fracture was shown to be through the powder particles rather than around them, indicating the source of weakness to be in the internal structure of the copolymer.

The copolymer was expected to be cross-linked through divalent zinc ions and its insolubility and infusibility supported this. Cleavage of the ionic cross links with formic acid produced a zinc-

free linear copolymer of high molecular weight.

Addition of low concentrations of acrylic acid to the dough moulding monomer appeared to 'labilise' the cross links producing a more homogeneous moulding with adequate wet strength.

Toxicologically the zinc-containing materials are satisfactory and though zinc is extracted at a measurable rate in an aqueous system, this is very small and should be acceptable over the life of a denture.

In other respects the composite is quite satisfactory and though a marketable product is not claimed the system is considered worthy of further study.

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ACKNOWLEDGEMENTS

During the course of this study, expertise and apparatus outside the scope of the Department was needed on several occasions. I would like to take this opportunity to thank the people involved for their assistance:-

Mr Colin Price of Birmingham Dental Hospital -

for his help in radiographic testing and interpretation.

The Technical Staff of the Materials Research Department of Birmingham Dental Hospital -

for their help and the use of dental test equipment.

Dr John Evans, formerly of RAPRA Shawbury -

for his prompt evaluation of molecular weight parameters by gel-permeation chromatography.

The Physical Sciences Department of Wolverhampton Polytechnic -

for the use of their thermogravimetric analyser, on the untimely breakdown of our own instrument.

The Departments of Biology and Metallurgy of the University of Aston in Birmingham -

for providing photomicrography facilities not, at that time available within the Chemistry Department.

Special thanks must go to my sponsors Amalgamated Dental International Co Ltd for financing my study, and to my joint supervisors Dr Harold Wilson of Birmingham Dental Hospital, Dr Brian Tighe of the University of Aston, and Dr Frank Hybart,

formerly of the University of Aston, now of Glamorgan Polytechnic. Despite officially handing me over to Dr Tighe on his return to his homeland Dr Hybart did not lose interest in the project and maintained his level of involvement from afar.

Thanks too to all my friends and colleagues both at Aston and at home - their witticisms on the subject of false teeth proved to be as valuable a source of ideas as many a serious discussion!

Finally, for their understanding in allowing a degree of flexibility in working hours enabling me to arrange the typing and binding of this thesis, I thank my present employers Blundell-Permoglaze Limited.

To those who made it possible

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CHAPTER 1

INTRODUCTION

1.1 GENERAL BACKGROUND

At first sight it appears that a study in radiopaque polymeric materials is a purely academic exercise. This is not so. With the growth of the science of biomedical engineering a wide range of manufactured materials are being used in the human body. Of these a great many are metal and are therefore readily located by radiography, but a great many more are carbon chain polymers which exhibit a similar x-ray absorption to flesh and are therefore undetectable. Not only does this mean that implants such as plastic heart valves and artificial aorta cannot be observed after implantation, but also, any prosthetic device becoming displaced, or even plastic surgical instruments being 'lost', cannot be easily located prior to surgery for removal. Such is the case with the denture made from polymethylmethacrylate.

Though it may seem extremely unlikely for a denture to be found anywhere in the body other than the mouth many cases are reported of aspiration (into the oesophagus or lungs) or ingestion (into the stomach and digestive system) of partial dentures, or broken parts of full dentures (1-10). It would theoretically be possible to eliminate these occurrences by educating the public into the dangers of sleeping in dentures or wearing cracked or otherwise faulty prostheses but this could not provide a complete solution for several reasons:-

1.1.1 It is a feature of our motor-car-oriented age that many

of the casualties admitted to hospitals are injured in road accidents. One of the commonest injuries resulting from such accidents is a fracture of the jaw, or at least severe facial bruising from contact of the head with the car windscreen or interior trim. If the victim were wearing a denture it is probable that it would be shattered under this sort of impact, and the broken particles may become impacted in the soft tissue of the mouth, or may be swallowed or inhaled (2). In such a case, unless the denture can be reconstructed completely from particles recovered at the scene of the crash it is never certain whether or not fragments have found their way into the victim's body.

1.1.2 Though less common, cases are recorded of denture ingestion resulting from circumstances other than the wearing of faulty prostheses, the wearing of a denture during sleep, or violent accident (6,10). Such cases usually involve small partial dentures, though incidents are reported of ingestion of full dentures resulting from unaccountable circumstances such as epileptic convulsions.

1.1.3 Attempts to educate the public to safeguard their own health always seem to be viewed as applying to everyone except oneself. This is shown by the ineffectuality of contemporary campaigns on the dangers of cigarette smoking, and on wearing car seat belts.

Having established that dentures may be swallowed it still remains to be shown that they then pose a threat to the health of the victim. In fact in the majority of cases of ingestion the foreign body passes through the body quite normally and is excreted with no ill effects.

Similarly obstructions in the throat are usually readily removable by bronchoscopy (provided the patient has not asphyxiated prior to examination) (1).

Difficulties arise when the material becomes impacted somewhere in the body:- Impaction in the lung can lead to pneumonia, drowning of the lung, and, if the location is not known for surgery, death may result. Impaction somewhere in the alimentary canal can likewise have fatal results if the correct site for surgery is not located. Some success has been experienced in this area using modified 'barium meal' techniques (6,7) but the polished acrylic surface tends not to restrict the flow of the barium sulphate paste sufficiently for the method to be fully reliable (8,10).

Over a period of thirty years many deaths have been attributed to ingestion of denture base, and in all probability many more have gone undiagnosed because of the normality of any radiographs taken. In almost all of these case studies pleas are made for research into radiopaque denture base materials, even to the point of demanding government legislation.

These factors lead one to question the wisdom of such widespread use of a material so potentially hazardous. In order to appreciate the reasons for the almost universal use of polymethylmethacrylate as a denture base material, it is necessary to consider the relevant properties with respect to potential alternative materials.

1.2 DENTURE BASE MATERIAL - PROPERTIES AND POTENTIAL MATERIALS

The properties required of an ideal denture base material may be considered in two sections:- those relevant to the wear of the denture, and those involved in the material processing. All of these properties are detailed in British (11) and American (12) Standards specifications, the more important being:-

1.2.1 Properties in use - 1) Flexural strength

2) Impact strength

3) U.V. stability

4) Low moisture sensitivity

5) Dimensional stability

6) Non-toxicity

7) Colour stability

8) Satisfactory appearance.

1.2.2 Properties in processing - 1) Good flow properties in moulding

2) Minimal mould shrinkage.

These properties are all achieved to a very high degree by a metallic denture. In fact metallic dentures were first introduced in ancient Assyria when gold was used, and for certain specialised purposes, they are still in use today. It is obvious though, that a metallic denture can never be cosmetically satisfactory, and in addition, the processing of such materials is very difficult.

During the early part of the twentieth century dentures made from vulcanite, a hard rubber came into widespread use, these too, however could not be made aesthetically satisfactory, as a dark red-brown was the nearest attainable match to gum pigmentation.

In 1937, after cellulosic materials had shown little potential as denture base polymer, polymethylmethacrylate was examined, and found to excel in almost every respect (13). A transparent material, it could readily be tinted to match gum colours, and most importantly it was found to be very easily processed. A dough-moulding technique is employed, wherein a monomer : polymer solution of dough-like consistency is cured in a hand compression mould. The mould is tailor made in plaster of Paris from an impression of the patient's mouth.

As the plastics industry grew many new polymers were produced

and each in its turn was screened as a potential denture material (14-27). Though polycarbonate showed superior strength, and polyolefins and polystyrene were seen to be dimensionally more stable in an aqueous environment, these materials do not account for more than a few percent of the dental market. There is nonetheless a growing number of polymeric materials finding uses in dentistry (28-33), though most of the novel polymers are used in restorative applications (fillings) and fissure sealants, leaving polymethylmethacrylate dominant in denture applications. It is possible, by introducing long chain methacrylates as internal plasticisers, and ethyleneglycoldimethacrylate as a cross linking agent, to modify the physical properties of polymethyl methacrylate. This accounts for the differences between commercial denture materials available (34).

The fundamental reason for the choice of acrylics as the standard denture material is the dough moulding process. Most thermoplastics require processing by injection moulding, for which the plaster of Paris dental moulds are not well suited (35). Plaster of Paris has a compressive strength in the region of 26 Nmm^{-2} whereas, to withstand the closing forces involved, a figure of 100 Nmm^{-2} is recommended for injection mould materials. It is obvious that in such a 'one-off' system it would not be practical to fabricate moulds from tool steel. It thus follows that any successful new denture base material will, in the absence of an entirely new moulding system, be processable by the dough-moulding technique.

However, the material used for the base polymer in a denture has little bearing on the problem of radiopacity as all commercial polymers are almost totally transparent to x-rays. This is due to their being composed entirely of carbon, hydrogen and oxygen (and

perhaps nitrogen) atoms which all have atomic numbers less than 10 and thus will absorb x-rays very weakly.

It is necessary then to consider possible additives suitable for incorporation into denture base, which may confer an acceptable degree of radiopacity on the composite.

1.3 SUGGESTED RADIOPAQUE ADDITIVES

In the past most attention has been devoted to the incorporation of heavy-atom-containing fillers into the matrix. These can conveniently be considered under two sub-headings:

1.3.1 Macroscopic Fillers - some dental practitioners have recommended, as an interim measure, that silver wire (9), lead foil (3), or barium loaded yarn (9), be incorporated into a denture. Such a practice would offer protection only when a denture were swallowed intact, as on fragmentation particles containing no additive could break off. In fact the presence of such objects within the polymer matrix could well lead to increased risk of breakage due to stress concentration. In addition, should a crack appear in such a denture, exposure, of lead foil especially, to saliva constitutes a toxicity problem in itself. It is therefore felt that this practice offers little improvement and can introduce new disadvantages.

1.3.2 Homogeneous Fillers - (or more correctly uniformly filled materials, as any filled system consists of two phases, and as such cannot be truly homogeneous). At various times almost everything from gold dust (36) and ground dental amalgam (9) through commercial x-ray contrast media (36,37) to glass fibres containing barium and bismuth salts (38-43), and the powdered salts alone (44-50), have been tried as opacifying agents. None of these has been wholly

successful, though a material containing barium sulphate powder is on the market as 'Radiopaque Stellon' and success has recently been claimed using a barium glass (43,51).

However, all of the materials so far discussed have adverse effects on the physical properties of the polymer. In the commercial material mentioned the degree of radiopacity is not really adequate, as it is appreciated that a higher loading of barium sulphate has disastrous effects on the physical properties of the system.

1.4 REQUIREMENTS FOR ANY ADDITIVE TO DENTURE BASE MATERIAL

The essential requirements for any radiopaque additive may be summarised as follows:

1) Non toxic.
2) Compatible with the polymer at a concentration high enough to give the desired radiopacity.
3) The physical properties of the composite must still comply with the dental standards, with respect to physical strength, UV stability and dimensional stability both in moulding and in use in an aqueous environment.
4) Optical clarity must be maintained - in fact total transparency is not essential but on the other hand total opacity is unacceptable as the gum colour cannot then be matched realistically.
5) The composite must be readily processable by the dough moulding process.

These requirements would appear to be most readily attainable by a liquid additive. In fact work has been done on the incorporation of iodo benzene into polymethylmethacrylate (52) unfortunately

this material is a skin irritant, and, being able to leach out of the solid polymer, is likely to cause a reaction in the oral soft tissue. To prevent this leaching, and to improve still further the compatibility with methylmethacrylate the use of a polymerisable radiopacifier is suggested. Though this is the field which promises the most complete and satisfactory solution in the long term, it has been largely ignored in published work to date. Only barium acrylate and bili-tenebril (53) (a tri-iodo phenyl ethacrylate) have been subjected to any investigation and these not exhaustively.

Before surmising further on the nature of the ideal radiopacifying additive it is necessary to consider the mechanism of x-ray absorption.

1.5 THEORY OF X-RAY ABSORPTION

In previous studies, in the dental field, on radiopaque materials, little or no attention has been devoted to the mechanism of x-ray absorption, its quantitative measurement, or the prediction of the efficiency of a particular compound as an x-ray absorber.

Much of this data is available in various tables of physical constants (54-58) and is summarised below:

X-rays are absorbed by atoms in one of two ways, depending upon the energy of the radiation and the particular atom under consideration.

1.5.1 Interaction with the nucleus - 'Pair Formation'

In pair production the photon completely disappears on encountering the atomic nucleus, it is replaced by an electron and a positron. The mass of the electron/positron pair is created from the x-ray energy and any extra energy is exhibited as kinetic

energy of the particles. As a minimum energy for formation of this finite mass is required, and can be calculated from the Einstein relation $E = mc^2$ as equivalent to a 1.02 MeV photon, it follows that less energetic photons cannot interact in this way.

1.5.2 Interaction with electrons - 'Photoelectric effect'

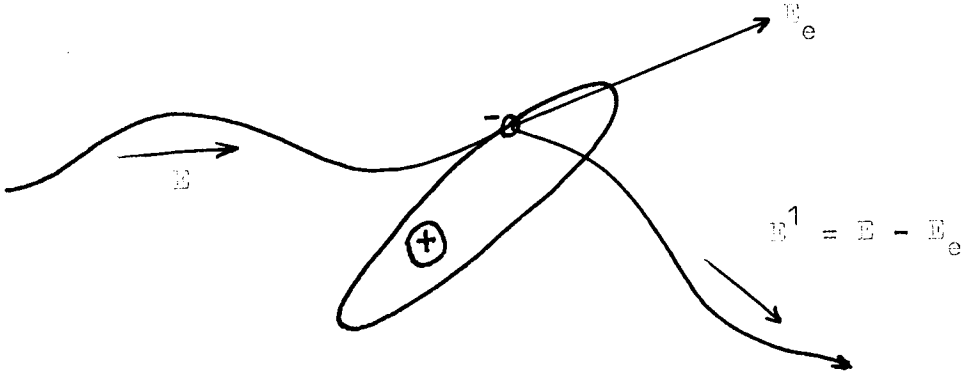
X-rays of fairly long wavelength (> 0.02 Å ; beam energy<1MeV) have photon energies appropriate to the energy level differences between successive electronic orbitals in an atom. Hence, if a particular electronic orbital is occupied, this electron will readily absorb an x-ray photon of the appropriate energy to jump into the next higher orbital.

As the photon energy is increased photons are absorbed by electrons in deeper orbitals of the atom. When an energy level is reached equivalent to the total binding energy of a particular shell of electrons there is an abrupt increase in absorption. This energy is termed the absorption edge for the electron shell and is equivalent to the energy required to eject an electron from that shell producing an ion. As the energy of the x-rays is further increased the absorption by the photoelectric effect decreases approximately inversely with the cube of the energy. This decrease continues until the absorption edge for the next deeper occupied electron shell is reached. Absorption by this mechanism usually predominates for x-ray photon energies <1 MeV and for all but the heaviest atoms is negligible above this value.

In addition to true absorption of x-rays one must also consider scattering effects:

1.5.3 Photons of energies exceeding the requirements of photo-electric absorption may either give a high energy electron on ejection from its orbital, or its excess energy may be reradiated as a

lower energy photon. This production of secondary radiation is known as 'Compton Scattering'.



It may appear that this process effectively reduces the absorption by re-radiating absorbed x-rays. However as lower energy radiation is more readily absorbed this is not the case.

These then are the main absorption processes which an x-ray photon may undergo on interaction with an atom, others do exist but these contribute less to the whole and are less easily explained. The relative importance of these processes is summarised in Graph 1.1.

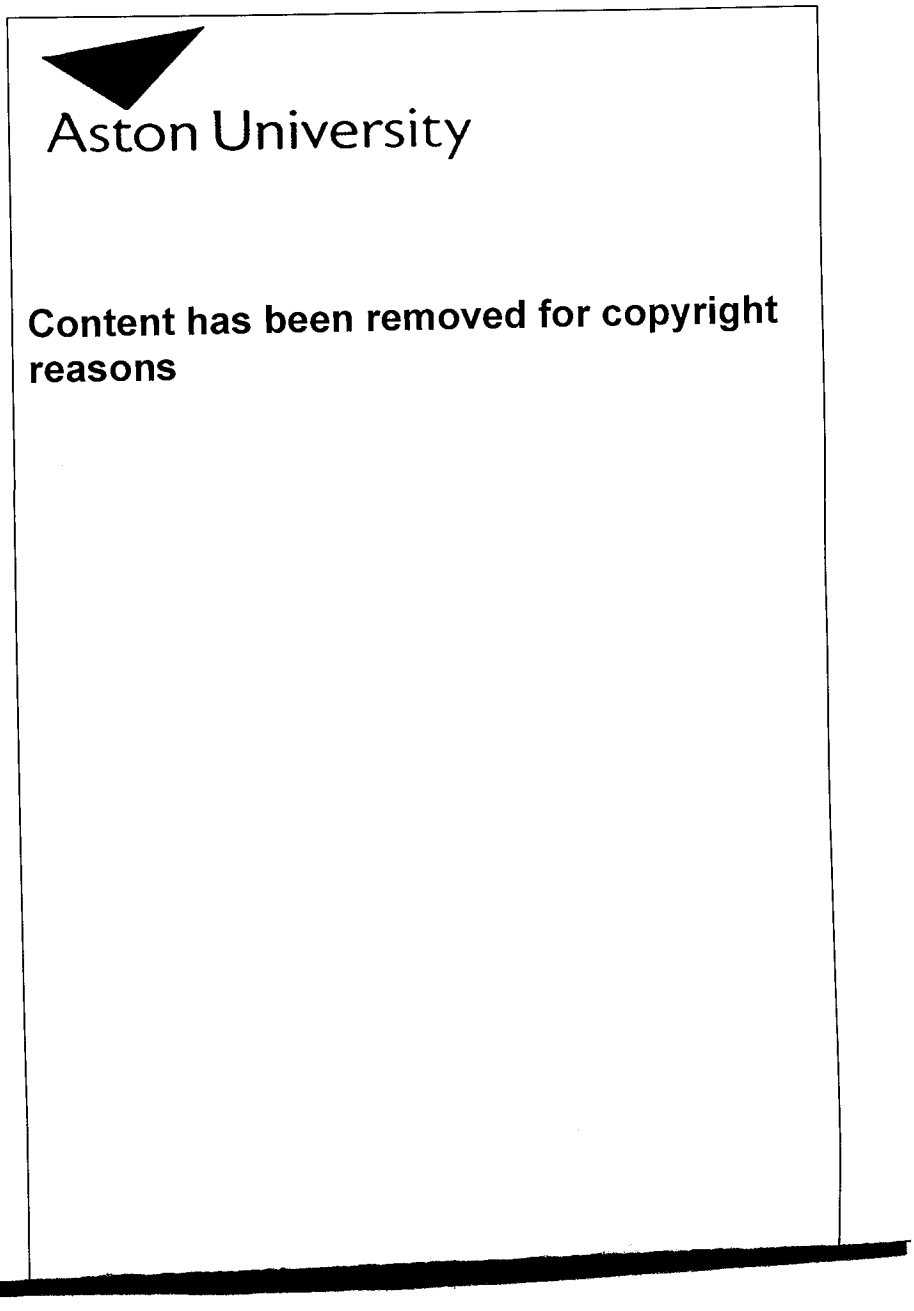
Almost all clinical radiography is performed using beam energies 150 KeV, and at this level it is at once apparent that the predominant absorption effect is photoelectric. A scattering component may account for $\sim$ 10% of the attenuation coefficient, but pair production is totally absent.

Having established the processes involved in x-ray absorption by one atom, one finds that the scattering component is almost impossible to quantify and separate from the total. It is for this reason that in quantifying the x-ray permeability of a material, one includes the scatter with the absorption and defines an attenuation coefficient. In fact three attenuation coefficients are defined:-

1.5.4 Atomic attenuation coefficient (μ_A) - this is simply the sum of the photoelectric and scattering interaction probabilities as mentioned above and is expressed as the effective cross sectional

GRAPH 1.1

The contributions of the various absorption processes to the total attenuation coefficient for a typical heavy atom (Reproduced from 'The Non-Destructive Testing Handbook' by R McMasters)



area of the atom in barns (1 barn = 10^{-24} cm^2). For treatment of absorption in bulk specimens one must refer to the equation derived from observed behaviour:-

$$I = I_o e^{-\mu_L d}$$

I = transmitted intensity I_o = incident intensity

d = thickness of absorber (in cms).

1.5.5 μ_L - Linear attenuation coefficient: this is defined as $\log_e \frac{I_o}{I}$ for 1 cm thickness of absorber. However this parameter depends on the density, and more particularly on the state of the material (μ_L for a gas is ca 10^{-23} whereas for a solid it may reach 10^4). In fact the graph of μ_L vs atomic number is very similar to that of density vs atomic number (see graphs 1.2, 1.3). As a compensation for this behaviour the equation is modified:-

$$I = I_o e^{-(\mu_L/_p)\, dp}$$

where p = density.

1.5.6 μ_L/p - Mass attenuation coefficient - this is defined as the logarithmic attenuation by 1 gm of the absorber, having a cross sectional area of 1 cm^2. Graphs 1.4, 1.5 show the effect of atomic number on the atomic, and mass attenuation coefficients, for an x-ray beam produced in a 15 kV tube.

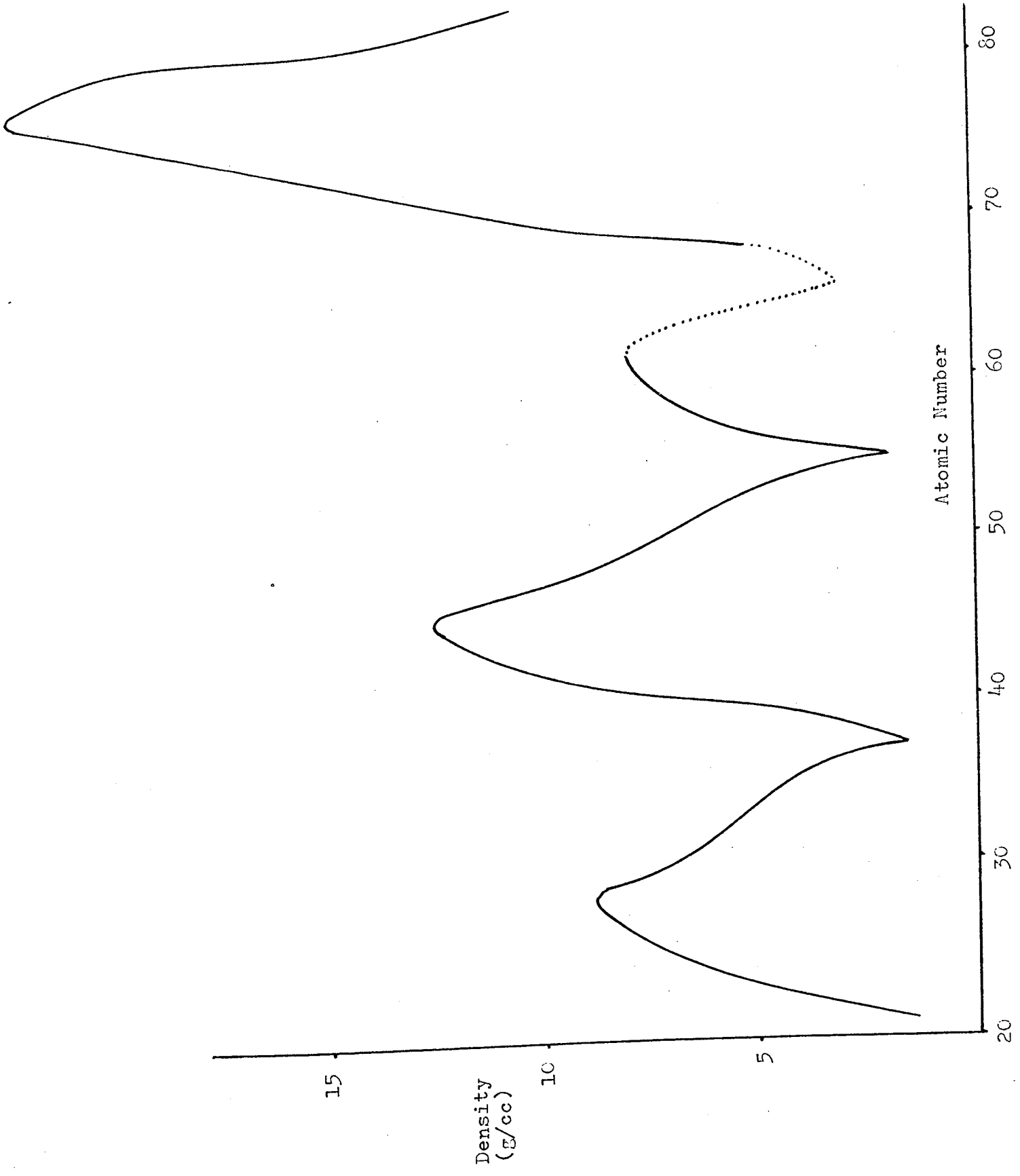
1.5.7 Prediction of Absorbing Behaviour

The mass attenuation coefficient defined above is not solely useful as a quantification of observed experimental data, it can also be used to predict the behaviour of untried materials using the formula

$$\mu_{TOT} = \sum \mu_i x_i$$

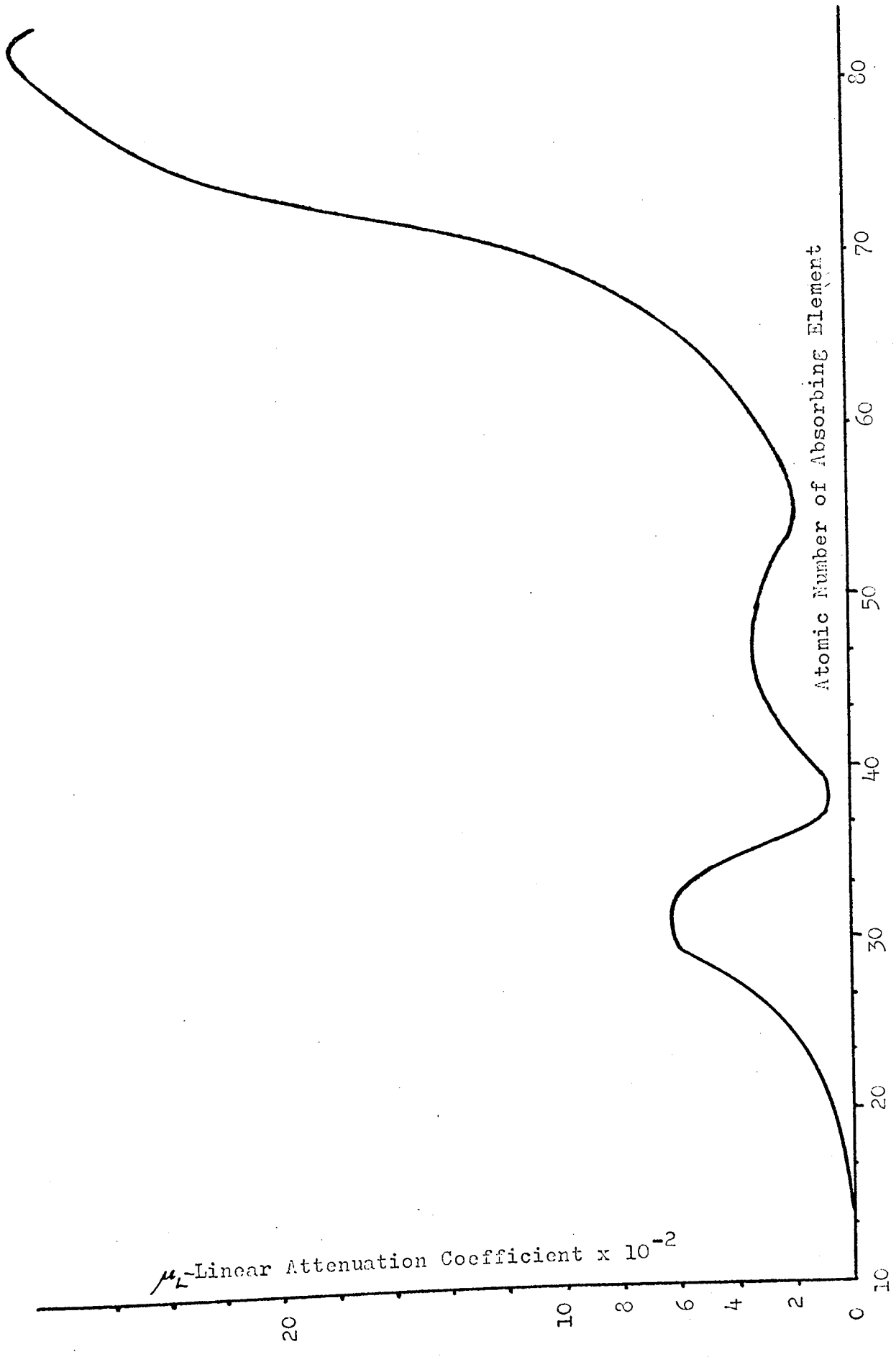
GRAPH 1.2

The density of the elements as a function of atomic number



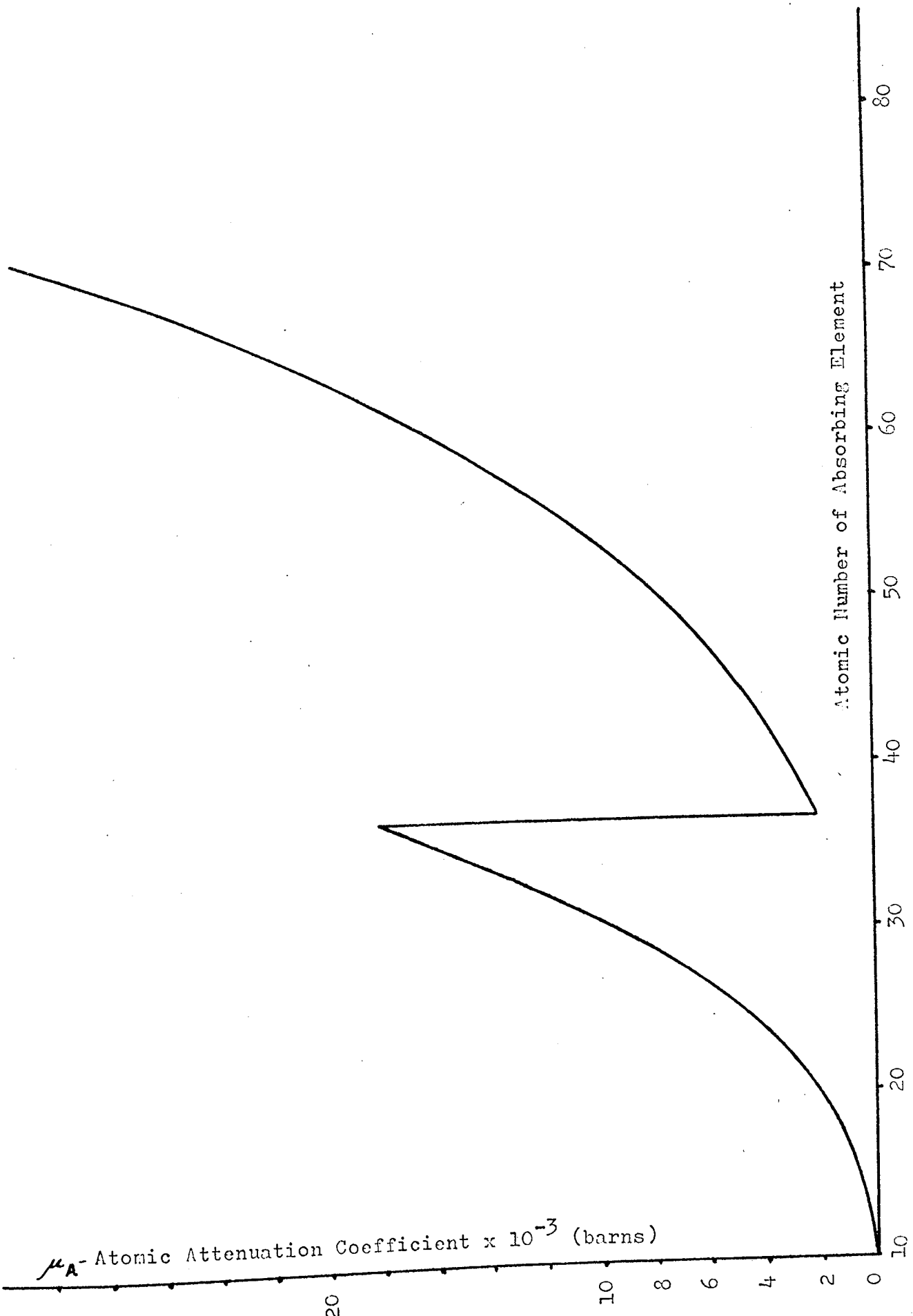
GRAPH 1.3

The linear attenuation coefficient as a function of the atomic number of the absorbing element (15 kV X-ray beam)



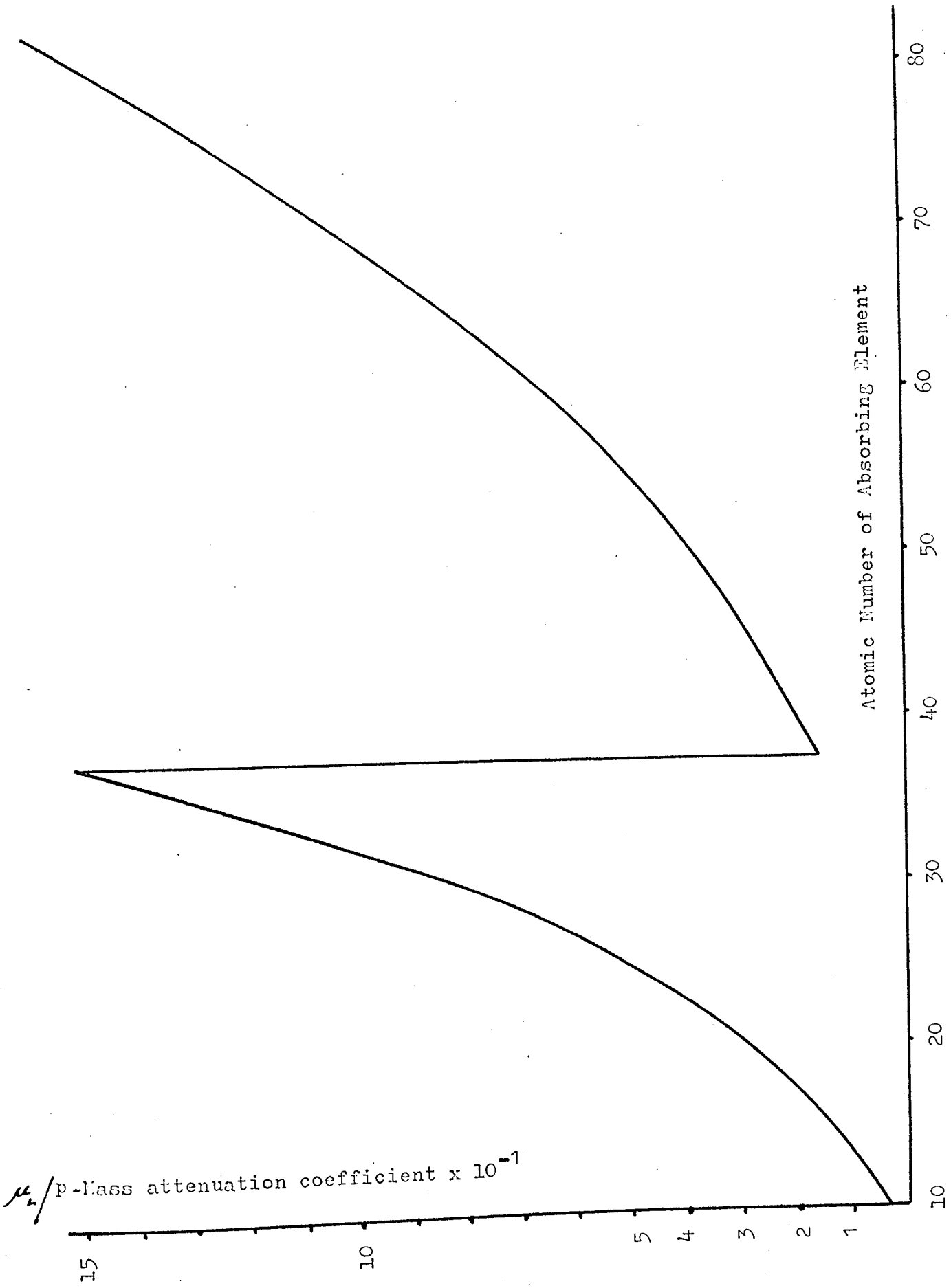
GRAPH 1.4

The atomic attenuation coefficient as a function of the atomic number of the absorbing element (15 kV x-ray beam)



GRAPH 1.5

The mass attenuation coefficient as a function of the atomic number of the absorbing element (15 kV x-ray beam)

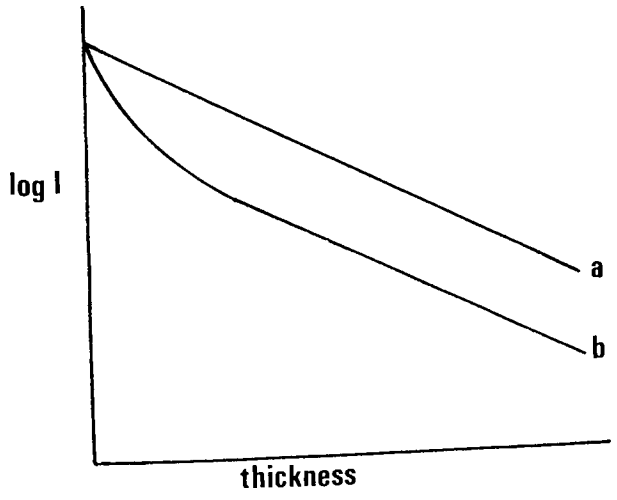


where μ_i = mass attenuation coefficient of atom i,

and x_i = weight fraction of atom i in the material.

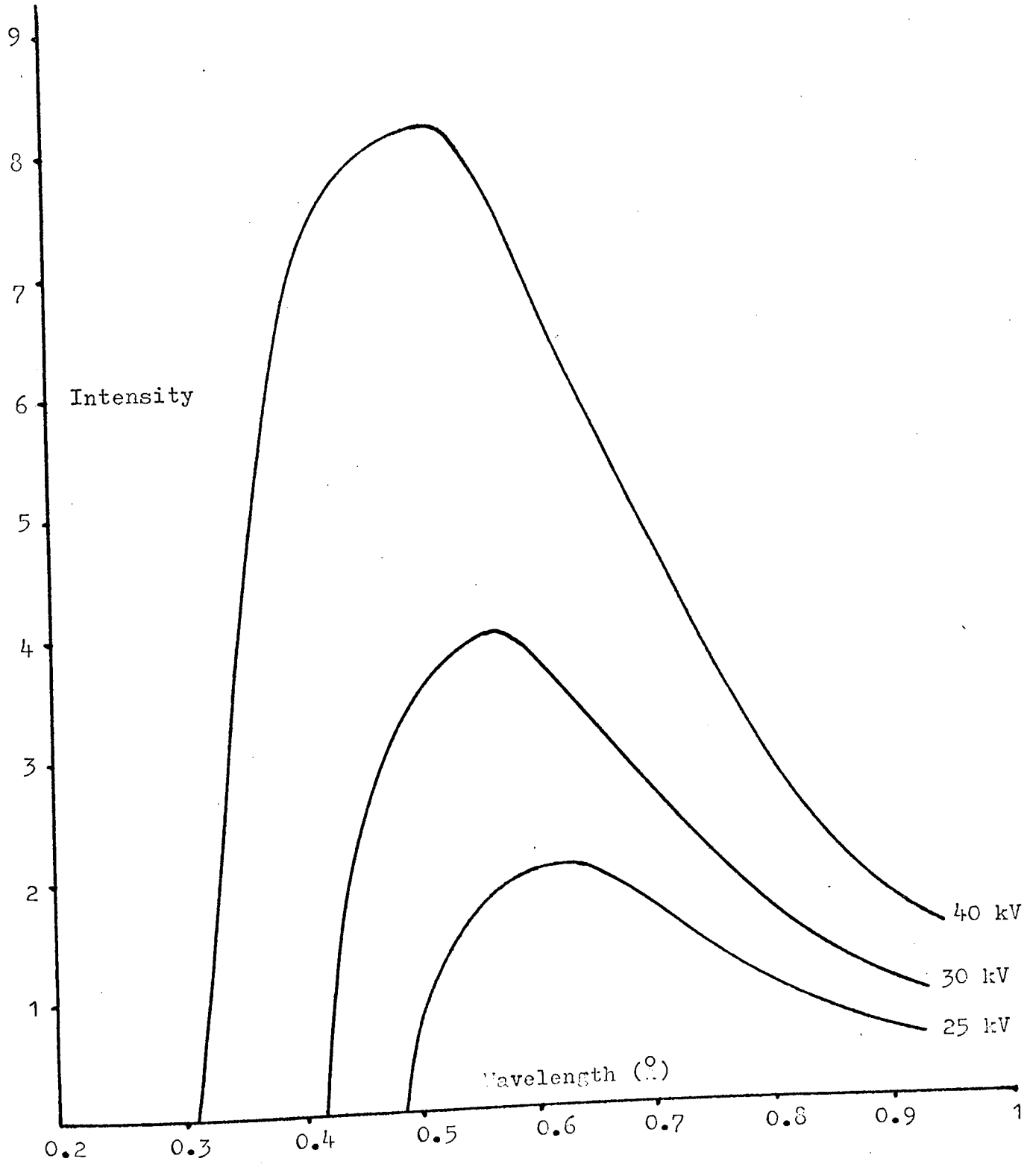
1.5.8 Quality of X-ray Beams

It must be emphasised that all of the above equations are only strictly true for monochromatic x-ray beams. These in practice are only easily obtainable from radio-isotope emissions. X-rays from discharge tubes are invariably composed of a wide spectrum of wavelengths. Typical emission envelopes are shown in Graph 1.6. X-ray beams are described either by wavelength (Å) or beam energy (KeV). In an x-ray tube radiation is produced by electrons striking a target. These electrons, due to collisions, may have any energy up to that corresponding to the applied voltage. The wavelength of the most energetic x-rays produced is easily calculable as $\frac{12.35}{KeV} = \lambda$ min and this corresponds to the sharp cut-offs in Graph1.6. It will be seen that most of the radiation has a wavelength within 0.5 Å of the shortest produced, and a long tail-off is exhibited to long wavelength. We have already seen that long wavelength x-rays are most readily absorbed, and this leads to useful absorption behaviour. If log (transmitted intensity) is plotted vs thickness of absorber for a homogeneous x-ray beam (Graph 1.7), a straight line results (a). If the same is done for a heterogeneous beam (b) absorption is stronger than expected at first but levels out to a straight line parallel to the first. This beam has had its longer wavelengths preferentially absorbed, and behaves



GRAPH 1.6

Typical emission spectra for x-ray tubes operating at 25 - 40 kV potential - minimum wavelength = $\frac{12.35}{kV}$



homogeneously in that absorber - it is not truly homogeneous and will not necessarily behave so in other media. This is the principle employed in filtering x-rays with copper or aluminium filters, giving a beam which for most purposes may be considered to be monochromatic. Thus, for given absorbing species and wavelength one can calculate the mass attenuation coefficient. Likewise if the desired mass attenuation coefficient is specified and the beam wavelength known an element can be selected and its concentration calculated to meet the requirements. Unfortunately such a simple solution is not possible due to the diversity of instruments in use in clinical radiography. Typical instruments give beam energies in the range 45-150 KeV. It is obviously not possible to standardise all equipment for radiography, and excessive filtration may remove too much of the useful part of the beam, but at least it is possible to compare prospective materials using effectively monochromatic beams at the development stage. Too much work on radiopaque denture material has contained no quantitative data whatever on x-ray absorption. Neither beam energy or filtration is stated in most cases, and the degree of absorption judged by eye in comparison with a similar radiograph of bony tissue.

1.6 ESTABLISHMENT OF SUITABLE ATOMS FOR CONFERRING OPACITY TO CLINICAL X-RAYS ON ACRYLIC POLYMERS

Thus far the mechanisms of x-ray attenuation have been expounded, along with characterisation of x-ray beams. The interrelation between atomic number (Z) of the absorbing atom and wavelength of incident radiation has not yet been considered:-

As the major contributor to absorption in the clinical wavelength range is the photoelectric effect it is readily seen that more occupied electronic orbitals will mean more opportunities for

interaction with the radiation. Thus in general terms, the higher the atomic number (and hence number of electrons) the more absorption edges will be found and the wider the energy range over which high attenuation is observed. Hence the preference for lead screening to absorb the maximum radiation possible.

Due to differing nuclear attractive forces, the energies appropriate to expulsion of an electron from an equivalent orbital in different atoms will not be equivalent, this is shown in Graph 1.9. Thus we are now in a position to select atoms which will have an absorption edge within the clinical spectrum, and hence achieve maximum absorption.

Traditionally x-ray contrast media have contained elements of high Z ($\geq$ 56) eg barium, iodine. Graph 1.8, showing the variation in mass attenuation coefficient with radiation wavelength, for a variety of elements, shows that, though having the required absorption edge, these elements are not better than lighter elements such as bromine and zinc over the whole range. Elements of $Z < 30$, eg calcium are inefficient absorbers.

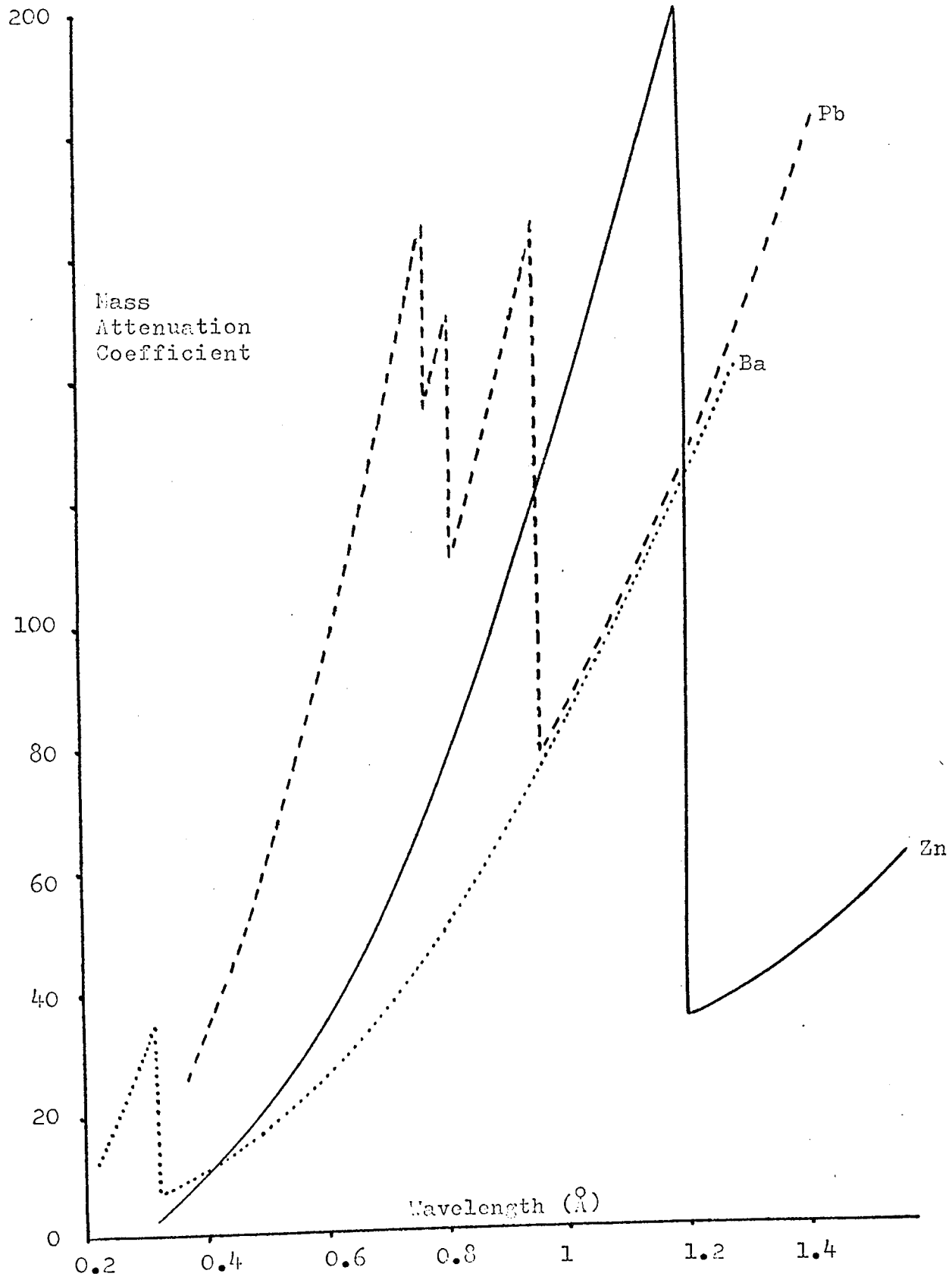
It is thus predicted that previously unstudied elements $30 \leq Z < 56$ will prove to be worthy of consideration as radiopacifying additives. Having established the likely nature of suitable radiopacifying additives, one must consider their potential toxicity and compatibility with the acrylic polymer matrix.

1.7 TOXICITY OF POTENTIAL RADIOPAQUE MATERIALS

Barium sulphate has long been in use clinically in the form of the 'barium swallow' for radiographically locating obstructions in the gastro-intestinal system. This is somewhat surprising as barium is a highly toxic metal (it has been suggested that 1 g of

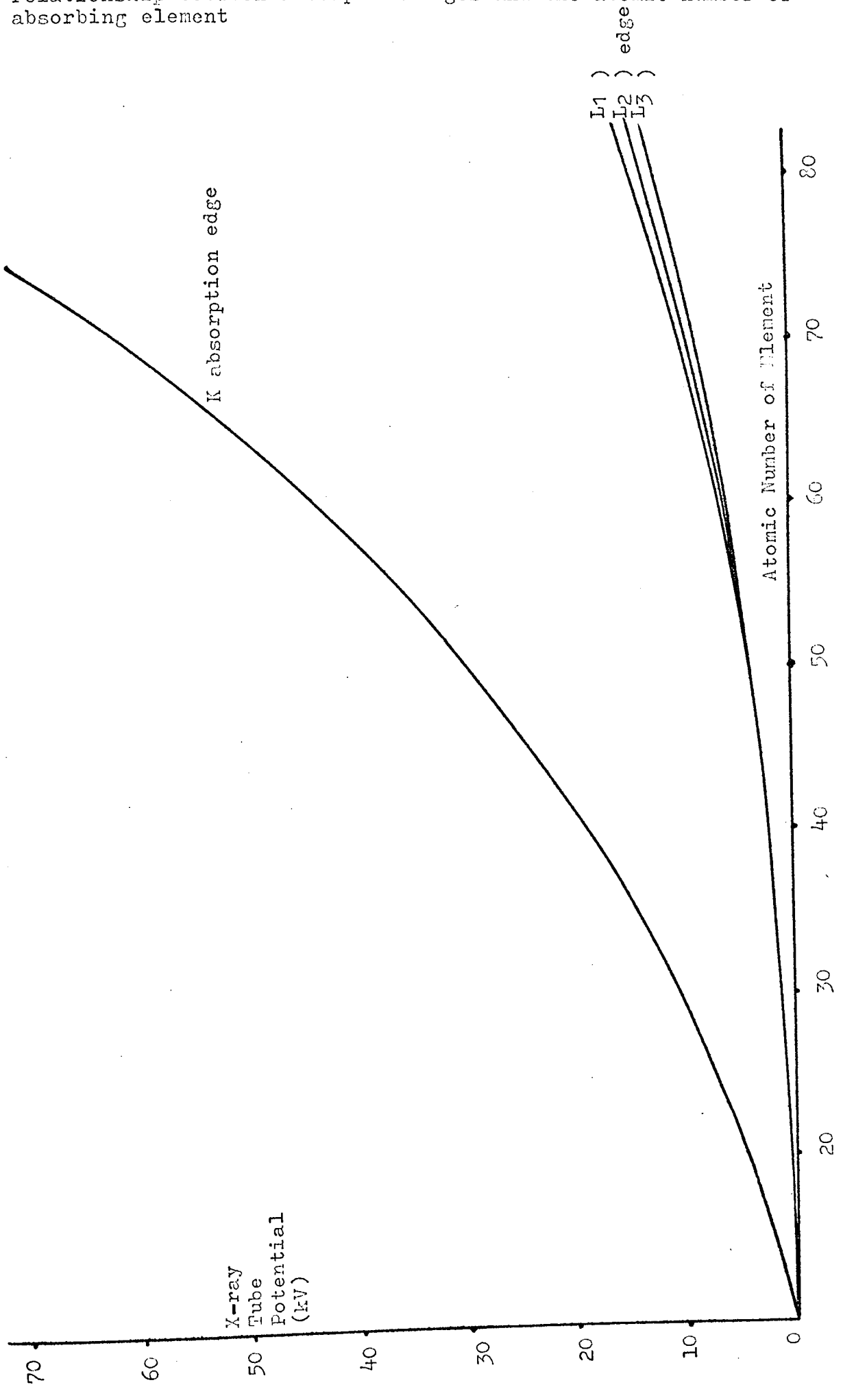
GRAPH 1.8

The absorption behaviour of zinc, barium and lead towards x-rays of wavelength 0.2 - 1.4 Å



GRAPH 1.9

The relationship between absorption edges and the atomic number of the absorbing element



barium chloride would be fatal to man, causing gastro entiritis and heart spasm). However, barium sulphate is virtually insoluble in water (0.00029% at 37°C) and even in the acidic environment of the stomach the solubility is low (0.006% in 3% HCl). More recently, other barium compounds such as the fluoride (solubility 0.12% at 25°C in water, and more in dilute acids) and the acrylate (solubility 14.3%, 25°C) have been suggested as potential additives to dental acrylics. The composite containing the fluoride has been found to give no adverse tissue response in animals, and presumably the acrylate would give a virtually insoluble polymer. However, as a denture is to remain in the mouth for periods of many years, it is felt that complete confidence cannot be put in a material which may constantly be releasing sub-toxic doses of barium into the body (59). It is therefore suggested that a completely satisfactory radiopacifying additive should either be totally insoluble in body fluids (eg contained in a glassy material) or should be inherently non toxic.

Applying these criteria to the range of elements suggested by radiographic considerations, one arrives at the conclusions summarised in Table 1.1.

The generalised conclusion obtained from examination of potential toxicity is that, with the exception of the halogens and the alkali metals, the heavier the atom the more toxic it is likely to be.

It seems logical then to concentrate effort on compounds of elements with the lowest toxicity consistent with adequate x-ray attenuation. Strangely enough these elements are the ones which have been least studied in the past as they have been considered ineffectual as x-ray absorbers.

TABLE 1.1

THE TOXICITY OF POTENTIAL RADIOPACIFYING ELEMENTS

Element	Z	Elemental Toxicity	Suitable Compounds
(Calcium	20	Low	All)
Zinc	30	Low, safe at 2000 ppm in diet	All
Bromine	35	Low in general	Bromides, some organic materials
Strontium	38	Low, similar to calcium	All
Silver	47	Toxic at high concentrations	Insoluble compounds
Cadmium	48	Low toxicity in inorganic compounds	Some inorganic compounds
Tin (60,61)	50	Generally toxic	Some individual compounds cleared toxicologically
Antimony	51	Toxic	Insoluble compounds
Iodine	53	Low in general	Similar to bromine
Caesium	55	Very low, similar to potassium	All
Barium	56	Toxic	Insoluble compounds
Lead	82	Toxic	Insoluble compounds
Bismuth	83	Toxic	Insoluble compounds

Note

a) The toxicity stated is obviously only valid for stable compounds of low reactivity, and assuming the contribution to the toxicity from other chemical groups in the compound to be negligible.

b) Although it is stated in Table 1.1 that soluble compounds of some materials would not be toxic, it is obviously undesirable to use an additive which may be leached out of the composite, as the radiopacity would thereby be reduced.

Before a final decision is made on which compounds are worthy of experimental assessment, it is necessary to consider how compatibility with the acrylic polymer matrix may be optimised.

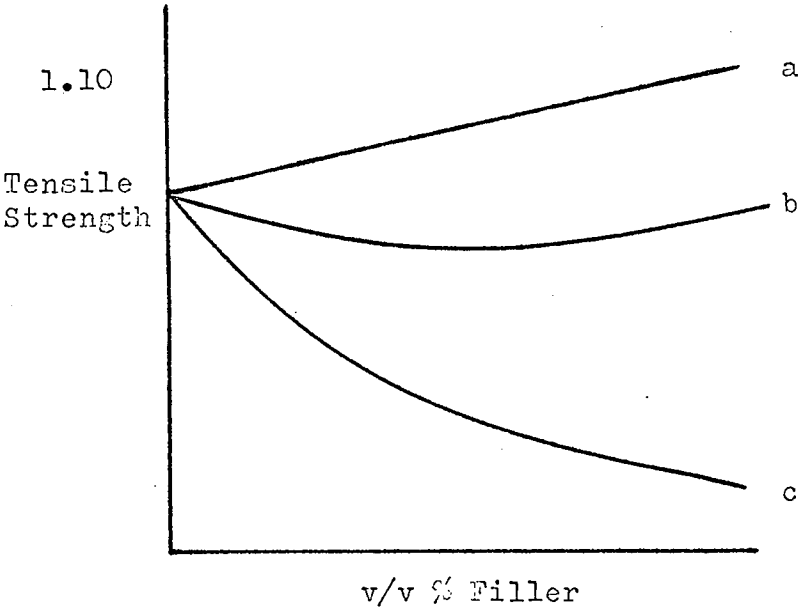
1.8 COMPATIBILITY

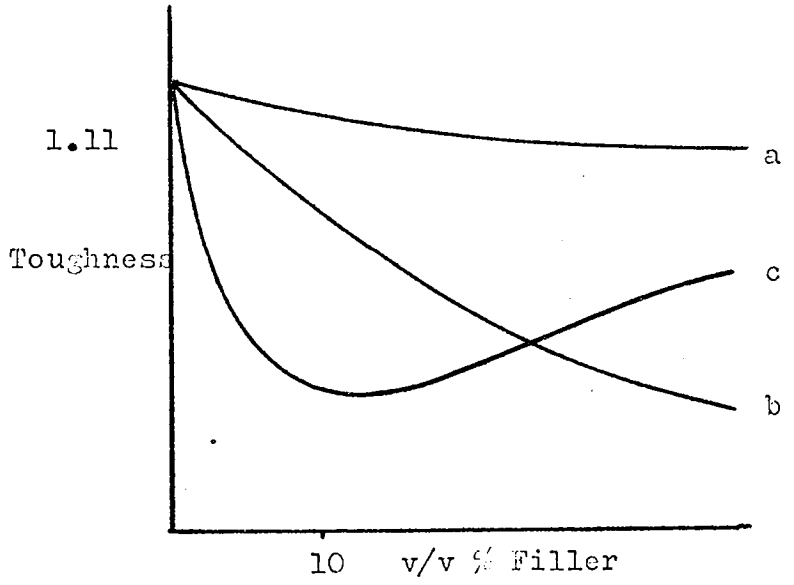
It has already been mentioned that inorganic fillers in realistic concentrations cause excessive deterioration in physical properties. Quantification of the effects on physical properties of fillers of varying compatibility with the polymer matrix has been published by Kenyon and Duffy (62). This work was performed using glass microspherical fillers, with and without a vinyl silane surface treatment. The polymer phase was an epoxy resin, but the two phase system is analogous to any powder filled polymer composite. The various parameters involved in tensile failure are summarised in graphs 1.10, 1.11, 1.12 as functions of the filler loading expressed in terms of volume per cent. It is apparent that for a non interacting filler, the first 10% loading has the greatest effect upon the mechanical properties of the composite. In fact commercial Radiopaque Stellon is loaded to about 8% v/v in the interspherular phase with inert barium sulphate. My own previous studies on this system showed that, viewed in the optical microscope, there was little visible change in structure above 10% v/v loading, but in the range 0-10% v/v a gradual deterioration in homogeneity was apparent (63).

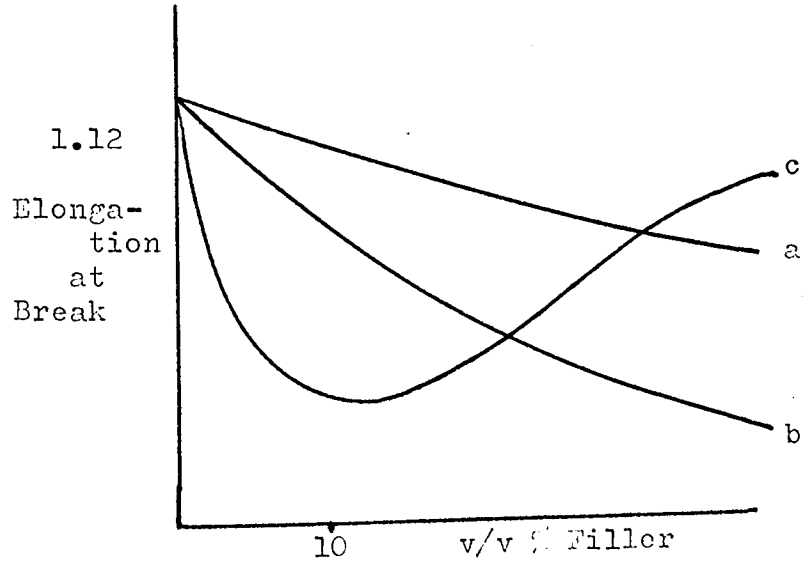
It is seen then, that even relatively low concentrations of inert fillers can have seriously deleterious effects on the composite. What materials then may be considered as compatible, or at least interacting, radiopacifiers?

GRAPHS 1.10 - 1.12

The effect of increasing loadings of filler with a) good adhesion
b) poor adhesion, and
c) no adhesion to the polymer on parameters in tensile failure (62)







1.9 RADIOPACIFYING ADDITIVES SUGGESTED ON COMPATIBILITY CRITERIA

The matrix into which the additive is to be incorporated is organic, and it is polymeric. Therefore the ideal compatible additive should also be organic and polymeric, and should resemble the molecular structure of acrylic polymers as closely as possible. Alternatively it should be a non-leaching plasticiser type compound, though such a material would be expected to be less permanent as an absolutely non-leaching non-bound additive is virtually impossible to achieve. In addition, the ideal material should contain the highest possible percentage of heavy atoms, thereby permitting the smallest possible loading to be employed to achieve adequate radiopacity. It is understood that any suitable material must be stable to the oral environment, as well as conforming to the required standards.

Possible suitable compounds are as follows:-

1.9.1 Heavy Metal Salts of Polymerisable Acids

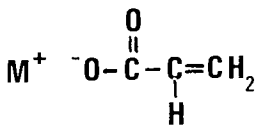
When thinking of linking a heavy metal atom into a methyl methacrylate network, the most obvious compound to try is the metal acrylate (or methacrylate). These salts are readily preparable in the monomeric form (63-67) simply by reacting the acid with the metal oxide, hydroxide or carbonate either in aqueous or methanolic solution or suspension. The solid product is recovered by crystallisation or precipitation in acetone. Polymerisation of the solid materials is reported by γ-ray irradiation, but by no other initiation method (64-71). The properties of the polymers thus formed are not well characterised, with the exception of the alkali metal (72,73) compounds which find commercial use as viscosity modifiers. The metals discussed in the above references are

Acrylates	Ca, Ba, Li, Na, Rb, K
Methacrylates	Ba, Zn, Sn

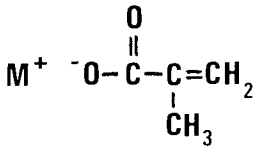
It appears that the multivalent metal atoms are responsible for ionic cross linking in the polymer, with the resultant thermal stability and solvent resistance. Polymerisation parameters are calculated, and the structure of the polymers determined, showing the absence of syndiotacticity normally associated with polyacrylic acid.

If the polyacrylate salt is required, this is most readily obtained by double decomposition with sodium polyacrylate in aqueous solution. The divalent metal polyacrylates are readily precipitated.

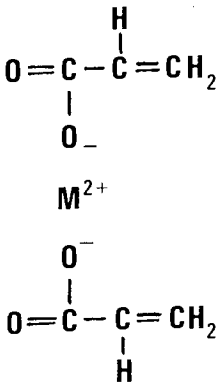
Due to the insolubility of the metal acrylates in other acrylic monomers, one cannot prepare copolymers directly by bulk techniques, however a method has been described (74,75). Moulding at 300°C; 5 tons in^{-2} of a powder blend of zinc oxide and a copolymer of acrylic acid and ethyl hexyl methacrylate yields a very tough, thermally stable (up to 400°C) solvent resistant polymer expected to find constructional use (74).



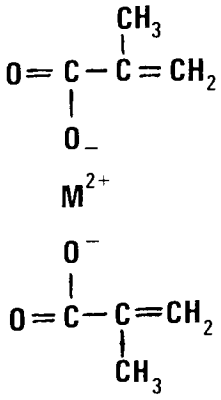
(i) monovalent metal acrylate



(ii) monovalent metal methacrylate



(iii) diacrylate



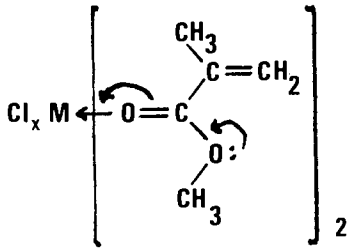
(iv) dimethacrylate

In terms of radiopacifying efficiency it is clear that monovalent metal acrylates (i) are preferable (3 carbon atoms per metal atom) but as will be seen later these compounds are too much affected by an aqueous environment. The best metal atom/carbon atoms ratio attainable with multivalent metal atoms is 1 : 6 with a diacrylate (iii).

Barium acrylate is in fact under consideration as a radiopaque additive for denture base (76).

1.9.2 Metal-Containing Soluble Complexes

It has been noted that polar monomers containing the carbonyl group are capable of dissolving and complexing Lewis acids (77-83). Particular attention has been devoted to the interaction between methyl methacrylate and zinc chloride (80, 81, 83) and tin (iv) chloride (81). The molar ratio in the complex may be 1 : 1 or 2 : 1 as represented simply below:



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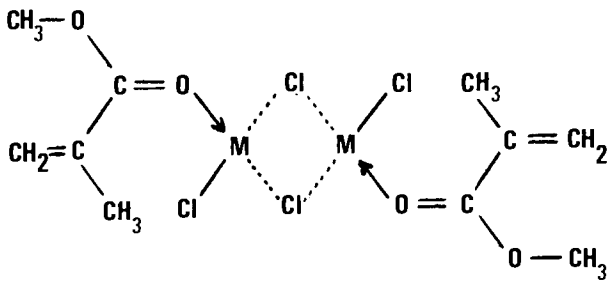
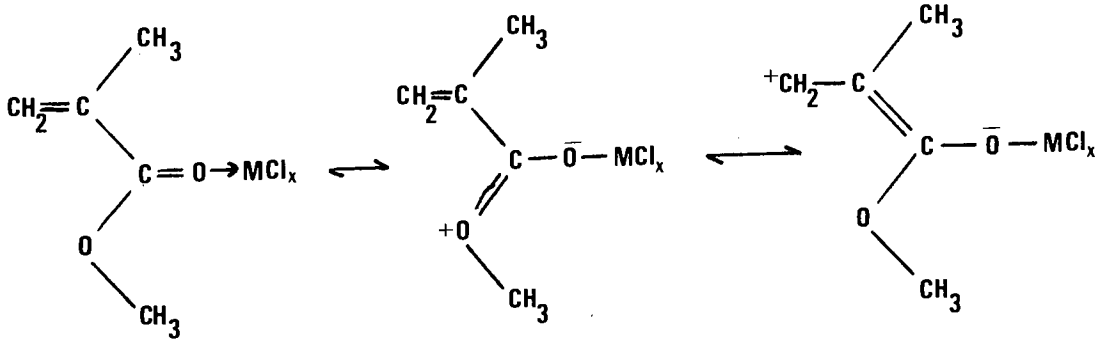


though resonance structures are postulated:



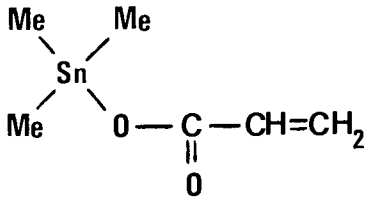
Even this does not fully describe the structure of the complex. The high viscosity and ability to produce a stereodirecting effect led Bamford et al (80) to postulate the formation of loose trimers and tetramers. Molecular weights from vapour pressure depression results supported this. Presumably it is due to this pre-alignment that the rate of polymerisation is so enhanced. It appears that ionic initiation does not account for this as shown by Okuzawa (81) who found that free radical inhibitors still prevent polymerisation. The unstabilised complex is so reactive as to be unstable to light and cannot readily be stored even in a refrigerator. The complex is also very hygroscopic, reminiscent of zinc chloride itself.

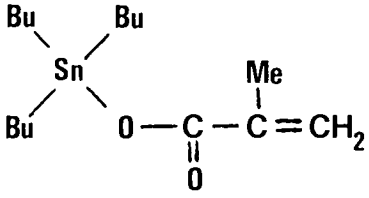
Of the polymer little is reported except that it is broken down by hydrochloric acid, losing the metallic component, and that the resulting polymethyl methacrylate is of very high molecular weight ($M_n = 2 \times 10^6$). Due to the general low toxicity of zinc compounds a slight degree of leaching in water could be tolerated in a denture, but the extent must be established. These complexes do not contain a very high weight percent of metal atoms (best is $Zn\ Cl_2\ C_5\ O_2\ H_8$) but they are worthy of consideration for their total compatibility with methyl methacrylate, and not least for their cheapness to make.

1.9.3 Metal Containing Covalent Compounds

1.9.3.1 As an extension of the work on $SnCl_4$ complexes Yamada (84) and Montermoso (85) produced similar work using covalent alkyl stannyl acrylates as model compounds to investigate the nature of the stereospecificity in the polymerisation. Preparation of the monomers is equally straightforward as that for the simple acrylates, but starting from alkylated tin oxide. Polymerisation

may then be carried out either in bulk at high temperature, in benzene with azo-bis-isobutyronitrile (AZBN) initiator at 30°C or in water emulsion. Substitution of the tin with alkyl groups leads to increased stability of the metal in the polymer (90% HCl 90°C, 3 hrs needed for removal) and precludes the possibility of cross linking. The resulting polymer could well show a toughening effect when incorporated in poly methylmethacrylate. Compounds investigated have been di- and tri-methyl and butyl stannyl acrylate and methacrylate. The disubstituted material can still cross link through the two acrylate groups, but the tri alkyl compounds all give linear elastomeric polymers.



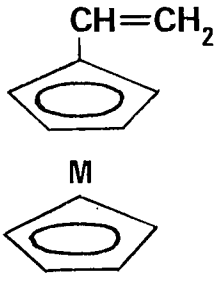


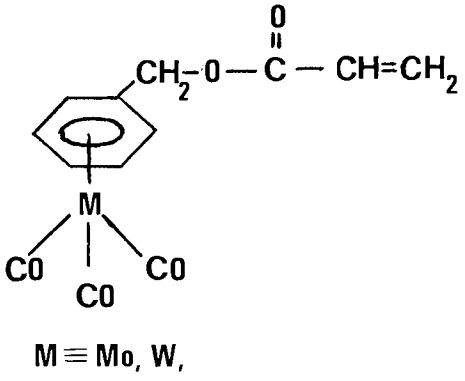
Obviously the methyl substituted acrylate will give the highest concentration of metal atoms.

This route to a radiopaque material seems very promising providing the material is non toxic and does not prove too expensive.

In fact this is the route chosen by Amalgamated Dental International Ltd for investigation in their own laboratories. So as not to duplicate work it was agreed that tin compounds should not be studied further at Aston.

1.9.3.2 In the field of purely covalent metal containing polymers, most attention has been devoted to compounds of the following general formulae:-

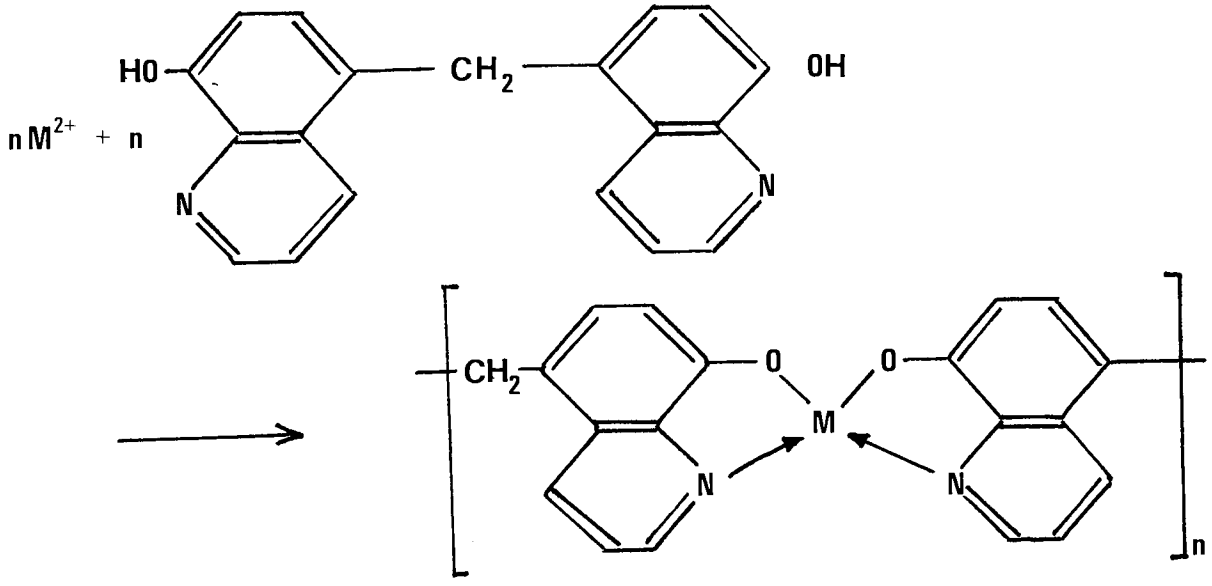




(i) vinyl metallocene (86-89)
M ≡ Fe usually

(ii) π-benzylacrylate metal tricarbonyl (86,90)

(i) and (ii) polymerise in ways analogous to styrene and acrylic esters respectively.



(iii) chelate polymer (91)

Compounds of types (i) and (ii) would apparently be suitable for copolymerisation with methyl methacrylate. However, the bonding required for the formation of such compounds restricts the choice of metal atom to for example iron, chromium molybdenum and tungsten, all of which are either toxic or insufficiently opaque

to x-rays. On the other hand, the chelate type polymer (iii) can be produced from most divalent metals, but due to its insolubility only low molecular weights are achieved. In addition, it is immediately apparent that the concentration of metal atoms is very low (general formula $M\ C_{19}N_2O_2H_{12}$) which would give unacceptably low radiopacity at realistic polymer compositions. This type of polymer is under scrutiny for semiconductor applications, but would appear to be inappropriate for denture materials.

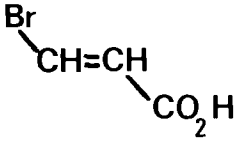
1.9.3.3 The best known class of covalent organo-metallic compounds is of course the simple R-M type or R-M-X, eg the Grignard reagents much used in preparative organic chemistry. Potentially polymerisable compounds of this type have been characterised, but tend to be extremely reactive towards water, air, etc (92,93).

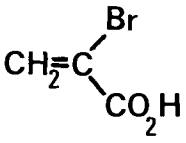
Should the polymer be prepared, there is no reason to suppose that it would be any more stable than this, though the hydrolysis product would presumably be the ideal dispersion of zinc oxide in polyethylene. The fundamental reactivity of compounds of this type is accompanied in most cases by correspondingly high toxicity (eg organomercury, organocadmium and organolead compounds). Thus, despite the relatively high heavy atom content of simple organometallics, they are not, in general considered to be suitable for denture base additives.

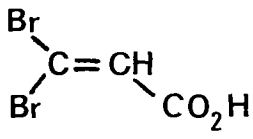
1.9.4 Covalent Non-Metallic Compounds

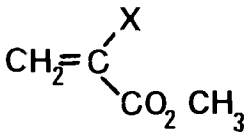
In order to minimise the change in mechanical properties of the denture base, it is logical to seek a heavy-atom-containing

monomer whose structure closely resembles methyl methacrylate. An iodo-acrylate would be just such a compound but no reference can be found to work on this material. However, on examining the properties of analogous chloro and bromo compounds the behaviour can be predicted.

(i) 

(ii) 

(iii) 

(iv) 

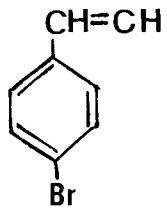
x ≡ Cl or Br (98-100)

Of these compounds, the monomer (i) was used by the US Army as a defoliant in Vietnam, the polymers derived from (ii) and (iii) are unstable with respect to HBr loss, and the monomers (iv) are intensely poisonous causing eye and lung damage. The chloro-compound in (iv) is commercially polymerised to yield a fire resistant, scratch resistant polymer otherwise very similar to polymethylmethacrylate. Lowering the volatility of these compounds by incorporating a long side chain (eg n-hexyl) reduces their toxicity considerably. In general the chloro-compounds are stable, but the bromo compounds quite readily lose HBr, presumably in a manner similar to the HCl loss in PVC degradation. It would therefore appear most unlikely that iodinated acrylic polymers would be sufficiently stable for commercial use. As would possibly be predicted, other types of brominated or iodinated vinyl polymers

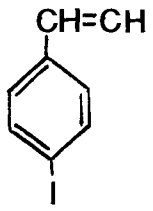
are similarly unstable. Thus vinyl bromide and vinyl iodide are well known compounds (101) but the polymers are unstable with respect to hydrogen halide loss and consequent discolouration (101-103). This degradation is rapid only at temperatures above 130°C but in view of poly vinyl chloride's poor colour stability in normal use (in the absence of stabilisation) it is inconceivable that the bromide and iodide should be stable.

However this does not mean that halogenated comonomers on the whole are unacceptable. Thus far only aliphatically substituted compounds have been considered, but in an aromatic environment the halogen atom is more stable.

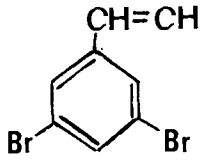
Considering the halo-styrene compounds



(a) (104)

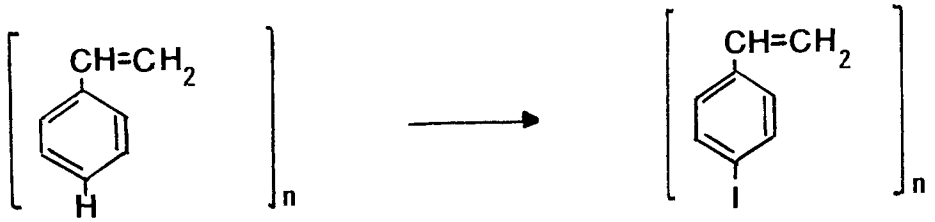


(b) (105)



(c) (106,107)

(a) and (b) the p-halostyrenes are moderately easy to prepare (104) and polymerise (105) and are quite stable, though the stability of the resulting polymer is not described. This same polymer may be obtained directly however, by halogenation of polystyrene, as described by Braun (108).

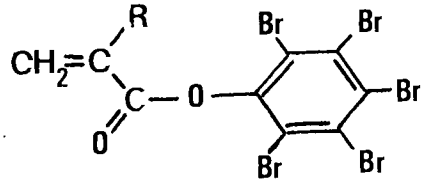


Iodination is effected by an iodine/iodic acid system kept at 90°C in nitrobenzene solution for 25 to 30 hours. The reaction proceeds to over 90% of theoretical, and yields a product described as

"a light yellow glassy solid, soluble in benzene chloroform and tetrahydrofuran and swollen by ether". The stability of the iodine in this environment also is in doubt as it is reported that the polymer solution in benzene "turned red on exposure to strong light". Though whether this was established as due to dehydro-iodination or some other reaction is not known.

In this iodination reaction it should be noted that no main chain substitution occurs, and all the iodine goes into the p-position. The lack of main chain reaction would appear to allow for iodination of styrene : methylmethacrylate copolymers without attack of the aliphatic groups. This would then provide an easy route to an iodinated copolymer suitable for dental use. However materials of this type do not really contain enough of the heavy atom unless employed at very high concentrations. Compound (c) m, m^1, dibromostyrene could prove to be a more satisfactory material. This compound was investigated (106, 107) as a flame retardant for use in polyester resins and was shown to be acceptably stable, and to copolymerise readily with methylmethacrylate to yield a transparent material.

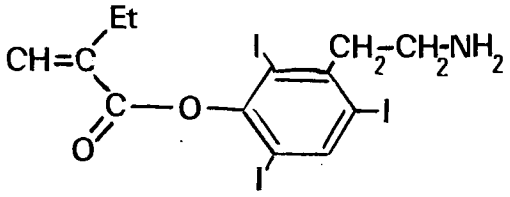
It is logical to extend the range of halo-aromatic monomers from styrene analogues to different acrylic esters.



R ≡ -H or $-CH_3$

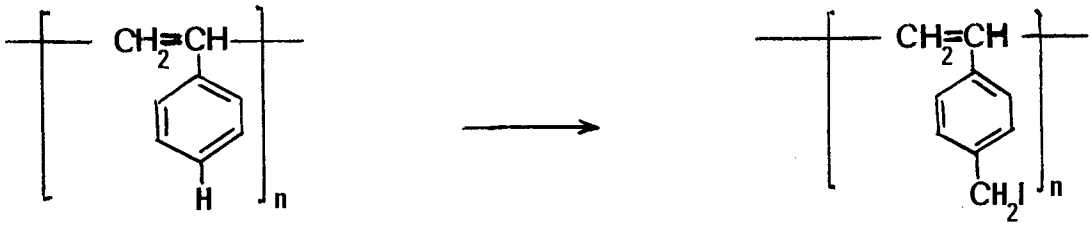
If R≡ $-CH_3$ this material, pentabromophenyl-methacrylate is almost the best additive imaginable with respect to heavy atom content. It is in fact on the market as a flame retardant, (109) though at

considerable expense. No details of the properties of this compound in copolymerisation are available. Other such compounds, tribromophenyl acrylate and 2,4,6 triodo 3 amino ethyl phenyl-ethacrylate (the afore mentioned bili-tenebryl, shown here) are



on the market, though at very high prices and with little known of the polymerisation properties.

There is one further reaction of polystyrene which may possibly be of use:- (110)



the halomethylation is accomplished by iodo methyl methyl ether (CH_3 O CH_2 I), catalysed by zinc iodide, over a period of ten days. The iodine is very readily replaced by more reactive halogens, and, in fact is very readily replaced by many groups, thus accounting for its commercial significance (as an intermediate in ion exchange resin synthesis). This compound would thus appear to be of little value.

These then are the polymerisable additives available for consideration, though in all cases further study is necessary as very little work has been done on the physical characteristics of the polymers as opposed to the polymerisation parameters.

Before correlating the requirements from toxicity screening and x-ray studies, with available polymerisable materials, it is worth commenting on non interacting fillers.

1.9.5 Inert Fillers - Modification

It has already been stated that the use of inert fillers in a denture material is unsatisfactory because of loss of transparency and flexural strength. These disadvantages are aggravated by the fact that thus far the filler has always been added at the dough moulding stage and is consequently confined to the 'holes' between the prepolymer spheres. The fact that very little homogenisation results from the flow of the viscous dough has already been established microscopically (63). If the filler could be incorporated into the spheres two and a half times the amount of filler could be used before the overall loading approached that between the spheres if addition is carried out at the doughing stage. The problem then is to incorporate filler particles into polymer spheres as they are produced in a suspension polymerisation process. As many monomers are found to be strongly adsorbed onto mineral fillers (silica, kaolin, asbestos, clay and glass) and may be graft polymerised onto them, (111,112) it would seem far from impossible to incorporate fillers in this way.

Despite the prospects opened up by this phenomenon it is vastly preferable to achieve a totally homogeneous polymer, which is possible only with a copolymerisable additive. It is therefore intended to return to considerations of inert fillers only if the production of suitable copolymer systems proves impossible.

1.10 SELECTION OF MATERIALS FOR STUDY

Studies of the general trends in radiopacity and toxicity of

simple compounds, along with the more detailed survey of heavy atom containing monomers lead to a position where a choice of compounds worthy of further study may be made.

To summarise, the criteria arrived at in the consideration of the various parameters are as follows:

RADIOPACITY The effectiveness of atoms as absorbers of x-rays increases with increasing atomic number, and is very low below atomic number Z = 30 (zinc). However in the wavelength range involved in clinical radiography, the absorption edges of zinc, bromine, caesium, silver, tin and other elements with $30 \leqslant Z < 56$ render these elements effective absorbers.

TOXICITY In general, the lighter the atom the less toxic are its compounds likely to be. Simple compounds are less likely to be toxic than complexes.

CHEMICAL CONSIDERATIONS The best solution appears to lie in simple comonomers, to maintain a high heavy atom content and a high degree of compatibility with the polymer matrix. Simple Lewis acid complexes may be equally suited provided they are stable in an aqueous environment. Aliphatically halogenated monomers do not appear to be sufficiently stable for consideration.

Correlation of all data currently at hand suggest that the following compounds are worthy of study:-

(i) Zinc chloride - Lewis Acid Complex with methylmethacrylate.

(ii) Acrylates, methacrylates of:-

zinc, strontium, caesium, silver, tin (and tin alkyls).

(iii) Bromostyrene, dibromostyrene and more highly halogenated compounds if available.

(iv) Bromo- and iodophenyl acrylates and methacrylates, with as high a degree of aromatic halogenation as possible.

At this point it should be emphasised that some of these compounds may prove too expensive for commercial use (a tentative limit of £1 per pound is suggested). Though obviously if a material is found to be ideal in all respects, a price premium would be acceptable. This is a reasonable supposition as the major part of the cost of a denture is not the material, but the time taken by a skilled technician.

CHAPTER 2

MATERIALS AND STANDARD TECHNIQUES

2.1 CONTROL MATERIALS

2.1.1 'Stellon' ('New Formula Cross-linked') manufactured by Amalgamated Dental International Co Ltd was taken as a typical clear acrylic denture material. This material is a two part system, a suspension polymerised polymethyl methacrylate powder (40-150 μm) and a liquid monomer system. The monomer is methyl methacrylate containing 15% ethylene glycol dimethacrylate and inhibitor. The polymer phase contains sufficient residual benzoyl peroxide initiator to overcome the inhibitor and effect the cure of the dough moulding. A typical suspending system for dental polymer production is described by Halpern (113) as using 0.5-1.0% polymethacrylic acid and disodium hydrogen phosphate buffer in aqueous solution.

2.1.2 'Radiopaque Stellon' also manufactured by A D Int Co Ltd was taken as of the minimum standard acceptable in respect of physical strength and optical clarity of mouldings produced therefrom. The monomer system in this material is similar to that in 'Stellon', but the polymer powder has 8% barium sulphate powder blended with it. In addition a pink pigment is incorporated with the polymer powder.

2.1.3 'Microfine Barytes' - barium sulphate powder as used in 'Radiopaque Stellon', was supplied by A D Int Co Ltd and was employed as a control inert filler and x-ray opacifier in polymethyl methacrylate. This is a very fine powder, of particle size $\sim$ 1 μm.

In the commercial production of 'Radiopaque Stellon' mixing of 'Stellon' with 'Microfine Barytes' is effected by a sigma blade mixer followed by sieving to 80 mesh.

2.2 MONOMERS

2.2.1 Zinc Acrylate - Preparation of zinc acrylate was by a modification of the method of Restaino et al (65) - 90% of the calculated requirement of pure vacuum distilled acrylic acid was added to a methanolic slurry of AnalaR zinc oxide (25% solids). During addition the slurry was well agitated and maintained at less than 20°C to prevent premature polymerisation. The excess zinc oxide was then filtered from the slightly viscous solution in a stainless steel pressure filter under a pressure of 12 psi of nitrogen. The resulting clear solution was then concentrated in a rotary evaporator under vacuum at room temperature to the point of crystallisation and then cooled in ice to obtain the solid product. The zinc acrylate was then filtered off, washed with ether and dried under vacuum at 50°C.

Prior to the adoption of this method stoichiometric neutralisation was employed. Under these conditions the filtration step was necessary only to ensure the exclusion of dust from the product, and could be accomplished quite readily in a Buchner filter. However when produced in this way the zinc acrylate invariably contained 1-2% acrylic acid (determined by the weight loss at 150-250°C on thermogravimetric analysis). At no stage during the preparation was the methanolic solution of zinc acrylate allowed to stand for an extended period. This was because of the production of methyl acrylate and zinc hydroxide:

$$Zn\left[O-\overset{O}{\overset{\|}{C}}-CH=CH_2\right]_2 + 2CH_3OH \longrightarrow Zn(OH)_2\downarrow + CH_2=CH-CO_2-CH_3$$

This reaction was observed to take place over a period of a few days, being apparent by the precipitation of zinc hydroxide, and the characteristic smell of methyl acrylate.

In an effort to eliminate this possibility of ester production the preparation was attempted in other solvents, but only water was a sufficiently good solvent for zinc acrylate, and this led to the production of the dihydrate rather than the desired anhydrous salt.

Estimation of the purity of the product was made by complexiметric titration of the zinc against 0.05M E D T A using xylenol orange indicator in a solution buffered to pH 10 with hexamine. (114) The zinc content of the material was also determined by thermogravimetric analysis (pyrolysis to zinc oxide) and atomic absorption analysis, both of which techniques will be discussed later.

In view of the anticipated rate of usage of zinc acrylate a 2 kg custom synthesis was arranged with Wychem Ltd according to the above method. Analyses of this material and the laboratory preparation are presented in Table 2.1.

Potassium Acrylate and Zinc Methacrylate were also prepared in methanolic solution as described above.

2.2.2 Caesium Acrylate was made similarly, though starting from the carbonate (ex Koch-Light, 99% pure) instead of the oxide. In this case it was found that rapid polymerisation occurred if the drying temperature exceeded 50°C.

TABLE 2.1

PURITY OF ZINC ACRYLATE

Test	Lab Prepared	Wychem Product
Zinc Content (EDTA)	31.8% (100% pure)	31.5% (99.1)
Zinc Content (AA)	31.5% (99.1)	31.35 (98.6)
Zinc Content (TGA)	31% (97.6)	30.8% (97.1)
Methanol Insoluble Material	0	0.6 - 0.9%
Volatiles (Weight loss at 120°C for 24 hours)	1.2%	2%
Acidity (Measured by the dissolution of zinc oxide by a methanolic solution of the zinc acrylate as it percolates through in a sinter)	0	1.2% Acrylic Acid

2.2.3 Strontium Acrylate was prepared as a precipitate when acrylic acid was added to a methanolic solution of strontium hydroxide (AnalaR).

2.2.4 Silver Acrylate was prepared by digestion of silver carbonate with acrylic acid. The insoluble product was filtered off and recrystallised from hot water. The acrylate crystallised as white dendritic crystals. Study of this material (and other silver compounds) was abandoned when the instability of the compound was realised. The crystals had turned black during one day's exposure to daylight.

Any other materials used which were not standard laboratory reagents will be described where appropriate.

2.3 ROUTINE TEST METHODS FOR DENTAL EVALUATION

2.3.1 Mould Preparation As mentioned earlier dental moulds are individually made for production of each moulding. An identical system, except of course in the shape of the pattern used, is employed to prepare a mould for the production of test blanks.

2.3.1.1 Using sheets of dental modelling wax (paraffin wax) a model is prepared 70 mm x 35 mm x 3mm.

2.3.1.2 The wax positive is invested in plaster of Paris in the bottom half of a dental flask such that only the top surface is exposed, flush with the plaster surface. In order to prevent air bubbles occurring at the plaster/wax interface some of the plaster is first heaped onto the blank, and the remainder used to overfill the flask. When the plaster is beginning to set the wax blank plus plaster is pressed into

the flask and the excess plaster removed with a palette knife.

2.3.1.3 The exposed surface of wax and plaster is coated, after setting, with 'Teepol' to act as a release agent. Excess is washed off under a tap.

2.3.1.4 More plaster is applied to the surface, and to the upper half of the flask. As soon as it is possible to invert the upper half of the flask the two are mated, and hand pressure applied to squeeze out the excess plaster.

2.3.1.5 After allowing twenty minutes for setting the flask is opened by a sharp tap with a hammer and a twist of a knife blade in the joint.

The wax blank is removed from the mould by melting out in a jet of boiling water.

2.3.2 Preparation of the dough:- Polymer powder (10 g) is added to monomer (4 g) in a porcelain container and the lid put in place (mixing is in this order to exclude air pockets). The mixture is stirred intermittently until the consistency is such as not to stick to a dry finger tip.

2.3.3 Moulding:

2.3.3.1 Both surfaces of the mould are coated with aqueous sodium alginate solution which forms a release film of calcium alginate at the plaster surface.

2.3.3.2 The polymer dough is kneaded in the fingers into the rough shape of the mould cavity and placed in the bottom half of the mould.

2.3.3.3 A sheet of wet cellophane is placed over the sample, the top half of the flask positioned, and pressure applied in a hand press - this operation is termed 'trial closure'.

2.3.3.4 The flask is re-opened, the cellophane removed and excess flash trimmed off.

2.3.3.5 Alginate solution is re-applied to the upper half of the mould which is then replaced. Pairs of flasks are then clamped in spring loaded jigs (plate 2.1) to exert a constant pressure.

2.3.3.6 The jig is placed in programmed air oven to undergo a curing cycle of:

7 hours delay to complete homogenisation and flow of the dough followed by:

3 hours at 85°C to polymerise the monomer (Graph 2.1).

The jig is then left to cool to room temperature.

This cycle is conveniently carried out overnight, the samples then being ready for removal the following morning.

2.3.3.7 When cool the flasks are removed from the jig, opened with a knife and the cured plaque of polymer prised out.

As the surface quality of the polymer produced is not of paramount importance (see sample preparation) it has been found possible to re-use a mould up to four times before deterioration becomes excessive.

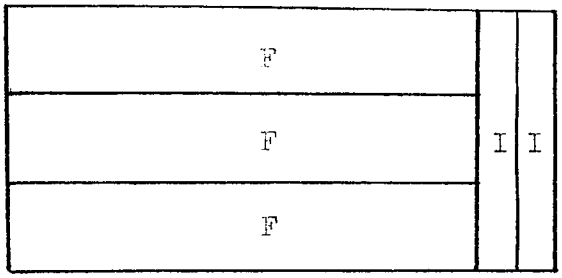
This procedure was found to be somewhat less than satisfactory for moulding formulations containing hydrophilic materials, due to interaction with the water present in the alginate solution and on the cellophane. As a dry replacement for these separating media thin (25-50 μ) polythene or polyethylene terephthallate (Melinex) films were used on both sides of the cavity.

2.3.4 Sample Preparation

The standard sample size for flexural strength determinations

PLATE 2.1 DENTAL MOULDING FLASKS IN A TRIAL CLOSURE PRESS

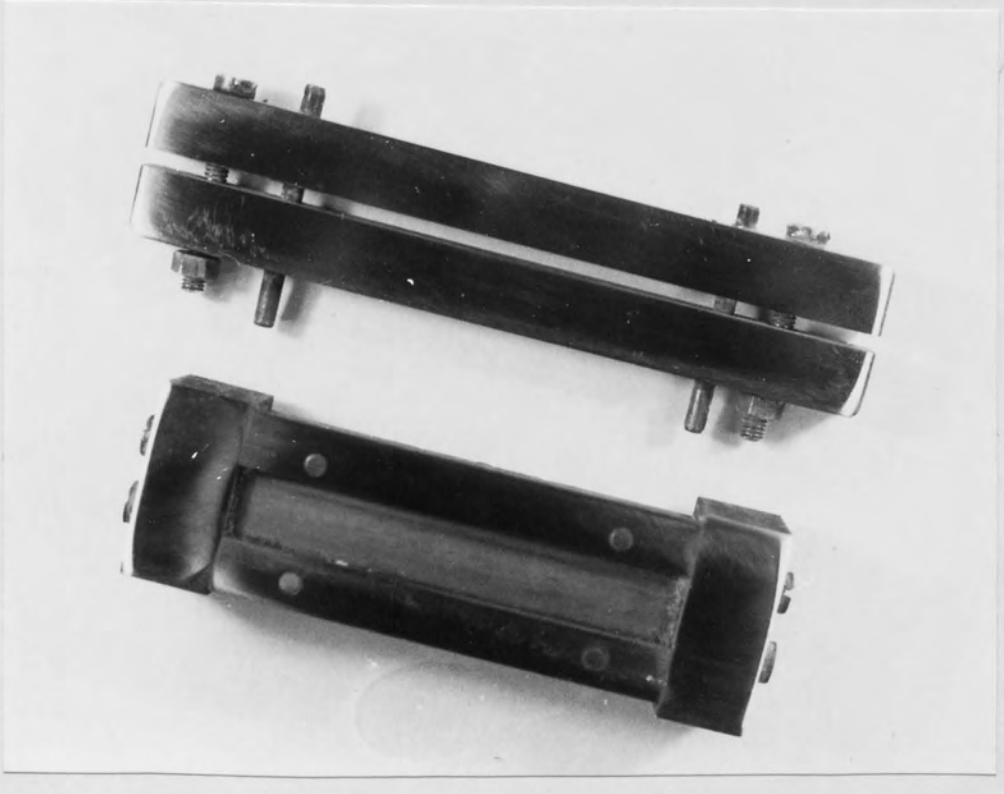
is 60 mm x 10 mm x 2.5 mm and it is convenient to use the broken halves of these for the qualitative tests of UV stability and x-ray absorption. For the quantitative physical test results to be mutually comparable the cross sectional dimensions must be identical. In order to achieve such consistency in dimensions hardened steel sizing jigs (plate 2.2) are used giving dimensions 10 $\pm$ 0.05 mm x 2.5 $\pm$ 0.05 mm. Prior to this final sizing the polymer plaques are roughly cut, using a hacksaw, into two impact specimens 5 mm wide and three flex samples 11 mm wide x 60 mm long (as at left).



2.3.4.1 Flexural Strength Samples - Each flex test piece in turn is mounted in the 10 mm jig so as to overlap on each side. The excess material is then rubbed off on waterproof silicon carbide paper on a plate glass bed under a stream of water. Grade 280 C paper is used for rubbing away the bulk of the material, and 500 A to give the final finish. The specimen is then removed, placed in the cavity of the 2.5 mm jig and, with frequent turning of the sample, rubbed down as above on successively finer grades of paper, again finishing with 500 A.

The standard dental testing technique now requires that each test piece be immersed in distilled water at 37^{o}C for seven days. In fact of the three test pieces cut above one was immersed in water as directed, one was tested dry and the remaining sample kept in reserve in case of premature failure of either of the others. A further point of deviation from British Standard procedure is in the number of specimens tested. Owing to the large number of

PLATE 2.2 HARDENED STEEL SIZING JIGS FOR FLEXURAL TEST SAMPLE PREPARATION



formulations to be tested, and the time consuming sample preparation techniques single specimen test results will be quoted. It is not felt that this will lead to gross inaccuracy as more emphasis will be placed on modulus figures which are not 'notch-sensitive' than on the more scattered ultimate failure strengths. The process of operating with five test samples for wet testing (as per BS D64/13854), and five for dry testing, through all stages from mould preparation to interpretation of results is considered too time consuming for the value of the extra results produced. Flexural strength testing is, after all, only one aspect of the evaluation of potential materials and as such until an otherwise ideal material is produced is not worthy of such attention. Even so, provided it is not viewed as absolute, some useful information is provided by the ultimate strength results on such single samples.

2.3.4.2 Impact Strength Samples - Except for the fact that hardened steel jigs are not used, the preparation is similar to that described above. The 5 mm x 3 mm x 35 mm hacksaw-cut specimens are sized by hand using the fine (500 A) abrasive paper to 4 mm x 2 mm cross section. In order to achieve these dimensions with any degree of consistency frequent checks with vernier calipers, and ultimately a vernier screw gauge, are necessary. Once more one sample is soaked for 7 days in distilled water at 37°C, and one tested dry.

2.4 STANDARD TEST PROCEDURES (DENTAL)

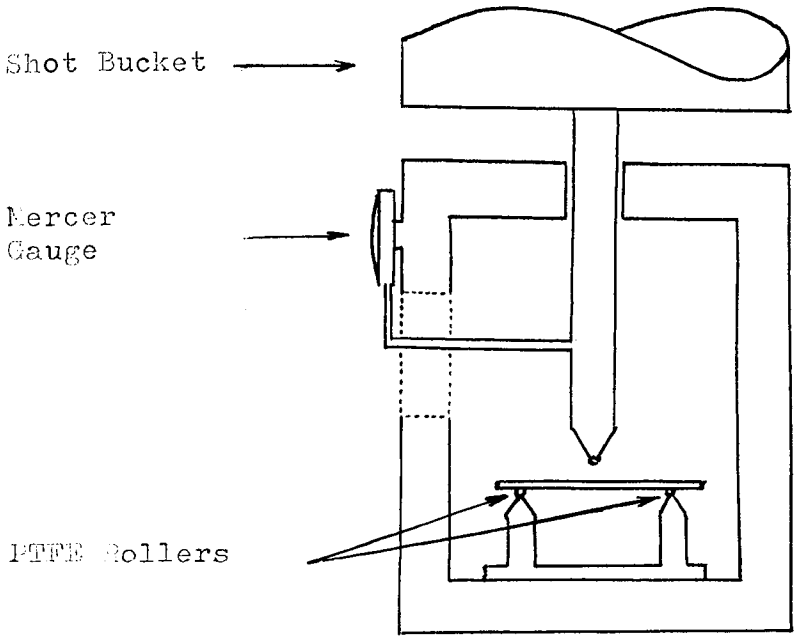
2.4.1 Flexural Strength Determinations

The test designated in the above British Standard employs three point bending as the mode of deformation, over a 50 mm span. The

loading force is supplied by lead shot being poured, at the required rate, into a bucket mounted on the top of the main ram (see Fig 2.1).

FIGURE 2.1

BRITISH STANDARD FLEXURAL TEST APPARATUS

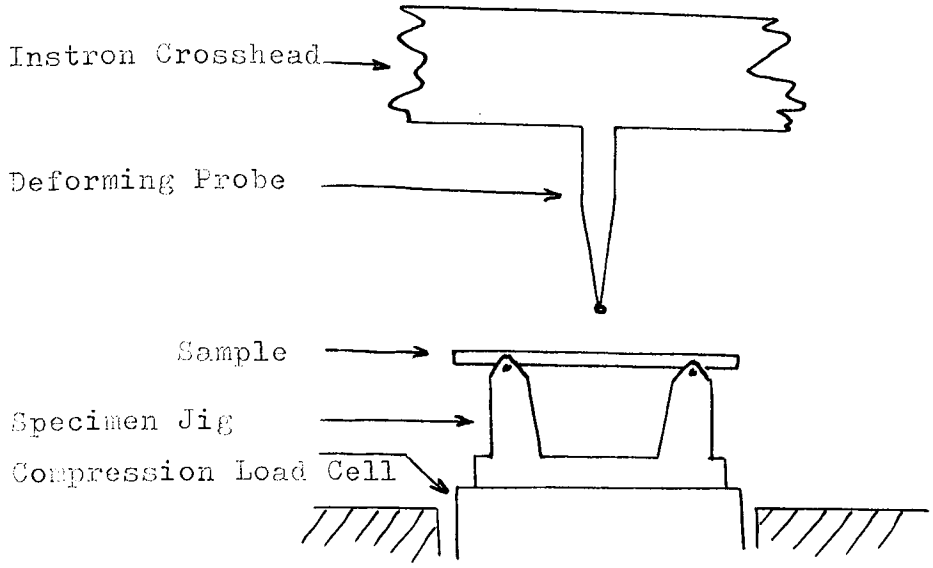


The deflection of the sample is followed on a Mercer gauge mounted on the frame. The basic simplicity and portability of this apparatus may commend it as a control instrument in a small dental research laboratory, but it is hardly ideal for research purposes. Instead, an 'Instron' tensometer equipped with a suitable compression load cell is used (plate 2.3). The designated standard testing jig fits quite conveniently into this instrument (see Fig. 2.2). The dental standard measures deflection at a constant rate of loading, and specifications are quoted on this basis. Initial load is specified as 1.5 kg, with an increase of 0.5 kg min^{-1} up to 5 kg. Deflection at this final load shall be 2-5.5 mm, and at the intermediate load of 3.5 kg, 0-2.5 mm (taking the 1.5 kg reading as zero deflection).

PLATE 2.3 THE INSTROM TENSOMETER USED FOR FLEXURAL TESTING WITH INSET SHOWING THE JAW ARRANGEMENT

FIGURE 2.2

EXPERIMENTAL APPARATUS FOR FLEXURAL TESTING



In contrast the 'Instron' test procedure measures increasing load on the sample while maintaining a constant rate of deformation. Though strictly speaking these test methods do not yield identical information the data required by the British Standard can be derived from the 'Instron' test.

The experimental parameters employed in the flexural testing were as follows:-

Bending Span	-	50 mm
Crosshead Speed	-	0.5 mm min^{-1}
Full Scale Load	-	100 N

(Chart Speed to give $\sim 45^{o}$ initial slope=100 mm min^{-1})

The cross sectional dimensions of the samples were measured immediately after testing at the point of fracture. Then using the formula

$$F = \frac{3PL}{2bd^2} \quad N\ mm^{-2}$$

Where F = Flexural Strength
P = Load at failure
L = bending span (50 mm)
b = width of sample
d = thickness of sample

the corrected flexural strength value is calculated. In this way any size variation between the samples is compensated for, though due to the sizing technique used, such variations should be minimal. The initial (tangential) modulus is also calculated and expressed in terms of Newtons per square milimetre (cross sectional area) per milimetre (deflection) ie Nmm^{-3}. A further parameter quoted is the deflection at break (mm).

Samples may also be described according to the shape of trace produced:-

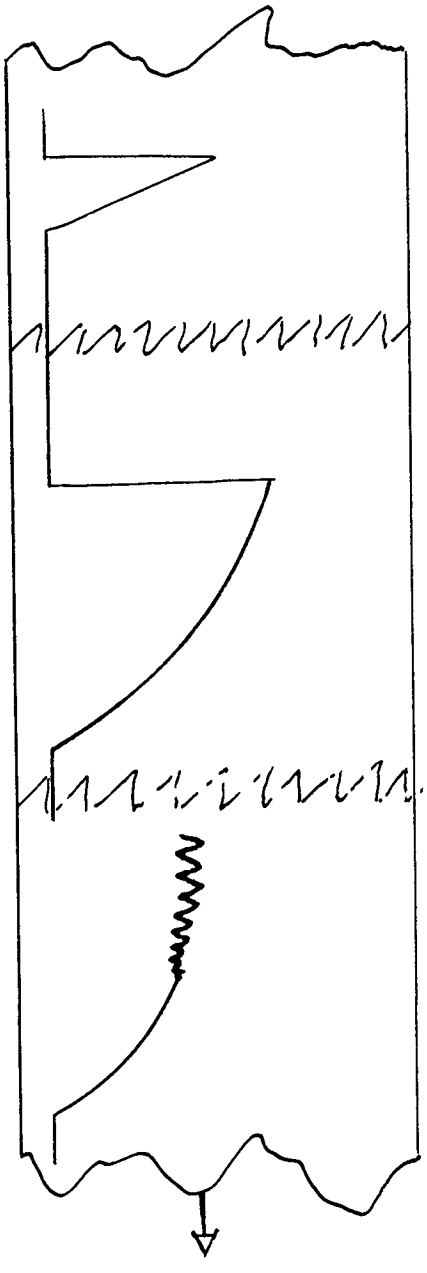


FIGURE 2.3

Brittle failure, possibly premature failure due to notch-sensitivity

FIGURE 2.4

Tough sample (large area under curve) ultimate brittle failure. (typical of dental acrylics)

FIGURE 2.5

Flexible sample - no failure deflection continues until the sample is pushed right through the supports.

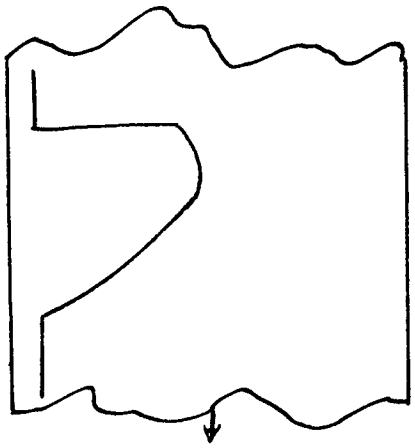


FIGURE 2.6
Progressive crack formation typical of formulations containing high loadings of mineral fillers.

2.4.2 Impact Resistance

The technique used at Birmingham Dental Hospital for measuring impact strengths is in fact simply a high speed version of the flexural strength test. However, owing to the degree by which the speed of test is raised, completely different instrumentation is required. The rate of deformation employed is 133 mm sec^{-1}, which is beyond the scope of the 'Instron', so a compressed air driven ram is used. However, the major problem involved is in recording the load on the sample as conventional x-y recorders have far too long response times. The solution is supplied by connection of the output from the load cell to a storage oscilloscope. The required information may then be read from the screen, or traced onto sheets of celluloid or photographed at one's leisure.

As in the flexural strength testing the sample dimensions are measured at the point of fracture, and the same formula used in calculation of the impact strength, (though in this case L = 20 mm).

Parameters calculable from this technique are as for flex testing, though the impact energy too is often quoted, this being obtained from a measurement of the area under the stress/strain curve.

Owing to the identical mode of failure employed it is felt that impact testing results may mirror those of flexural testing,

and thus offer little useful information. However, at least until this suspicion is vindicated or otherwise, both of the tests will be performed.

2.4.3 Radiological Assessment

As has been stated earlier there exists no standard technique for radiographic assessment of dental materials nor even for describing the degree of attenuation.

However, several test methods have been initiated by C Price (Birmingham Dental Hospital), the one used most extensively being as follows:-

Broken halves of flex test samples are mounted with their 10 mm dimension perpendicular to a photographic x-ray plate. On the same plate is mounted an aluminium step wedge as reference. This plate is then exposed for 4 sec to a beam from a 60 kV x-ray source, filtered through 6 mm aluminium (giving an effectively homogeneous beam $\lambda = 0.3294$ Å).

After processing the plate is examined with a photodensitometer, equating the absorption due to each sample with a certain thickness of aluminium.

Then, involving the equation

$$\mu_x \, t_x = \mu_y \, t_y \qquad \text{for identical absorption}$$

where u = linear attenuation coefficient, t = thickness for materials x and y respectively.

$$\mu_{sample} = \frac{\mu_{AL} \, t_{AL}}{t_{sample}} = \frac{\mu_{AL} \, t_{AL}}{10}$$

As μ_{AL} is available from tables, μ_{sample} is known.

It should be noted that this is the linear attenuation coefficient and is divided by sample density to give the mass coefficient.

A simpler technique of estimation which is currently under evaluation consists in immersing the sample in a series of aqueous solutions of x-ray absorbing salts. In a solution of identical attenuation coefficient a sample will not show up at all on a radiograph. Thus, once the solutions are decided upon and prepared no further measurement is required, simply a visual assessment of the radiographs.

Ideally, assessment of radiographic absorption should be carried out using every available x-ray source and all possible conditions of exposure. This is obviously totally impracticable and while it is accepted that the technique described above is restricted in its applications it does provide a useful comparison between the samples in the range to be considered.

There still remains the question of what is radiopaque and what is radiolucent? 'Radiopaque Stellon' is generally considered to be of somewhat less than the minimum required radiopacity. As figures are never quoted on this subject it is difficult to assess the ultimate extent of this investigation. However it now seems that a universally acceptable standard would be "having the x-ray absorbence of 20% barium sulphate-filled polymethylmethacrylate". This implies a desired mass attenuation coefficient $\mu/_{\rho} = 0.714$ calculated as described earlier at $\lambda = 0.3294$ Å.

Knowing this figure, it becomes possible to calculate the required concentration of any potential absorbing species in polymethyl methacrylate.

Correlation of experimental x-ray data with theoretical calculations

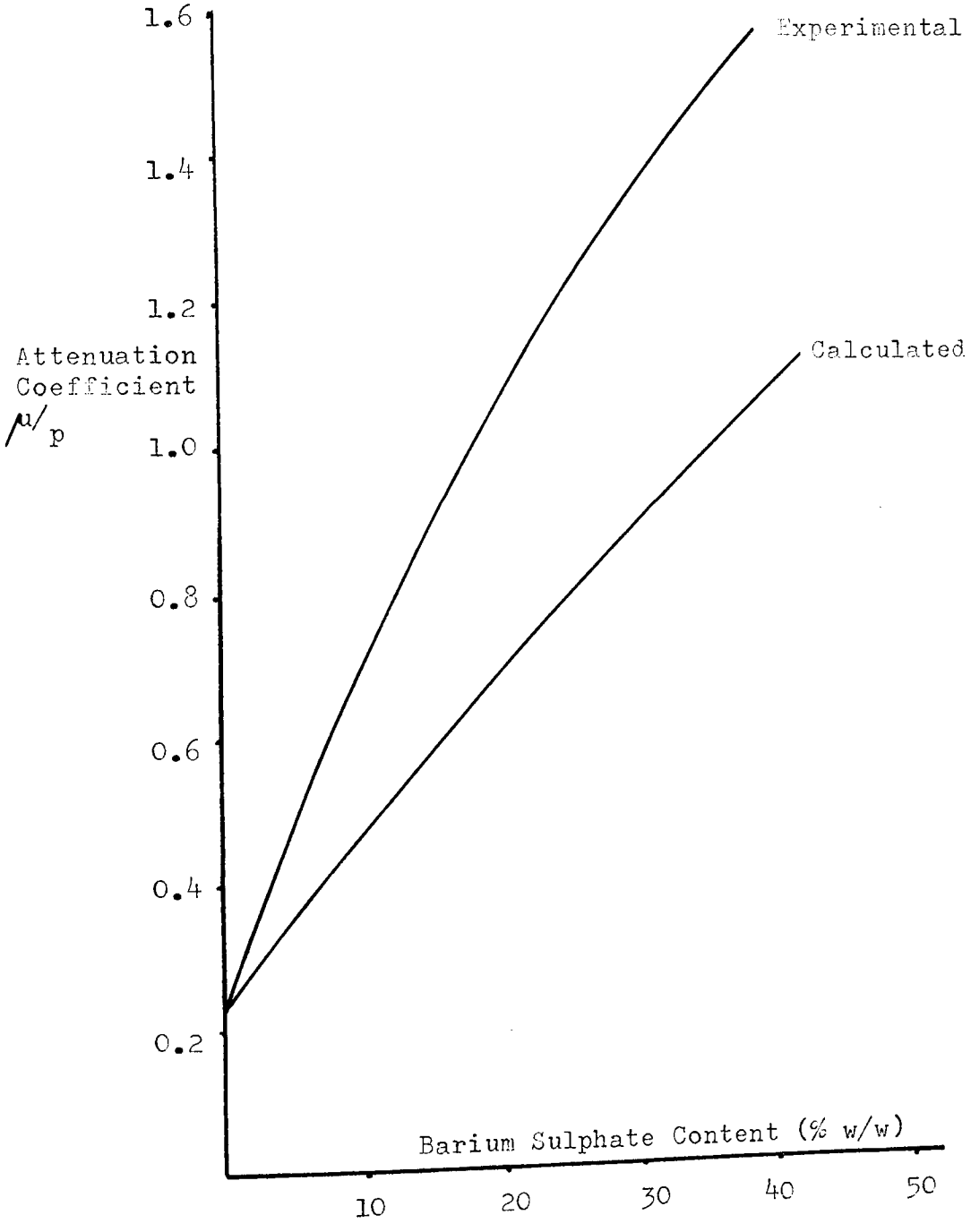
If the mass attenuation coefficient of a composite is really as readily calculated (for a given x-ray wavelength) as indicated

in the previous chapter, it should not be necessary (for research purposes) to subject specimens to radiography as prediction is easier. In order to test the validity of these calculations experimental and predicted values of the mass attenuation coefficient were compared on polymethyl methacrylate samples containing varying loadings of barium sulphate. Experimental values were determined as described above using the 60 kV (peak) tube with heavy filtration to produce a linear logarithmic absorption curve of effective wavelength 0.3294 Å. The results are presented in Graph 2.2.

It is seen that at higher concentrations of barium sulphate the experimental attenuation coefficient deviates increasingly from the theoretical value. In fact this behaviour is equivalent to an effective lengthening of the x-ray wavelength as the concentration of heavy atom increases. This is born out by Graph 2.3 in which the effective wavelength of the beam was calculated from the observed total attenuation coefficient. In order to do this it was assumed that the mass attenuation coefficients of carbon hydrogen, oxygen and sulphur remained constant over the range involved, and that of barium was the only variable (this is not strictly true but the effect due to barium vastly exceeds that of the other elements). Thus effective wavelengths were calculated which, at each concentration, would fit the theoretical coefficient to the experimental value. The reason for the increasing effective wavelength is not known, but the near linearity of the curves of Graph 2.2 indicate that the beam is behaving monochromatically (since a graph of log (transmitted intensity - I) vs thickness of absorber is equivalent to one of $-\mu$ vs concentration of absorbing species in a non absorber). Why then should each successive increment in barium

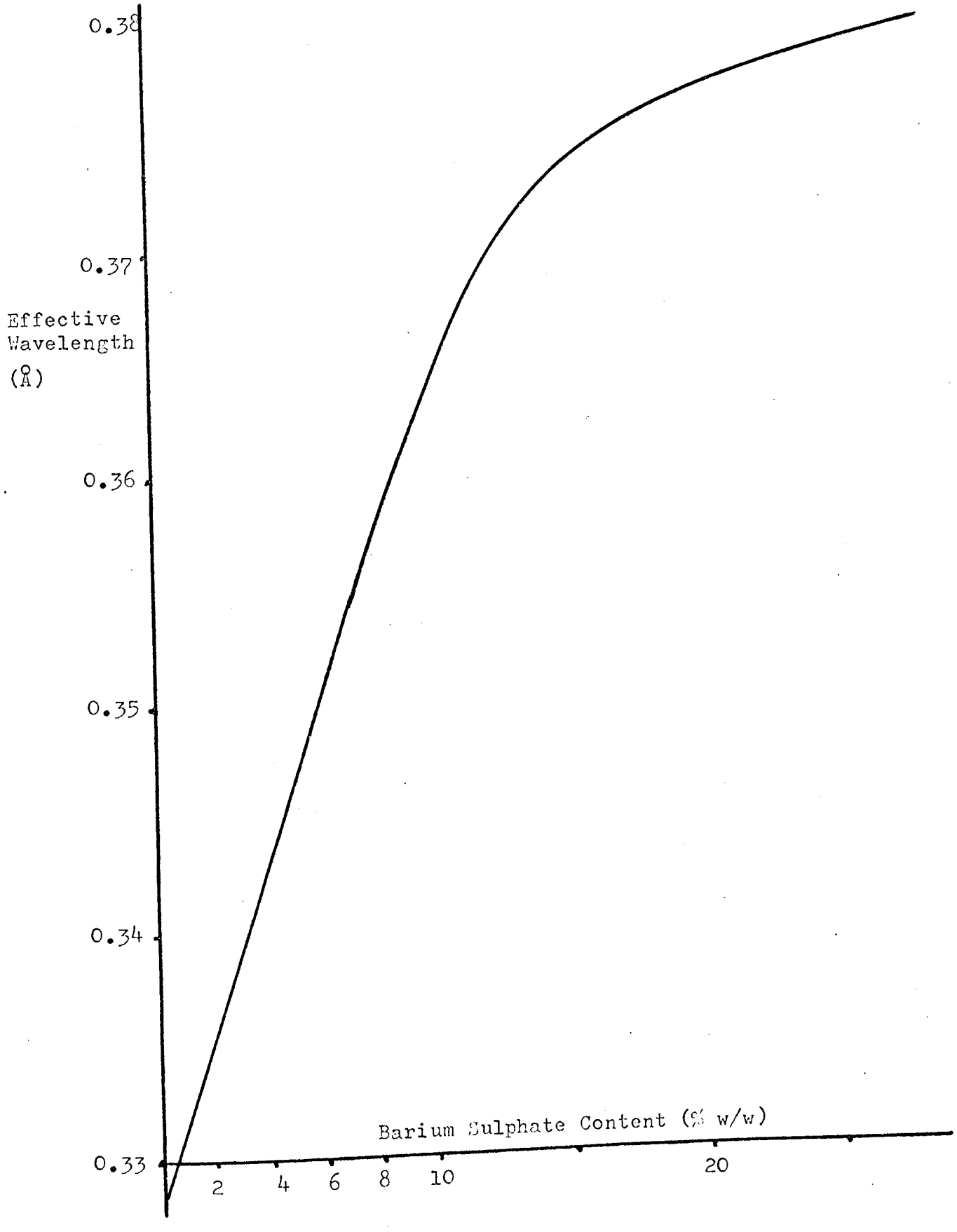
GRAPH 2.2

Calculated and Observed Mass Attenuation Coefficients for Composites Containing Barium Sulphate Filler



GRAPH 2.3

Calculated Effective Wavelengths to Fit the Observed Attenuation Coefficients for Barium Sulphate Filled Composites



concentration have a greater effect than its predecessor? It is reasonable to assume that, at very low concentrations of heavy atom, most of the incident radiation which is scattered at low angle in the forward direction ultimately reaches the film (or detector). At a higher concentration each heavy atom except for those in the surface of the specimen will be able to interact with this scattered radiation and being of lower energy it will be more readily absorbed. Thus the more barium atoms present the greater the absorption over and above that expected purely on a concentration basis. It is felt that this observation is probably not original, though no reference was found to such behaviour in the literature. (A comprehensive literature search of all radiographic and nuclear physics journals was considered outside the scope of this investigation).

It appears then, that even for an effectively monochromatic x-ray beam it is not possible to calculate the attenuation coefficient for a composite material with absolute accuracy. However, for a preliminary screening of prospective materials these calculations provide a valuable technique.

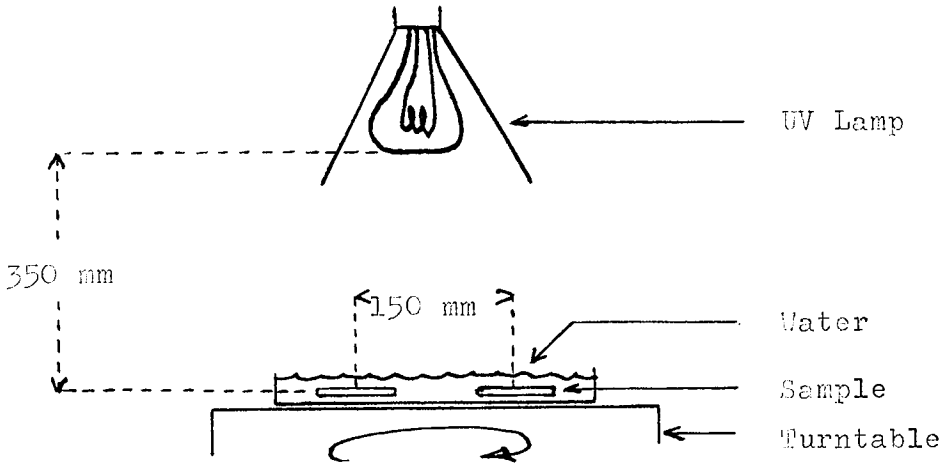
2.4.4 Ultra Violet Stability

Though included in the British Standard specification, this test is very rudimentary and subjective - The broken flex test specimens are immersed in a shallow dish of distilled water and rotated beneath a tungsten filament mercury discharge lamp. The power source for the turntable is identified by the recommended speed of rotation - 33 rpm.

Exposure is continued for twenty four hours, and the relative discolourations judged by eye. Any perceptible deterioration

FIGURE 2.7

UV TEST APPARATUS



being cause for concern, but the limit of acceptability being "perceptible with difficulty when viewed in daylight".

It is only anticipated that this test shall be a go/no-go elimination technique, especially for the halogenated monomers, and as such it is probably adequate. It would however be preferable to set the test on a quantitative basis by a simple photometric technique. The problem of calibration against a standard observer, and the wide variation in optical clarity of the unexposed specimens complicate the issue. In view of its lack of fundamental importance to this project development of this test is not considered worthy of study, it will thus be performed as recommended.

2.4.5 Optical Qualities

Two standards are quoted for denture base - "unpigmented base shall be crystal-clear, translucent base shall be translucent". A standard of translucency may be provided by the ability to read through a specimen laid over a page of typescript. Thus "if it is possible to read through a 2.5 mm thick sample, it shall be deemed translucent, otherwise it is opaque". (BS 2487).

2.4.6 Water Sensitivity

Specifications for water absorption on dental acrylics are made with reference to the 24 hour immersion at 37°C of a sample 1 mm thick. In view of the large number of extra mouldings required for this test, a determination was made on the 2.5 mm thick specimens, though 24 hours was not sufficient time to achieve equilibrium. It was thus decided that in general, water content should be determined on the weight increase of the soaked flex test specimens over 7 days. However, even this figure is not wholly adequate, and selected samples were soaked to equilibrium (constant weight). Samples of the same material with different cross sectional dimensions were examined to elucidate diffusion characteristics.

Weighing was carried out daily for one week, then weekly until constant weight was achieved. For every weighing each sample was dried on a cloth, then waved in the atmosphere for 15 seconds to evaporate any water remaining as a surface film.

In order to achieve the varied cross sections, new plaster moulds were cast on wax models 50 mm x 50 mm x 1 mm and 50 mm x 8 mm x 8 mm. In each case the surface was smoothed on 500 A emery paper prior to testing to achieve physical uniformity.

At the end of the test the samples were deswollen under vacuum at 70°C to constant weight.

Testing by this method means that no material will come within the standard, but a meaningful figure is obtained for scientific evaluation.

2.4.7 Wedge Moulding

In addition to the routine mouldings produced, samples of selected formulations were moulded in the form of wedges 5 mm x 5 mm

tapering to a chisel point over a length of 40 mm. By this means it is hoped to show qualitatively any of the common moulding defects. It is also apparent that in translucent formulations such wedges give a semi-quantitative estimation of translucency. If a wedge is placed over a line of typescript the thickness at which optical translucency is lost may easily be assessed.

As in the previous cases, the model for the wedge mould was fashioned in wax.

2.4.8 Histological Screening

In order to establish, with confidence, the non toxic nature of otherwise promising material, in vivo testing was required. This test was performed as a service by Birmingham Dental Hospital.

Small (2 mm x 2 mm x 5 mm) samples of dough moulded material, with the emery smoothed surface, were implanted beneath the skin on the back of laboratory rabbits. After periods of 3 months and 1 year animals were sacrificed, and the medium and long term tissue response assessed.

Owing to the nature of the test it was felt undesirable to use it as a fundamental screening technique. Thus, as stated above, such a procedure was only called upon when in other respects a formulation looked very promising. It will thus be seen that only one formulation was submitted for such an examination.

2.5 NON DENTAL TESTING TECHNIQUES

Where established laboratory procedures have been employed these will be referred to at the appropriate point. The tests to be detailed here are those most extensively employed, which in most cases have been adapted to fit the requirements of the project.

2.5.1 Thermogravimetric Analysis

The varying degree of cross linking of the dough mouldings, either from the ethylene glycol dimethacrylate, or other difunctional monomers in the system, renders the product insoluble in normal solvents. It is thus very difficult to analyse these materials in the conventional manner or by spectroscopy. However, it is known that methyl methacrylate polymers readily depolymerise at temperatures in excess of 250°C to leave no residue at 450°C (Graph 2.4). Thus, provided the comonomer or filler is stable at these temperatures, or undergoes a stoichiometric pyrolysis to stable products, an analytical technique is suggested.

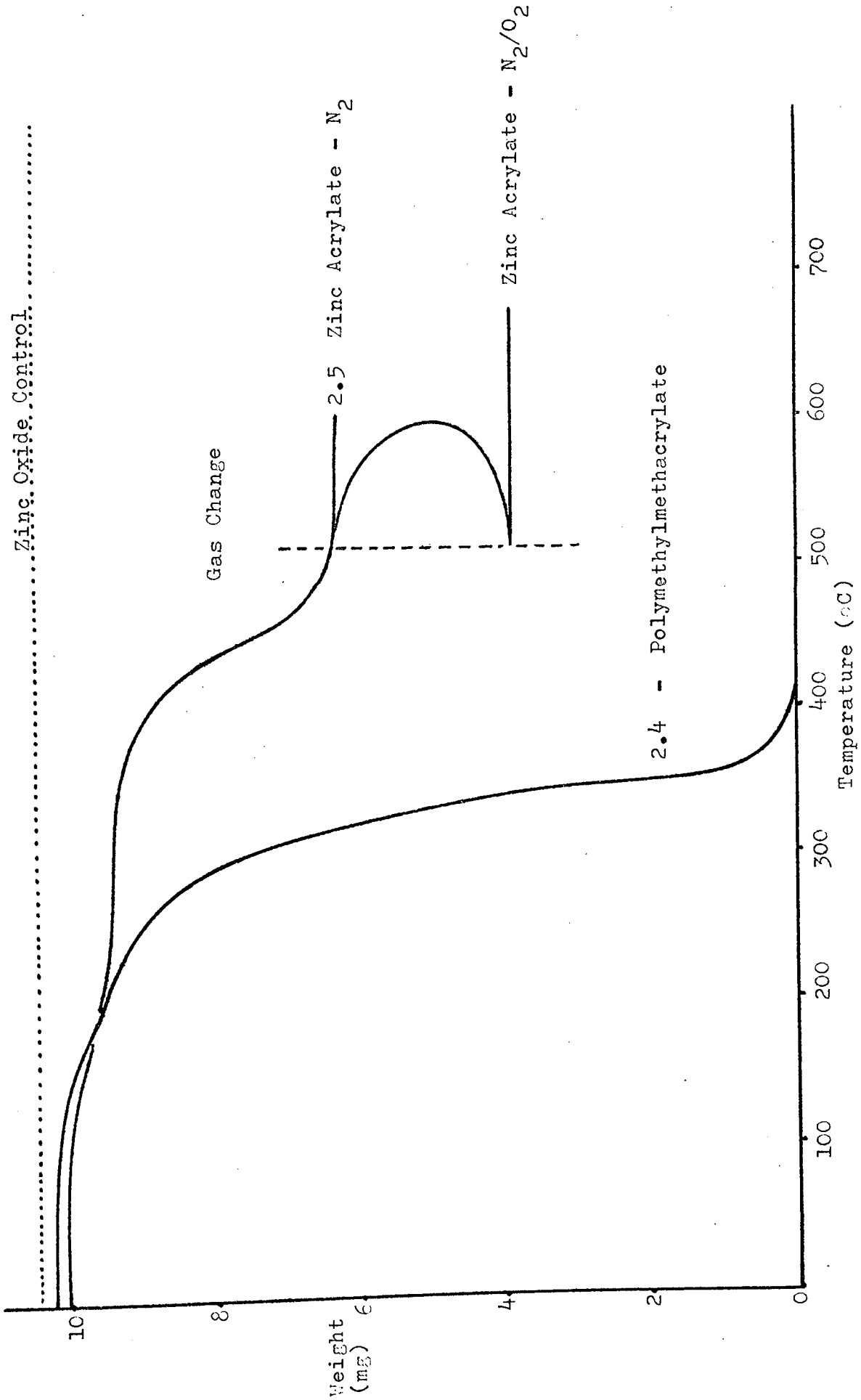
It has been found that zinc oxide is quite stable at temperatures up to greater than 800°C, it has also been found that zinc acrylate will pyrolyse quantitatively to zinc oxide if the correct atmosphere is employed for the pyrolysis. Under nitrogen, pyrolysis occurs to a virtually constant weight, but not to zinc oxide as some char remains (Graph 2.5). On the other hand an oxygen atmosphere leads to loss of the sample as it explodes, as does the use of air.

The technique finally arrived at for zinc estimation was as follows:

A DuPont 900/950 thermogravimetric analyser was set up for 10 mg full scale deflection, 20°C per minute heating and 100°C per inch recorder sensitivity. The gas inlet was connected, via a two way valve, to cylinders of nitrogen and oxygen. Pyrolysis of the sample was then commenced using a gentle flow of nitrogen ($\sim$ 5cc/min) and continued to constant weight ($\sim$ 500°C). At this point the gas valve was adjusted to give a vigorous (though not so much as to disturb the sample) flow of oxygen to burn off the residual char. As the char burned off the sample was observed to glow red (the

GRAPHS 2.4, 2.5

Thermogravimetric Analysis (TGA) Curves for Compounds Fundamental to the Project



sample can be seen by looking along the silica tube into the furnace area) and the exotherm was clearly seen on the recorder (Graph 2.5). After the exotherm the residue showed no further weight loss, and if the furnace were opened hot the characteristic yellow of zinc oxide, fading to white as it cooled, was apparent. Calculation of the zinc content of the sample could then be made from the graphs.

An additional advantage of this estimation method is the fact that any residual solvent in a sample is not only detected, but measured in the early stages of heating.

The validity of this technique was checked by the parallel analyses of zinc acrylate mentioned earlier (Table 2.1).

In the later stages of the investigation a Stanton-Redcroft instrument was loaned (for which thanks must go to the Physical Sciences Department of Wolverhampton Polytechnic) owing to the breakdown of the DuPont instrument. Using the same instrument settings it was found possible to pyrolyse to an oxide residue in a single step by modifying the gas composition. The final mixture arrived at was 20% air in argon, ie approximately 5% oxygen. The results obtained on the two different instruments were identical within the limits of experimental error. This error was assessed at $\pm$ 2%, with respect to zinc content, by repeated pyrolyses on the same sample.

It was at one time hoped that a more precise heavy atom determination technique would be provided by radiography. As has already been established however, this could only be sufficiently accurate if a truly monochromatic x-ray source were available. This would necessitate the use of γ-emitting radioisotopes and as a

consequence would lose its relevance to the project as a whole.

.2.5.2 Extraction Studies

In order to establish the possible long term effects of new polymers in the oral environment it is necessary to assess the extent of extraction of any soluble materials.

It has already been established that the only compounds worthy of consideration for inclusion in denture base are either insoluble in water, or non toxic. A denture though may be in an aqueous environment for a period of many years, during which time it is conceivable that all the radiopacifying agent may be lost. Owing to the long time period involved, any measurements made over realistic periods will necessarily be very small, and thus require sensitive techniques of measurement.

The inherent insolubility of the brominated monomer-type formulations in water implies that loss will not be significant. In fact there should be little difference in behaviour to that of pure polymethyl methacrylate where the only material lost is any residual monomer which is rapidly removed on initial immersion. Extraction studies are thus to be centred on the metal polyacrylates. Special attention is devoted to the zinc polyacrylate systems, as zinc acrylate is very soluble in water ($\sim$ 40%).

As such small quantities are involved it is not possible to estimate extracted material by volumetric analysis (such as the EDTA complexiметry described earlier) though the initial screening was performed on this basis.

Volumetric techniques can be used to estimate zinc contents of 100 mg in the sample aliquot. The expected order of concentrations to be encountered is 0.1 - 1 mg. The analytical technique

accepted for this concentration range is dithizone colourimetry.

Polymer samples (flexural strength test pieces were used except where surface area or type was being studied) were immersed in extractant solution at 37°C. This extractant, which was generally water, except when other specific systems were being investigated, was changed weekly for analysis. It was found convenient to use 40 ml of extractant : 1.5-2 gm polymer, thus allowing for making up to 50 ml in a volumetric flask prior to analysis.

The analytical procedure employed was a simplification of that described by the Society for Analytical Chemistry (115). (It was possible to simplify this procedure due to the absence of interfering metal ions from the sample solutions.) A calibration curve was first prepared as follows:-

AnalaR zinc sulphate was dissolved in deionized water and diluted such that 1 ml ≡ 1 µg Zn (0.004398 g $ZnSO_4$ $7H_2O$ per litre). Into five separating funnels was pipetted 1, 2, 3, 4, 5 mls of this solution respectively and a sixth treated as a blank. 1 ml of $N/_1$ hydrochloric acid was added to each, and diluted to 10 ml. Sodium acetate/acetic acid buffer solution (5 ml) was then added, followed by sodium thiosulphate solution (1 ml 25%). Dithizone solution (4 mls of 0.005% solution in AnalaR carbon tetrachloride) was then added and vigourously shaken. The carbon tetrachloride layer was run off after settling to be replaced by fresh dithizone solution, until no colour change was apparent. Finally the aqueous sample was washed with carbon tetrachloride (1 ml). The combined organic extracts were then shaken with successive 10 ml portions of sodium sulphide solution (AnalaR) to destroy uncomplexed dithizone. This was continued until, after settling the aqueous layer was clear and the organic layer pink. The carbon tetrachloride layer was then

washed with water, dried with anhydrous sodium sulphate, filtered and made up to 25 ml in a standard flask.

The absorption of the solutions thus prepared was measured in a 10 mm glass cell for the absorption peak at 532 mμ using pure carbon tetrachloride as a reference. The instrument used for this measurement was a Unicam SP 700 UV/visible spectrometer. The absorption curve a little each side of 532 mμ was examined so that the peak position was confirmed. Optical densities of the samples were then plotted against zinc concentration to give a calibration graph.

As the zinc content of the unknown extractant solutions can not be assessed prior to testing, and the useful range of this technique is small, several different runs were performed on each sample.

Aliquots of 0.5 ml, 2 ml and 10 ml of the unknown were treated in an identical manner to the standard samples above. If the concentration was in the required range a figure for optical density was obtained, and hence, from the calibration curve, a value for the zinc concentration. If no zinc were detected even in the 10 ml aliquot the concentration must be less than 0.1 $\mu g\ ml^{-1}$, hence a longer extraction between tests was required. If the concentration was too high, even in the 0.5 ml aliquot, to appear on the calibration curve, a still smaller sample had to be taken.

It will be immediately obvious that this system of total change of extractant at weekly intervals may lead to long term inaccuracy. To give a graph of extracted zinc vs extraction time requires a summation of all the measurements up to the week in question. This means that the analytical error is cumulative and hence the absolute value for extracted zinc after a long period may

lack accuracy. However one must consider that in the oral environment the extractant (saliva) is constantly flowing over the sample (denture) and thus a stagnant system with small sample removal at intervals would not be relevant. In fact as a separate test a sample was left for an extended period in a stagnant extractant from which minimal samples were taken at intervals for analysis. The results are compared at the appropriate point (Ch 5). In fact the feature of critical importance in this extraction is the temperature as, to be relevant to use the test must be carried out at body temperature. A thermostatic water bath controlling at $37^{\circ}C \pm 0.2^{\circ}C$ was employed. This emphasis on temperature control precludes the use of soxhlet-type continual flow extractors, these being readily operable only at reflux temperature, or room temperature. However, in an attempt to establish the long term performance, accelerated extraction tests at $100^{\circ}C$ in a soxhlet extractor were performed. Analysis of the eluted material was made by the colourimetric method described above, samples being extracted from the flask at hourly intervals for the first day, and twice daily thereafter. Once again, as the approximate concentration of zinc was not known, a range of sample sizes was taken so as to ensure that one would lie in the range of the calibration curve.

This analytical technique is very tedious and time consuming, but once the appropriate skills were mastered the results were very reproducible. However, once the value of these results was seen, and the prospect of continuing the extractions over a period of a year or more appeared, a more automated analytical method was sought. This was achieved in the use of an Atomic Absorption Spectrometer. Zinc ions, excited in a flame absorb radiation of 213.9 mμ, and this absorption provides the basis for a very sensitive

analytical method. As in the colourimetry, standard solutions are required for calibration, in this case a solution containing 100 $\mu g\ ml^{-1}$ Zn^{2+} was employed. This was further diluted to give a range of concentrations from 1 $\mu g\ ml^{-1}$ to 20 $\mu g\ ml^{-1}$ Zn^{2+} which were then subjected to analysis. Atomized droplets of the test solution were injected into an acetylene/air flame and the absorption at 213.9 mμ recorded. A graph was then plotted of absorption against concentration. Unknown samples were then similarly injected into the flame and the zinc content read from the calibration graph at the appropriate absorption. The accuracy of this method, like the colourimetry is confined to a narrow range of concentrations, 1 - 20 $\mu g\ ml^{-1}$ and suitable dilutions must be made of samples exceeding 20 $\mu g\ ml^{-1}$.

The instrument employed for these determinations was a Perkin Elmer 303 Atomic Absorption spectrophotometer. In order that a mutual check on accuracy could be made, for several weeks samples were analysed by both methods. Agreement was found to be excellent and thus the colourimetric determination was discontinued in favour of Atomic Absorption Spectroscopy.

2.5.3 Microscopy

In order to gain a more detailed understanding of the structure of dough moulded materials both optical, and stereoscan electron microscopy were employed. Both of these instruments are well known but the sample preparation techniques are worthy of description.

2.5.3.1 Optical transmission microscopy: In order that polymer samples, or indeed any samples, may be examined by transmission microscopy they must be transparent. Also, as the depth of field is so limited at high magnification definition is improved by having a very thin sample (in fact at this sort of thickness most materials

exhibit the required transparency).

Thus samples 3 mm x 3 mm x 15 mm were cut from a dough moulding and mounted on the sledge of a base sledge microtome. A series of sections 10 μ thick were then cut. These sections were formed tightly rolled, and broke up at any attempt to unroll them. The procedure adopted for flattening and mounting the specimens was as follows:-

The rolled sample was floated on a drop of boiling glycerol heated on a glass slide over a low Bunsen flame. At this temperature the stresses in the matrix relaxed and the sample uncurled to lie flat on the surface. The sample was then transferred to a clean slide, covered with a cover glass and examined under the microscope using objectives of several powers. The microscope used was an Olympus 'Vanox' which is also equipped for metallurgical incident light illumination:-

2.5.3.2 Optical incident light microscopy: In order to examine the mechanism of crack propagation and failure in polymer samples, the fracture surface was inspected microscopically. A small chip (approx 3 mm x 3 mm x 1 mm) having as uniform a surface as possible was broken from a dough moulded plaque with the aid of a pair of pliers. This was then mounted on a microscope slide with the fracture surface uppermost and horizontal. Mounting was achieved using a small piece of plasticine into which the sample was embeded. Examination was then made under various filters, with and without crossed polars and at a range of magnifications.

As an extension to the range of conditions offered in incident light microscopy, stereoscan electron microscopy was also used in the examination of surface structures.

2.5.3.3 Stereoscan Electron Microscopy: For the examination of fracture surfaces samples were prepared as above by breaking off a chip from a plaque. This was then mounted on an aluminium 'stub' using 'Araldite' or other non-volatile adhesive (to safeguard the vacuum system of the instrument). Owing to the insulating properties of polymers they are essentially transparent to an electron beam and thus will give no image. Thus in order to examine a polymer specimen by this technique, its surface must first be coated with a conductor. The method employed is a vacuum 'sputtering' system whereby a carbon or silver layer is built up on the surface from an arc struck between electrodes of the appropriate element in a high vacuum. Theoretically a monoatomic surface covering is adequate, but in practice the minimal complete layer is used which may well be much more than one atom thick. Over coating must be avoided as surface detail may be obscured.

The coated sample assembly was then inserted in the specimen chamber of the microscope, vacuum applied and examination commenced. Prolonged examination at high magnifications (> 1000 x) was not possible due to the heating effect of a concentrated electron beam. After approximately half a minute on a particular surface feature, distortion occurred due to melting and/or degradation. It was thus essential to photograph the image as soon as possible on location of a feature of interest, and to only employ high magnifications after a moderate power survey of the surface.

As well as fracture surface topography, this technique was used to examine both particle size and surface nature in powder specimens. In such cases mounting of specimens was achieved by heaping excess powder onto a smear of adhesive on a 'stub' followed by blowing off of excess powder. Coating with carbon was carried out as above.

In all cases, to economise on time and materials up to four different samples could be mounted on a stub, identification marks being scratched on the reverse side.

Where filler particles were not readily identifiable from the appearance of the display on the screen an x-ray spectrometer was employed to identify the elements present. A point of light could be steered on the cathode ray tube to the position in question. The x-rays emitted from this point due to excitation by the electron beam were then collected in an ionisation chamber and a spectrum displayed. The elemental structure of this area could then be determined from the known characteristic emissions of elements. However, it is felt that the value of this device is reduced by its over-sensitivity, such elements as silicon, sodium, chlorine, and copper being detected in almost all cases. The origins of these contaminants can only be guessed at:- sodium chloride would appear to derive from perspiration though every effort was made to avoid touching the actual fracture surface; silicon and copper, unless present in all the materials employed, which seems highly unlikely, can only have arisen from atmospheric dust.

2.5.4 Molecular Weight Determinations

Wherever polymer products of a suitable nature were produced, gel permeation chromatography (gpc) was performed to measure the molecular weight, and assess the molecular weight distribution. When cross linked polymers were produced, wherever possible systems were devised to remove the cross links and submit the resulting linear polymers to gpc to determine chain lengths. Such systems will be described where appropriate.

A flow rate of 1 ml min^{-1} of a solution of the polymer in

inhibited tetrahydrofuran was employed, and the eluted fractions examined by viscosity measurement. The column used was calibrated against a standard sample of polystyrene. In the Mark Houwink equation:-

$$[\eta] = kM^a$$

where $[\eta]$ = intrinsic viscosity

M = molecular weight

k, a = constants.

For the standard polystyrene sample $k = 1.2 \times 10^{-4}$

$a = 0.71$

For polymethyl methacrylate $k = 1.28 \times 10^{-4}$

$a = 0.71$

These values were used for all acrylic copolymers. The calibration curve of eluted volume vs molecular weight of polymer is presented in Graph 2.6. These GPC analyses were performed by Dr Evans of RAPRA, Shawbury.

2.5.5 Density Measurement

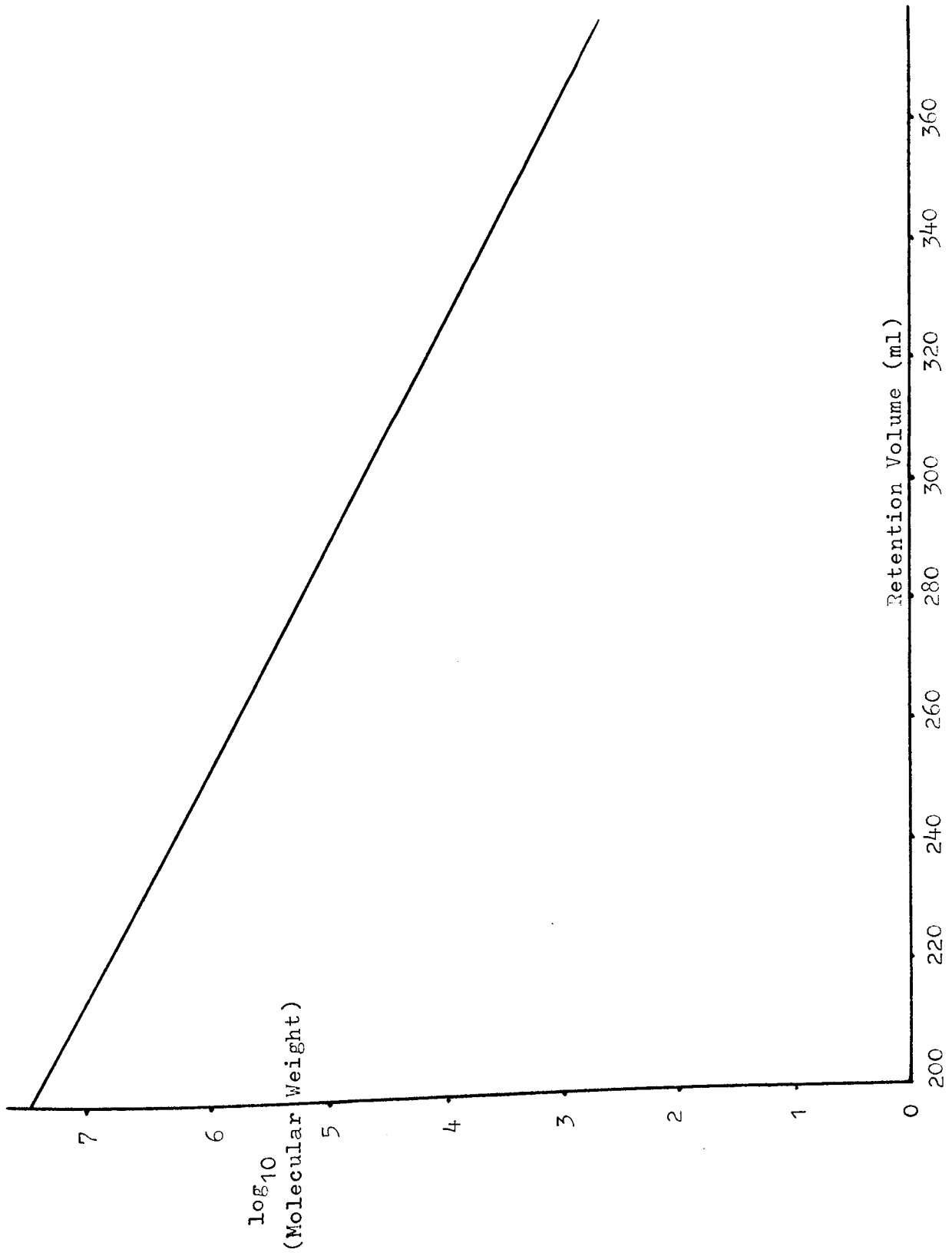
As mentioned earlier in radiographic estimation (2.4.3) the density of a sample is required in the calculation of its mass attenuation coefficient μ/ρ. Knowledge of the density also gives an insight into the homogeneity of polymer samples and the absence of porosity and bubbles.

On occasions when one or two formulations only were to be tested, their densities were measured by the traditional specific gravity bottle/water method.

When the number of specimens rendered it worthwhile a density gradient column was prepared using a carbon tetrachloride/n-heptane column. Concentrations were arranged so that the density at the

GRAPH 2.6

Gel Permeation Chromatography - Calibration Curve



top of the column was 1.00 gcc^{-1} (65% n-heptane) and at the bottom 1.59 gcc^{-1} (pure carbon tetrachloride). The column was calibrated with standard glass floats, and a calibration curve constructed. Unknown samples were then introduced and their density read from the curve at the point corresponding to the depth of flotation (measured with a cathetometer).

2.6 ANY FURTHER TESTS of less universal application will be described when relevant. This applies also to polymerisation systems, when their evolution is a point of study in itself.

CHAPTER 3

A PRELIMINARY APPRAISAL OF SIMPLE RADIOPAQUE MONOMERS

3.1 ZINC CHLORIDE : METHYL METHACRYLATE COMPLEXES

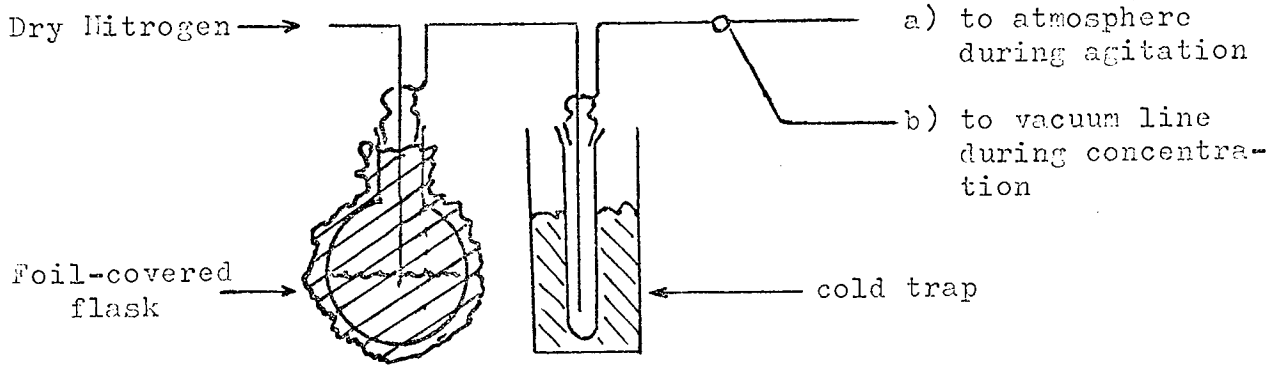
The existence, and potential radiopacity of the 1 : 1 and 1 : 2 Lewis acid : methyl methacrylate complexes has been described earlier. The calculated value for the mass attenuation coefficient $(\mu/_{\rho})$ at 0.3294 Å is 2.51 - 1.37. These figures assume that the entire polymer sample be composed of the complex and would obviously be reduced in a dough moulding process.

3.1.1 Preparation of the complex is fundamentally simple, but the extremely hygroscopic nature of zinc chloride, coupled with the reported instability of the complex necessitate special techniques. Thus, in order to avoid heating or contact with moist air, the following method was devised.

Zinc chloride (anhydrous, AnalaR) was weighed into a tared round bottomed flask. Any moisture absorbed during the weighing process was removed by drying under vacuum at 250°C for 3 hours. Dry nitrogen was then admitted to the vacuum oven and the flask was stoppered immediately on opening the oven. The dry weight of zinc chloride was recorded. The flask was then mounted on a vacuum line and methyl methacrylate monomer distilled in at 5 mm pressure until a molar ratio of approx 4 : 1 in favour of methyl methacrylate was achieved. During this operation the flask was cooled in ice and light excluded by wrapping in aluminium foil. When sufficient monomer had been collected the distillation was ceased and the

apparatus filled once more with dry nitrogen. To hasten the dissolution of the zinc chloride agitation was required and the most satisfactory technique found was a brisk stream of dry nitrogen from a capillary gas-bleed.

After several hours of such agitation the solution becomes clear, though on occasions a slight insoluble residue remained (which, when present, was filtered off and weighed, presumably being zinc hydroxide from hydrolysis of the chloride). This solution was then concentrated by applying a vacuum at room temperature while maintaining a flow of nitrogen. As the volume decreased, the



viscosity of the solution was seen to rise considerably. When approximately half of the methyl methacrylate had been removed (approx 1 hour) the flask and contents were reweighed. If the molar ratio of methyl methacrylate was still more than 2 : 1 concentration was continued, otherwise the complex was stored in the dark in a refrigerator.

It was not felt to be necessary to prepare the pure 1 : 1 or 2 : 1 complex, and as long as the composition lay between these limits it was considered adequate.

3.1.2 Polymerisation of the complex

When 0.2% benzoyl peroxide was added to the viscous complex

from above, and the solution warmed under nitrogen polymerisation was rapid. In fact even at 40°C a temperature normally considered to be too low for this initiator to be effective, the mass gelled almost instantly. A considerable exotherm was apparent, and ultimately a hard glassy polymer remained which gradually became reddish in colour as it cured. The poly complex thus formed was insoluble in, though swollen by; acetone, toluene, and methyl methacrylate, otherwise showing no interaction with common solvents. It appears then that the product is either cross linked, or of very high molecular weight. However, as the polymer had been produced in such an uncontrolled fashion, and in a form so difficult to handle, it was decided that this preparation was atypical and thus required modification.

Subsequently the dissolution of initiator was carried out at 0°C and the temperature raised slowly. The already viscous liquid was seen to become still more viscous as the temperature was raised to 25 - 30°C. Care was taken not to allow the mass to gel, thus when the viscosity approached that of treacle (monitored by observation of the nitrogen bubbles rising from the gas bleed) the mass was 'dumped' into a large volume of vigorously stirred methanol. A curdy white precipitate was formed. The polymer was then filtered off, washed in fresh methanol and dried in vacuo at 60°C.

3.1.3 Assessment of the polymer

It has been stated before that the major area of doubt concerning this polycomplex is its hydrolytic stability. Logically then this is the first property to be investigated.

Water extraction:- To prepare samples of a suitable form for extraction a film casting technique was employed. A solution of polymer in chloroform (approx 15-20% w/v) was cast onto a clean

polished glass plate to a depth of 0.5 mm (achieved by surrounding the casting area with layers of adhesive tape up to this thickness). Drying overnight at room temperature yielded a film 0.1 mm thick which was further dried under vacuum at 60°C. A pure polymethyl methacrylate film was prepared from 'Stellon' polymer by an identical procedure. 50 mm squares of the two polymer films were then cut, weighed and immersed in distilled water at 20°C. The samples were removed, blotted dry on filter paper, and weighed, every five minutes for fifteen minutes, every fifteen minutes for one hour, every hour for one day, and daily thereafter. When equilibrium was achieved (5 days) the samples were removed to a vacuum oven at 80°C and the weighing routine repeated. The results are shown in Graph 3.1.

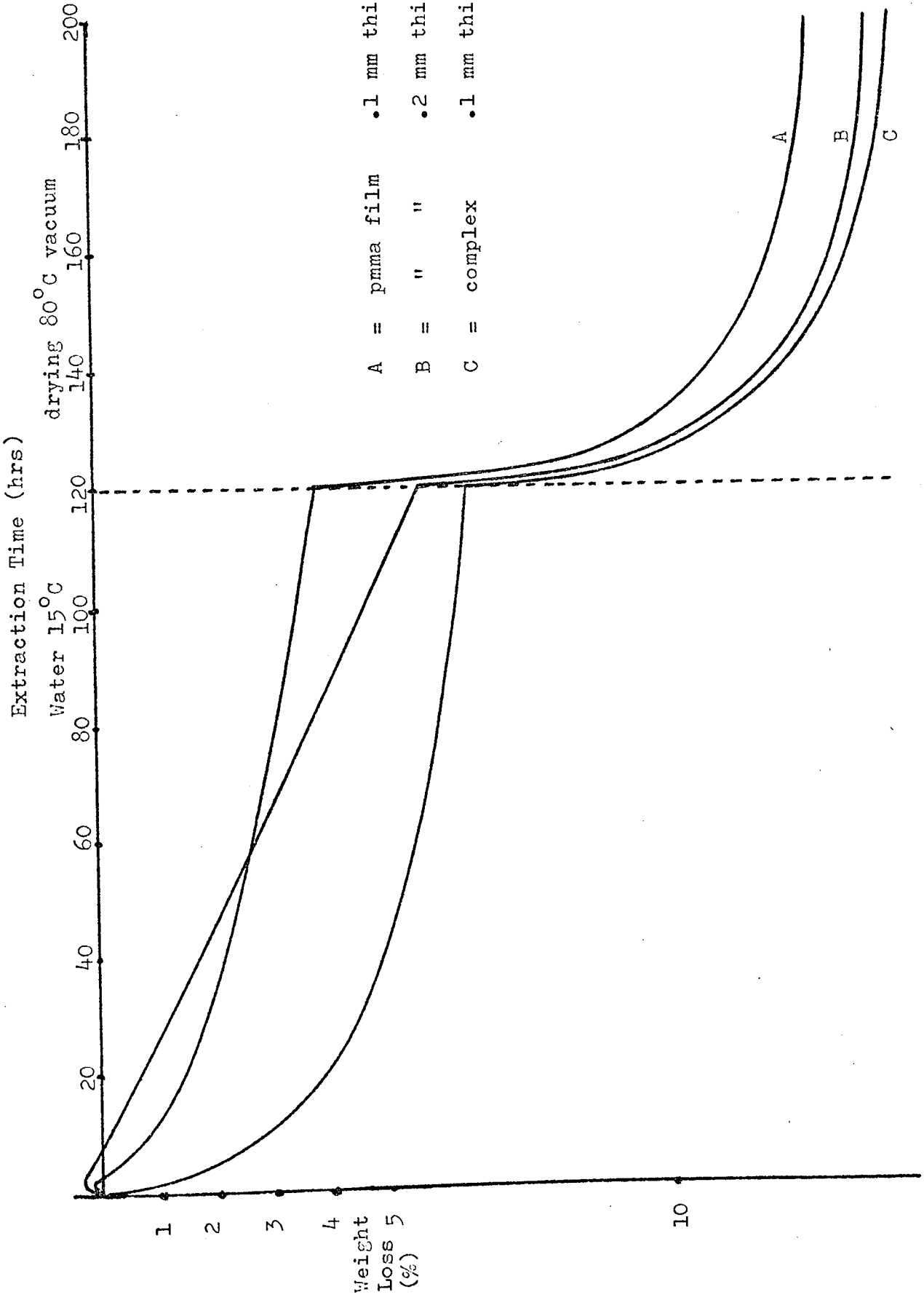
These curves are surprising in two respects; the high overall weight loss of the control specimen, and the relative similarity of the two final figures, if not of the intermediate curve shapes.

The excessive values for polymethyl methacrylate can only be explained by a considerable residual chloroform content, though this is surprising in view of the drying procedure used. Nonetheless as identical conditions were used in the preparation of both films their residual solvent contents should be comparable. This in turn implies that the film cast from the poly complex has a hydrolytic stability comparable to the control.

If this were a valid result it would mean that an ideal solution to the radiopacity problem was at hand. However, thus far the composition of the poly 'complex' film has only been assumed to be similar to that of the complex as prepared. The possibility of zinc chloride loss in the methanolic precipitation has not been considered.

GRAPH 3.1

Weight Loss of Zinc Chloride/Polymethylmethacrylate
Complex Films, Cast from Chloroform Solution, in Aqueous Extraction



It is known (78-81) that the zinc chloride is completely removed by methanolic hydrochloric acid. This provides a simple technique for estimating the composition of the polymer -

An accurately weighed specimen (approx 0.5 g) of the poly 'complex' was dissolved in AnalaR chloroform and reprecipitated in 2 : 1 methanol : hydrochloric acid. The precipitate was filtered in a tared sinter, washed well with methanol and dried under vacuum at 80°C to constant weight - NO LOSS IN WEIGHT WAS OBSERVED.

It appears then that all the zinc chloride was lost in the methanolic precipitation from the polymerisation system. This fact was borne out by the lack of residue in a TGA pyrolysis, and the identical similarity of refractive index with polymethyl methacrylate (Graph 3.2). The comparison of refractive indices was made on the film samples using an Abbe refractometer. The similarity extended over the temperature range 20 - 60°C.

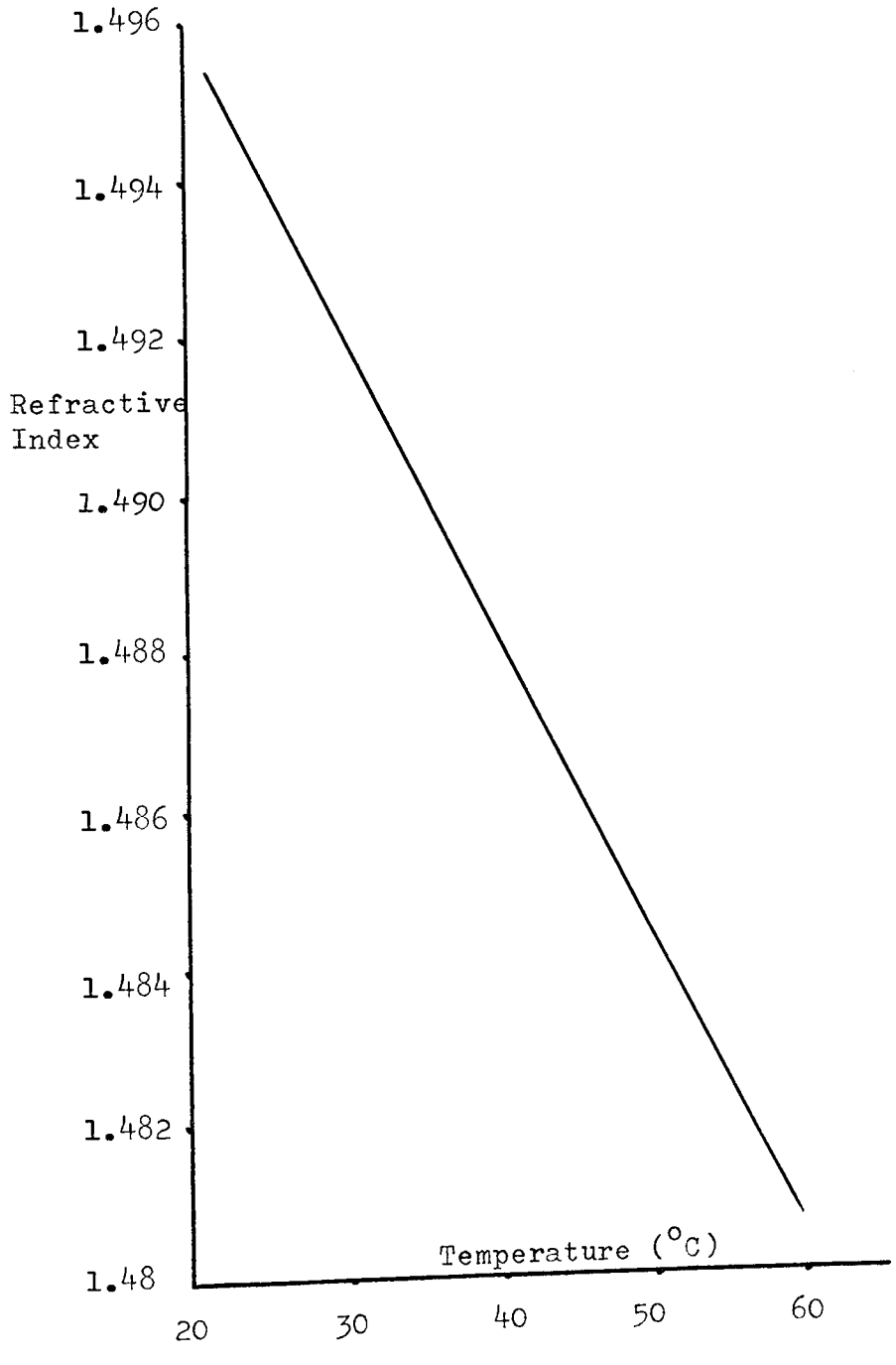
It was thus concluded that the polymer did not contain any zinc chloride.

In order to eliminate the zinc-losing step in the polymerisation, films were cast directly from the viscous partly polymerised syrup. Somewhat thicker films were obtained by this method as polymerisation continued at the same time as evaporation of monomer. The drying conditions for these films were modified to prevent premature contact with moisture. Thus an air oven at 60°C containing silica gel was employed overnight followed by 4 hours under vacuum at 80°C.

After drying, the films (two were cast, one 2.0 mm thick, and the other 0.5 mm) were transparent, though yellowish when viewed from the edge. Owing to extreme brittleness it was not possible to release the films from the glass whereas the control film had

GRAPH 3.2

Refractive Index as a Function of Temperature for Polymethylmethacrylate, and the "Zinc Chloride Poly complex" Films



stripped through its own contractive forces. Being thus unable to remove more than a few tiny fragments, these films were set aside, and a new casting surface considered. However, after standing overnight in the atmosphere of the laboratory the films had lifted from the glass, and were rubbery, accompanied by a degree of opacity.

This change in properties was attributed to absorption of atmospheric moisture and thus the films were redried at 100°C under vacuum for several hours. After redrying the films regained their former transparency though residual water is evidenced by their more rubbery nature.

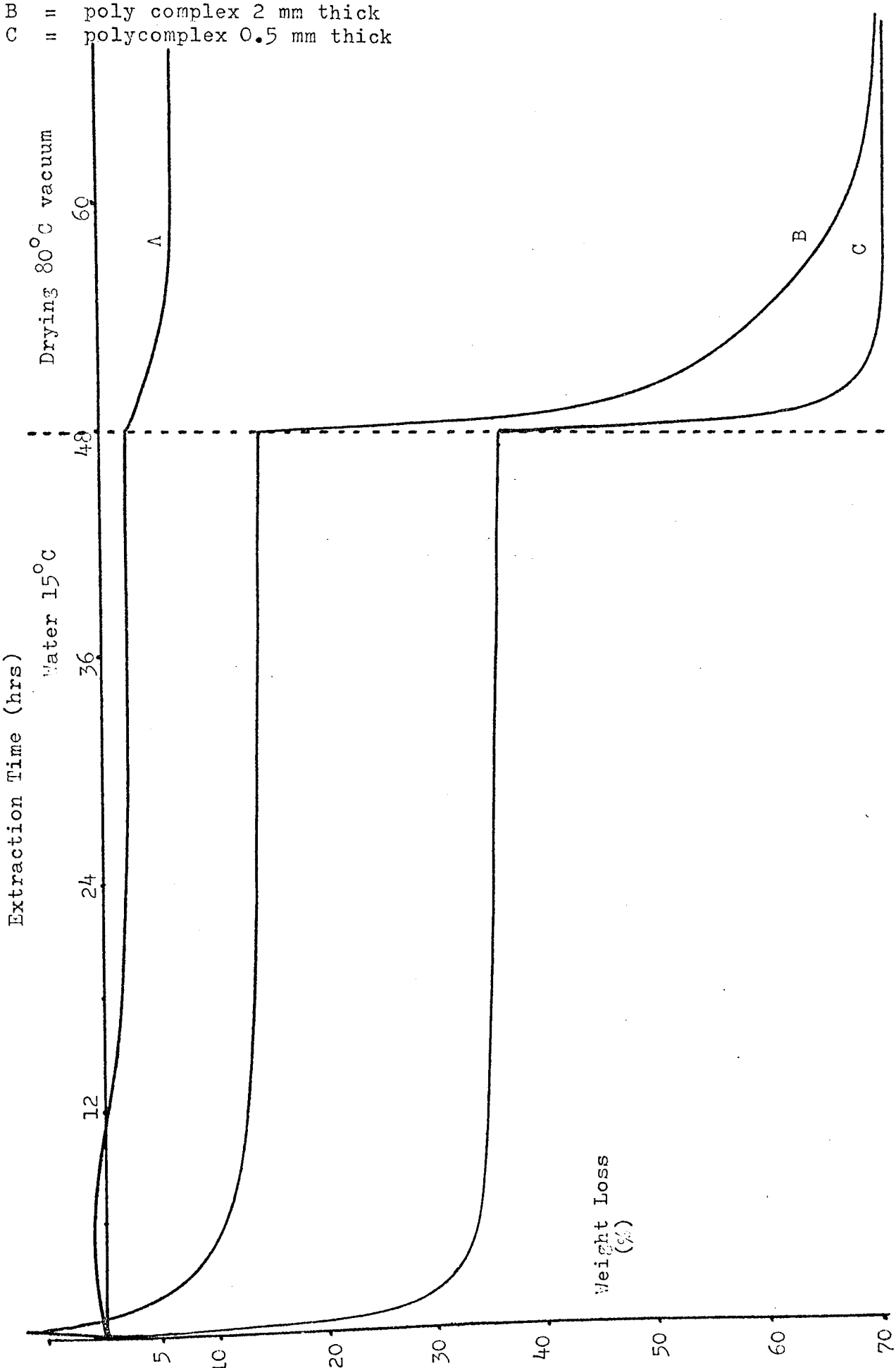
Extraction studies of these films were then carried out as described above, and the results are presented in Graph 3.3. Consideration of the weights of reactants used gives a molar ratio of 1.69 : 1 in the monomer in favour of methyl methacrylate. Due to the method used in the production of the films methyl methacrylate vapour was lost with the result that the dry films were enriched in zinc chloride. TGA pyrolysis of the dry films (Graph 3.4) revealed a zinc chloride content of 46% equivalent to a molar ratio of 1.07 : 1 in favour of methyl methacrylate.

Graph 3.3 shows that the final redried films had lost a massive 70% w/w of their original weight. As only 46% w/w water soluble material was present initially this figure must mean that the films contained a large amount of residual water before the extraction. A figure of 24% water is indicated by these results, which is surprisingly high even considering the known difficulty in dehydrating zinc chloride. In order to have confidence in removing all of the water a drying temperature in excess of 200°C would have been necessary. At such a temperature the stability of the polymer

GRAPH 3.3

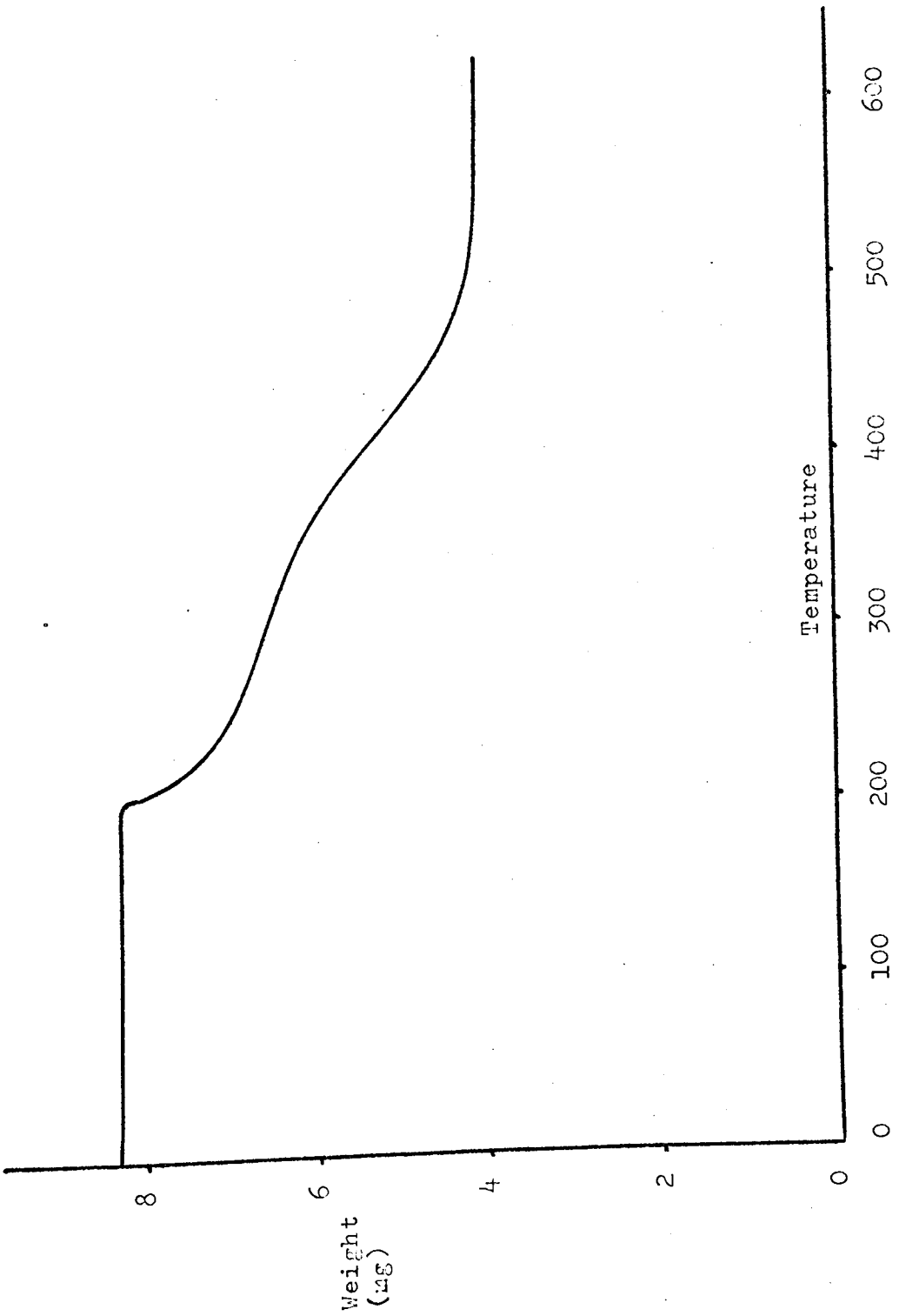
Zinc Chloride Extraction in Water, from a Film cast from the Poly complex in Methylmethacrylate

A = pmma control
B = poly complex 2 mm thick
C = polycomplex 0.5 mm thick



GRAPH 3.4

Thermogravimetric Analysis of the Zinc Chloride/Methylmethacrylate polycomplex



would have been questionable.

A check on the polymer composition was achieved by gravimetric analysis: - Accurately weighed polymer samples from the pre-extraction films were dissolved in further methyl methacrylate monomer. The polymethyl methacrylate was then precipitated in methanolic hydrochloric acid as described above. The dried, weighed precipitate yielded the polymer composition from the polymethyl methacrylate viewpoint. Analysis of the zinc chloride-containing solution from the precipitation gave the composition from the opposite approach. After suitably neutralising and buffering the solution, ammonium hydrogen orthophosphate solution was added to precipitate the corresponding zinc salt, which was washed dried and weighed. The results of these analyses are as follows:

polymethyl methacrylate	41.6% w/w
zinc chloride	44.5% w/w
	86.1% w/w

It must therefore be assumed that the remaining 13.9% was water left from the atmospheric absorption. Discounting this water gives a polymer composition of 1.27 moles polymethyl methacrylate : 1 mole zinc chloride, which is still within the limits for existence of the complex system.

However, regardless of the finer points concerning the analysis of the poly complex, the performance of the polymer was unsatisfactory in the extraction system. Qualitatively immersion of the film samples in water was accompanied almost immediately by the appearance of opacity. At the same time there was an increase in the plasticity of the polymer. On the other hand, after extraction to equilibrium, just one hour's drying at 100°C under vacuum

restored the original brittleness. The original transparency was not recovered even after extended drying for three days. The zinc content of the resulting dry films was sufficient to give a faintly positive result with dithizone colourimetry, but was inestimable by volumetric or gravimetric techniques. Zinc extraction may be regarded as $\geq$ 99% complete.

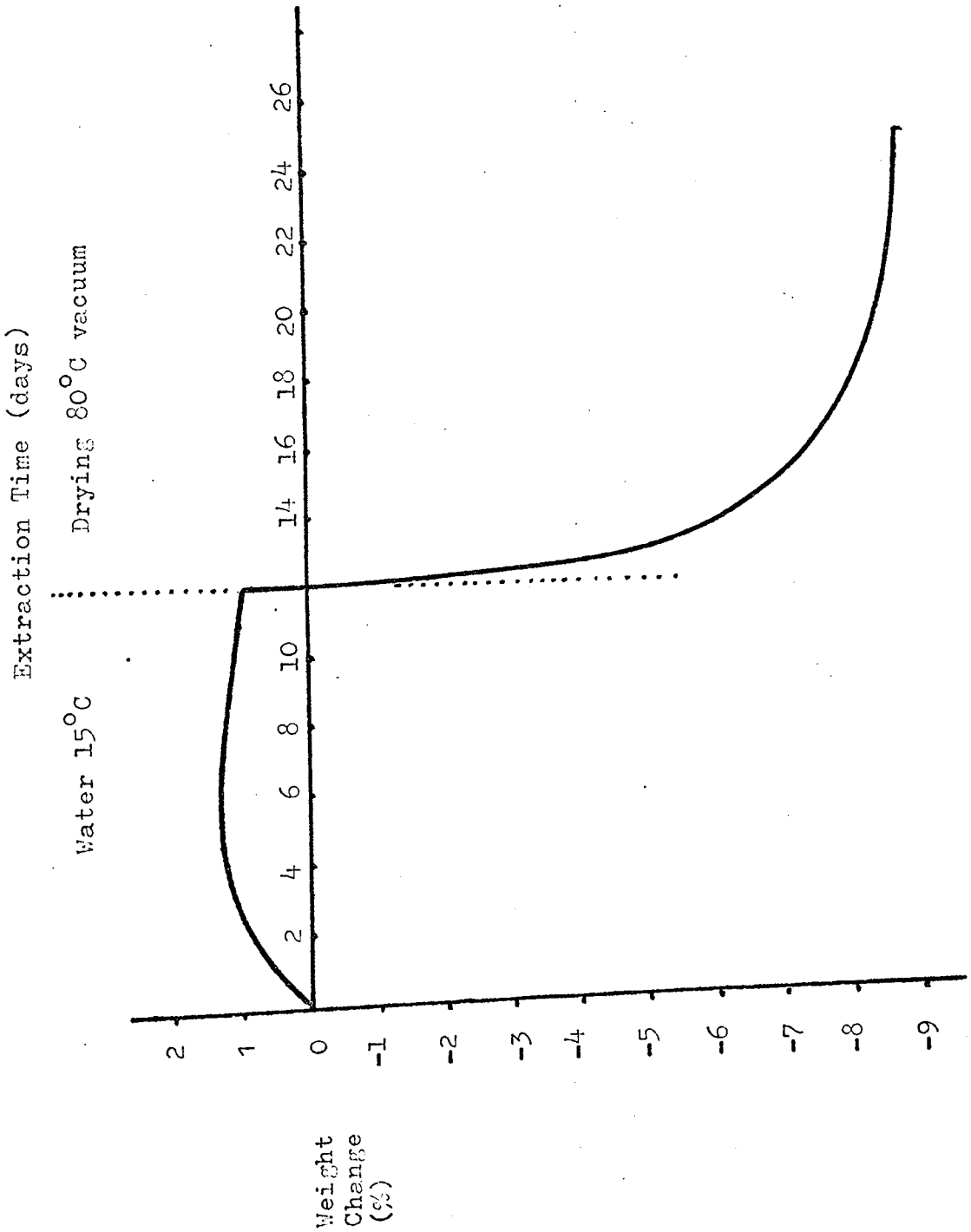
It is thus quite obvious that a denture base formulated on a zinc chloride/methyl methacrylate poly complex would lose all its radiopacity within a week or so of use (depending on the thickness of the various sections).

In addition to this investigation into the properties of films cast from the pure poly complex a dough moulded specimen was also prepared. In this system conventional 'Stellon' polymer was used and the complex formed the monomer phase (a ratio of 10 parts polymer : 4 monomer by weight was employed). The conventional moulding process was adhered to throughout except that the dough was handled through polythene film rather than in the bare hands. The moulding produced in this way was virtually indistinguishable from the control specimen in transparency. Radiography of this specimen yielded a value of $\mu/_p$ of 0.58, consistent with the expected zinc content of 5% Zn. However, as was the case with the pure poly complex the real test of suitability is the stability of the zinc chloride to aqueous extraction. A sample of the dough moulded material 50 mm x 3 mm x 2.5 mm was immersed in distilled water and weighed at intervals as were the film specimens. The results are presented in Graph 3.5.

In terms of preparation and polymerisation of the zinc chloride complex the reported characteristics were confirmed. The reactivity of the complex was considerably greater than that of uncomplexed

GRAPH 3.5

Zinc Chloride Extraction in Water from a Dough Moulding Containing the Polycomplex



methyl methacrylate, and the resulting polymer was of very high molecular weight ($\overline{M}n = 1.02 \times 10^6$). However, the stability of the complex has been found to be very poor in all systems containing solvents for zinc chloride. Thus methanol or water remove effectively all of the zinc chloride probably leaving behind a 'poronic' polymer structure. In view of this instability in an aqueous environment ZINC CHLORIDE WILL BE CONSIDERED NO FURTHER FOR A DENTURE BASE MATERIAL.

3.2 BROMINATED COMONOMERS

3.2.1 p-bromo styrene

Though it is not considered that p-bromostyrene is likely to be sufficiently radiopaque for dental requirements owing to its single bromine atom (though μ/ρ calc = 4.5) it is considered to be a useful model compound. Thus it is felt that should this simple material be suitable in all respects there will be no reason (subject to availability and price) why the di- tri- tetra and penta bromostyrenes should not be satisfactory.

p-Bromostyrene is totally miscible with methyl methacrylate and immiscible with water, thus being quite suitable (reactivity ratios permitting) for copolymerisation in bulk, solution or suspension systems. Reactivity ratios are reported as

r_1 (p bromostyrene) = 1.1; r_2 = 0.39 (116)

there should therefore be no difficulty in achieving high degrees of conversion with respect to p-bromostyrene.

It was decided that, to simulate the dental processes as closely as possible, a suspension polymerisation technique was preferable. Suspension systems are notoriously fickle in small scale preparations, and the optimum conditions of reaction vessel,

temperature, stirrer type and speed, as well as the suspending agents themselves are critical in avoiding coagulation.

So as to conserve the novel monomer, pure methyl methacrylate was used to evaluate a set of polymerisation conditions.

A 500 ml flanged, round bottomed flask was used throughout, equipped with a nitrogen bleed, thermometer pocket, and water cooled condenser. The preferred stirrer was a stainless steel three bladed propeller type which was polished before each polymerisation run. A high speed stirrer motor was used with a maximum speed of 10,000 rpm and a heating mantle and controller provided the heating source.

Suspending systems used were as follows:

I	Methyl methacrylate	75 g	
	Water	150 g	polymerisation 80°C
	ammonium phosphate ($(NH_4)_2HPO_4$)	0.27 g	
	Calcium chloride	1.2 g	
	.880 ammonia	4 ml	
	benzoyl peroxide	0.3 g	
II	Methyl methacrylate	70 g	
	Water	150 g	polymerisation 80°C
	magnesium carbonate powder	7 g	
	benzoyl peroxide	0.2 g	
III	Methyl methacrylate	450 g	After Halpern (15)
	Water	800 g	polymerisation 80°C
	sodium phosphate (Na_2HPO_4)	475 g	
	methacrylic acid	4 - 7 g	
	benzoyl peroxide	2.3 g	

IV	Methyl methacrylate	60 g	
	Water	150 g	polymerisation 65°C
	starch	4.5 g	
	azobisisobutyronitrile (AZBN)	0.3 g	

In all instances, stirring was continued as fast as was consistent with safety.

Only the starch stabilised system IV was found to give reproducibly good results with no tendency to coagulate in the later stages of polymerisation. It was therefore decided to maintain this system for all subsequent polymerisations.

By maintaining the temperature at 65°C for one hour, 80°C for a further two hours and 95°C for a final thirty minutes a polymer with no smell of residual monomer was obtained. After filtration, washing and drying the polymer was examined and found to be virtually identical to 'Stellon':-

Individual polymer particles were largely spherical and of size equivalent to 100 mesh ($\leqslant 150\ \mu$). The resemblance to 'Stellon' is more than one of physical form, graph 3.6 shows the almost identical similarity between their molecular weight distribution curves (obtained by gel permeation chromatography in tetrahydrofuran solution).

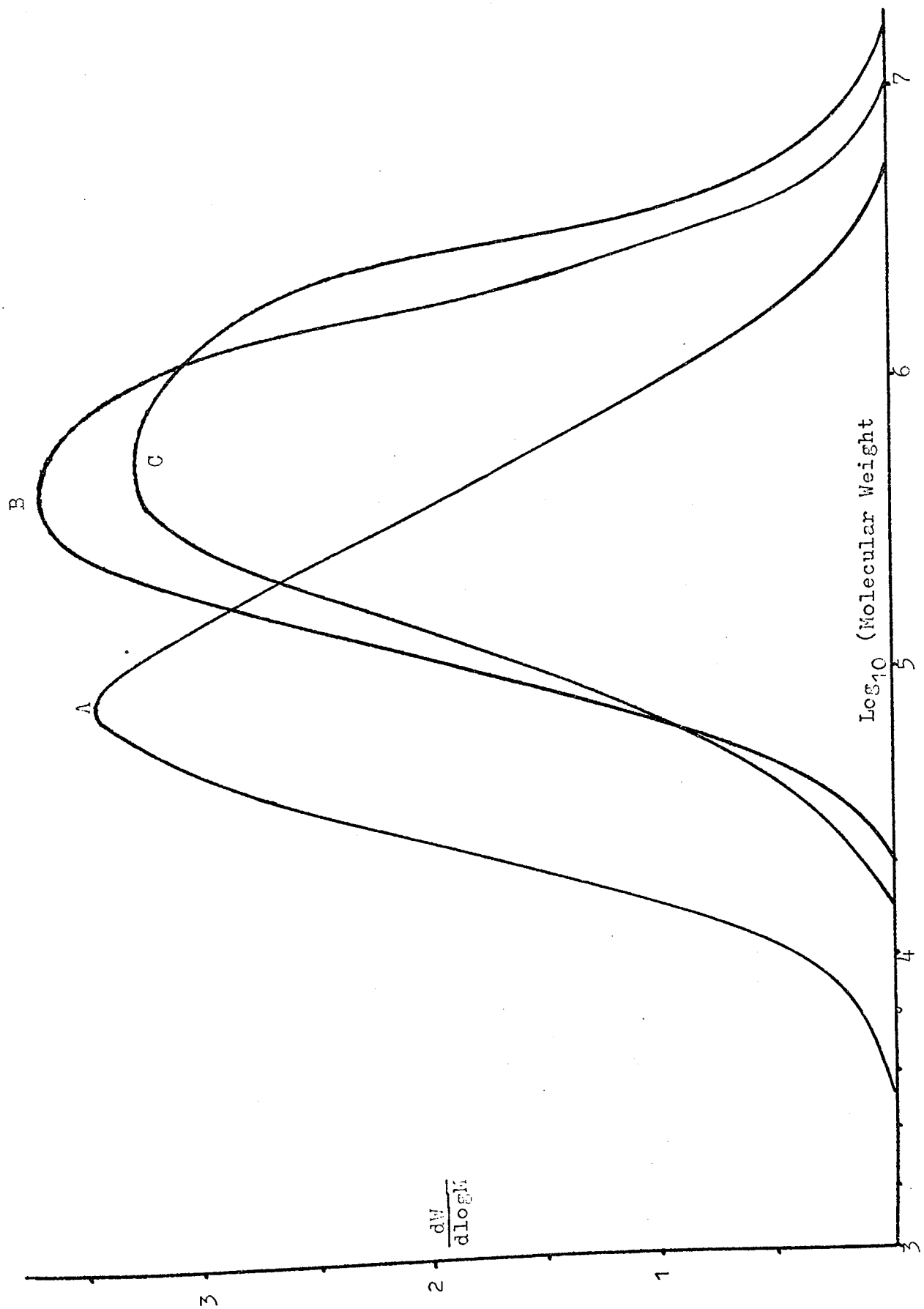
Having thus established the suitability of all the reaction parameters involved it was thought reasonable to investigate the possibilities of copolymerisation.

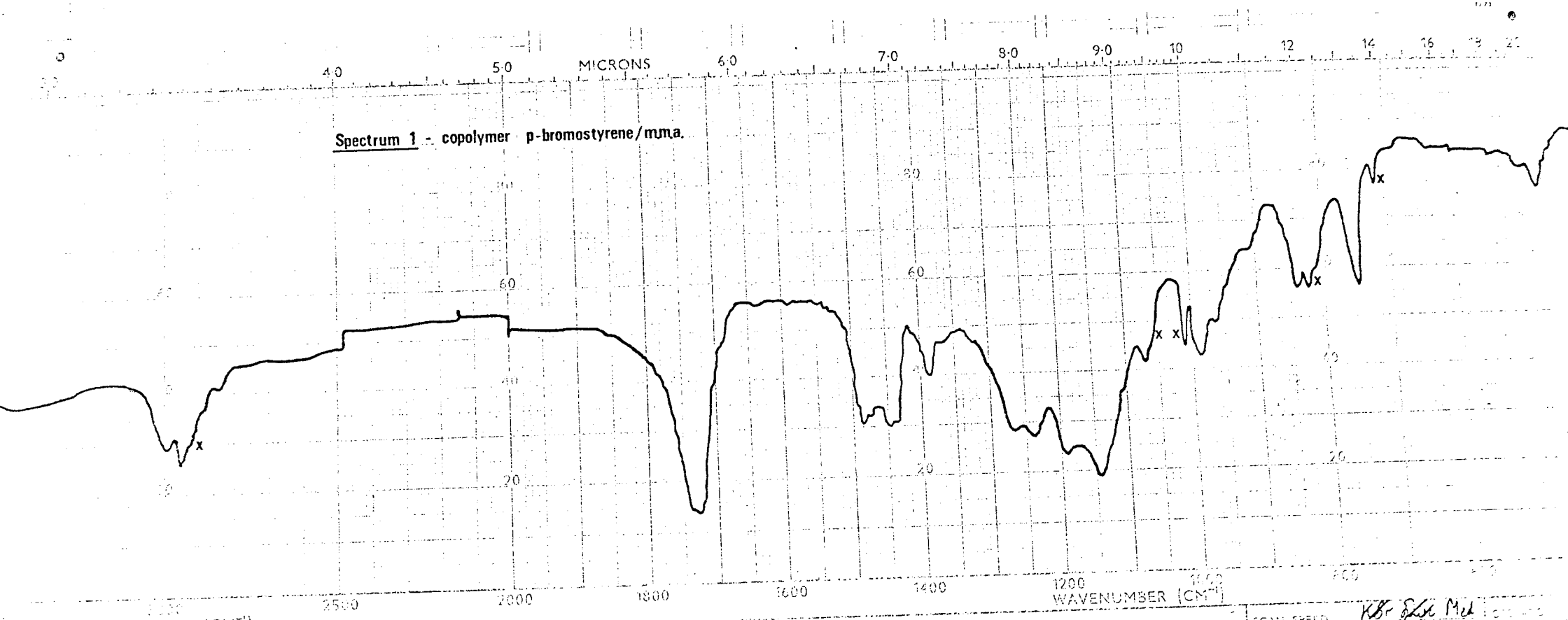
As only a small quantity of p-bromostyrene was available at this time it was decided to use the inhibited material as supplied without further purification. Gas/liquid chromatography did not show any appreciable impurities and thus this was felt to be justified. In order to overcome the inhibitor present the

GRAPH 3.6

Molecular Weight Distribution Curves of

A - p-bromostyrene/methyl methacrylate copolymer
B - laboratory prepared polymethyl methacrylate
C - 'Stellon'





mma pBrSt)

SOLVENT KBr Disc

CONCENTRATION –

CELL PATH –

REFERENCE Air

REMARKS

SCAN SPEED KBr Disc Mid

SLIT N

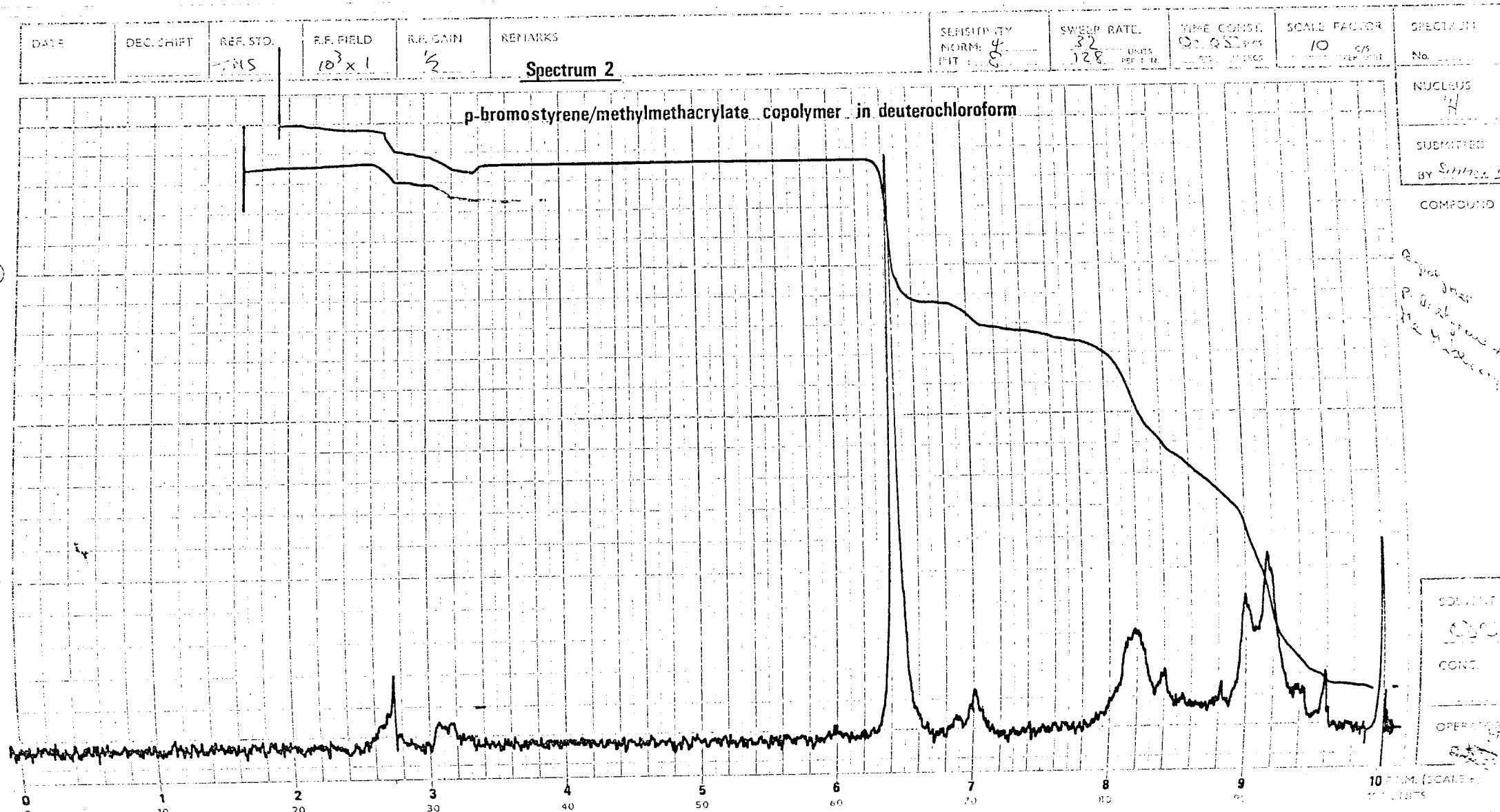
RPK/215/1032 457-5001

Intek

initiator concentration was doubled to 1% of the total monomers.

The previous polymerisation was thus repeated using an 85 : 15 mixture of methyl methacrylate : p-bromostyrene. The prescribed heating schedule resulted in a 92% yield of dry polymer, indistinguishable from the pure acrylic control. It is to be expected from the reactivity ratios that all of the p-bromostyrene is contained in the polymer and that any residual monomer is methyl methacrylate. However, depending on this fact, consideration of the weights involved could give a p-bromostyrene content in the copolymer of 7 - 17%.

The composition of the copolymer was examined spectroscopically. It was hoped that comparison of the absorption peaks in the infra-red region would be adequate. However, although the p-bromostyrene peaks at 9.9, 12.5 and 14 cm^{-1} are apparent in the spectrum of the copolymer (Spectrum 1) they are not sufficiently distinct for quantitative estimation. Nuclear magnetic resonance spectroscopy was more successful. The aromatic hydrogen atoms gave a resonance sufficiently remote from the aliphatic hydrogens to be readily identifiable despite the peak broadening and confusing effects from the random nature of the copolymer (Spectrum 2). Thus from the integrated curve 9.7% of protons are found to be aromatic, hence 17% derive from p-bromostyrene. This figure gives rise to a copolymer composition of 19.5 moles % p-bromostyrene or 11.5% w/w. Unfortunately, if the calculation is based on the sharp peak at 6.43 ppm (deriving from the $-OCH_3$ protons of methyl methacrylate) this yields a figure of 77.5% w/w methyl methacrylate. This figure is of course not consistent with the weights observed in the system. Indeed, if the small peak at 7 ppm is included in this calculation, the resulting copolymer composition obtained is 12% w/w p-bromo-


DATE
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TMS
R.F. FIELD
$10^3 \times 1$
R.F. GAIN
REMARKS
Spectrum 2
SENSITIVITY
NORM:
FIT:
SWEEP RATE
32
128
TIME CONST.
SCALE FACTOR
10
SPECTRUM No.
NUCLEUS
^1H
SUBMITTED BY
COMPOUND
p-bromostyrene/methylmethacrylate copolymer in deuterochloroform
0
1
2
3
4
5
6
7
8
9
10

styrene. Theoretical justification for this procedure is not apparent though it is feasible that when adjacent to p-bromostyrene units in the polymer chain the signal from the methoxy protons is shifted.

The 12% figure was confirmed to some extent by radiography of a dough moulded sample. This yielded a figure for $\mu/\rho = 0.61$ equivalent to a concentration of 8 - 10% p-bromostyrene in the moulding or 12 - 14% in the copolymer.

In terms of moulding properties the laboratory prepared polymethyl methacrylate behaved excellently, doughing and flow in the mould were very similar to the control. Unfortunately the moulded specimens were white and virtually opaque. This applied equally to the pure polymethyl methacrylate sample and the copolymer and can thus only be attributed to residual starch from the polymerisation. This fact is borne out by the transparency of bulk copolymerised samples both at 15% and 50% p-bromostyrene. (These polymerisations were effected in test tubes sealed under nitrogen and suspended for several days in a water bath at 50°C, after which the glass was broken away to yield polymer rods.) The doughing properties of the copolymer were somewhat less than ideal though acceptable. Absorption of the monomer by the copolymer particles was rather rapid, leading to some difficulty in achieving homogeneity and eliminating dry areas. However, having overcome this difficulty by more rapid mixing the resulting dough had excellent flow properties, though as mentioned above the resultant plaque was quite opaque. Physical property assessment of the specimens are summarised in Table 3.1.

From this table it is apparent that, though some spread is observed in results, there is no catastrophic deterioration in

TABLE 3.1

FLEXURAL STRENGTH OF P-BROMOSTYRENE COPOLYMER

Sample	Flexural Strength (Nmm^{-2})		Initial Modulus (Nmm^{-2})		Deflection (mm)	
	Dry	Wet	Dry	Wet	Dry	Wet
"Cross linked Stellon" Control	80	83	0.58	0.506	6.4	7.5
Laboratory prepared pmma	81.3	74.3	0.525	0.493	6.8	7.0
Copolymer	73.2	70.8	0.505	0.477	7.1	7.8
"Stellon"/ non cross linked monomer	82.1	84.3	0.66	0.52	6.8	7.0

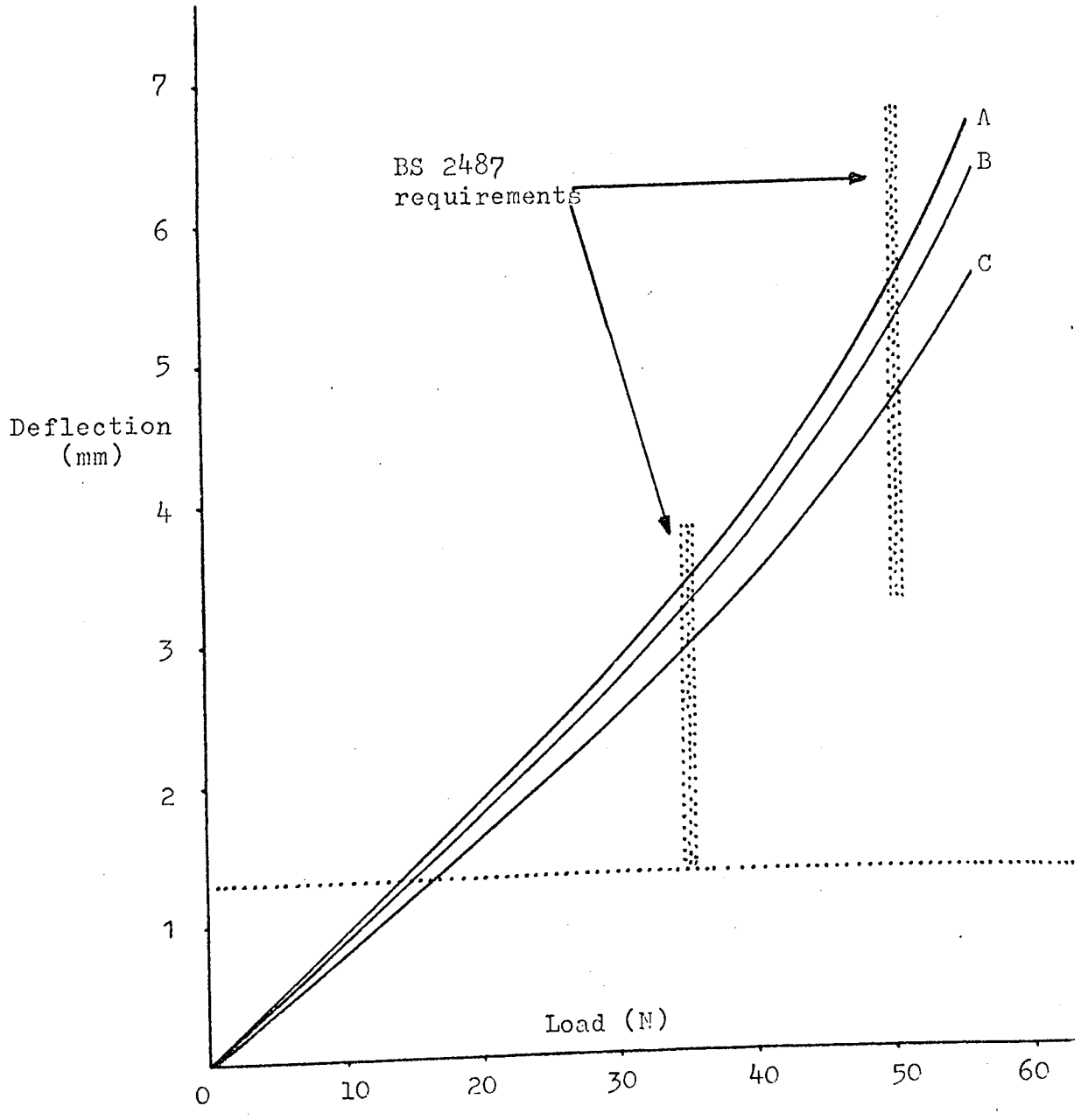
properties associated with the incorporation of p-bromostyrene in the polymer. Modulus values are virtually identical throughout and the deflection at break results are all quite acceptable. The slight depression in the flexural strength of the copolymer samples is not sufficient to be significant and the dental specification is still complied with (Graph 3.7).

The opaque samples produced would not be satisfactory from a dental standpoint, however it is felt that more attention to the polymerisation would produce a material capable of giving a transparent moulding. On the other hand the opacity of the sample implies absorption of visible light, and also presumably some portion of ultra violet light, hence the sensitivity of the standard UV stability test should be enhanced.

The major cause for concern about the properties of brominated

GRAPH 3.7

Stress/Strain Curves Related to British Standard Requirements for
A - pbromostyrene/mma copolymer
B - laboratory prepared pmma
C - 'Stellon'



polymers has been assumed to be their stability to UV radiation. No discolouration could be detected when the dough moulding of the p-bromostyrene copolymer was subjected to the standard UV stability test. In an attempt to produce more rigorous test conditions a 300 W UV lamp was used at a distance of only 10 cm from a stationary sample just covered with water. Owing to the heat build up in this system it was considered unsafe to leave for twenty four hours. However, three eight hour exposures over a period of three days produced only a barely visible colouration. This result was equally true of the dough moulding and the copolymer powder.

It thus appears that there are no reasons of physical significance which would preclude the use of brominated aromatic comonomers in dental acrylics. However, the properties of p-bromostyrene-rich copolymers are likely to resemble those of polystyrene rather than acrylics and in the same way would be unlikely to be a very widely accepted denture material. Thus, rather than having a high percentage of a monobromo- compound it would seem to be preferable to use a lower concentration of a more highly substituted material. It has unfortunately proved impossible to locate suppliers of polybrominated styrenes, even Laporte who used to use dibromostyrene as a polyester flame retardant had no knowledge of present availability. However, supplies of tribromophenyl acrylate and pentabromophenyl methacrylate were ordered from Polysciences Ltd. Despite the fact that these materials were advertised as commercial flame retardants the prices quoted would be prohibitive for dental applications. The order for tribromophenyl acrylate was cancelled on advice that 100 gm would cost £136! However it was still felt that one compound of this type should be considered and the pentabromophenyl methacrylate was chosen for its maximum bromine content.

3.2.2 Pentabromophenyl methacrylate

As supplied (at £36 for 50 g) the material was a brownish yellow powder. Recrystallisation from hot chloroform yielded virtually white needle crystals (mp 227°C) together with around 2 - 3% insoluble powder. The crystalline material thus obtained was only slightly soluble in cold methyl methacrylate, but more so at higher temperatures. Thus it was possible to dissolve 8% pentabromophenylmethacrylate (pbpma) in unstabilised methyl methacrylate at 45°C in a test tube, 0.5% Azobisisobutyronitrile was added and nitrogen bubbled through the solution. The tube was then stoppered and polymerisation effected at 55°C for three days. The resulting polymer was completely transparent though straw coloured. (Attempts to include higher concentrations of pbpma led to the appearance of crystals in the polymer.) After cracking off the test tube, the polymer rod was post cured at 100°C for twelve hours and then ground in a hammer mill to 80 mesh (180 μ).

This powder was then dough moulded in the normal way, and though the moulding characteristics were adequate the cured material was distinctly yellow and particulate. Physical properties of the moulding were as follows:

3.2.2.1 Mechanical Properties

	Wet	Dry	Stellon Dry	Stellon Wet
Flex Strength (Nmm^{-2})	60.2	64	80	83
Modulus (Nmm^{-3})	0.53	0.58	0.58	0.51
Deflection (mm)	4.1	4.1	6.4	7.5

3.2.2.2 Exposure to UV light in the standard test had no discernable effect on the already yellow material.

3.2.2.3 Radiography - μ/ρ of dough moulding - 0.79 (5.8% pbpma).

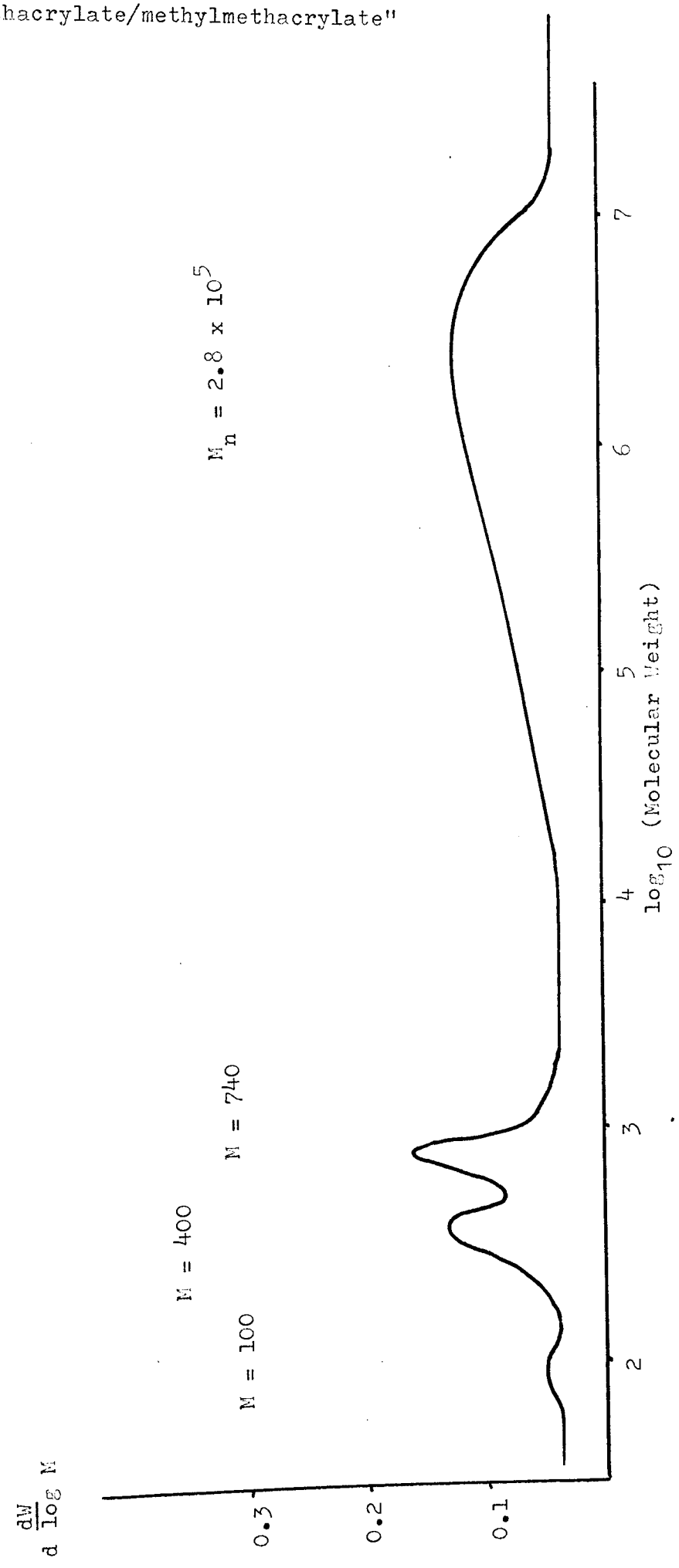
There is a marked increase in the brittleness of the polymer (shown in the drop in ultimate strength values and deflection at break), with little change in the modulus. This effect is more marked than would be predicted for a copolymer containing only 8% pbpma in view of the effects of a 15% p-bromostyrene copolymer. A low molecular weight was suspected of being the cause of the inferior properties. Gel permeation chromatography results however gave a figure of Mn = 2.8×10^5 and 4.2×10^5 for two separate polymerisations. This is effectively the same as that of 'Stellon' polymer (Mn = 2.49×10^5) and thus cannot be the cause of the weakness. However, consideration of the gpc curve (Graph 3.8) rather than simply the number average molecular weight suggests an explanation:- In each determination two peaks corresponding to low molecular weight material were evident, one at Mn $\sim$ 400 and the other Mn $\sim$ 740. The intensity of the peaks suggests a high concentration of these materials, though this may have been exaggerated by the preferential solution of low molecular weight material by the tetrahydrofuran solvent. A further small peak is seen at Mn = 90-100, this was almost certainly residual methyl methacrylate monomer. It was noted that the above two peaks could well correspond to a single species, the 740 peak being a dimer of the lighter one. However the empirical formula weight of pbpma is 557 (C_{10} H_5 Br_5 O_2) and even allowing for instrumental inaccuracy at low molecular weights this could not correspond to the observed peaks.

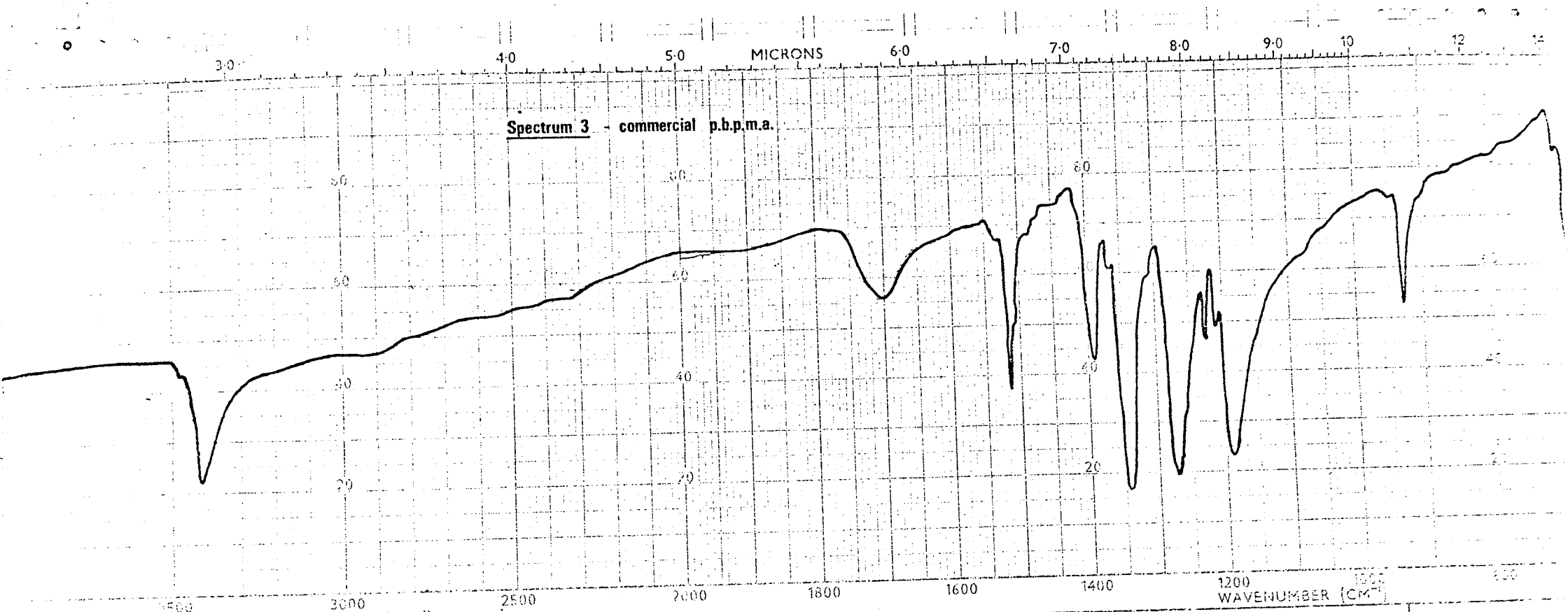
Thus the presence of a significant concentration of impurity in the pbpma is suggested.

I R spectra on the commercial and recrystallised pbpma together with the insoluble impurity showed startling results (spectra 3, 4,

GRAPH 3.8

Molecular Weight Distribution Curve for
"Pentabromophenylmethacrylate/methylmethacrylate"
Copolymer





2 commercial p b p m a

G. Simmons

SOLVENT KBr Disc

CONCENTRATION -

CELL PATH -

REFERENCE Air

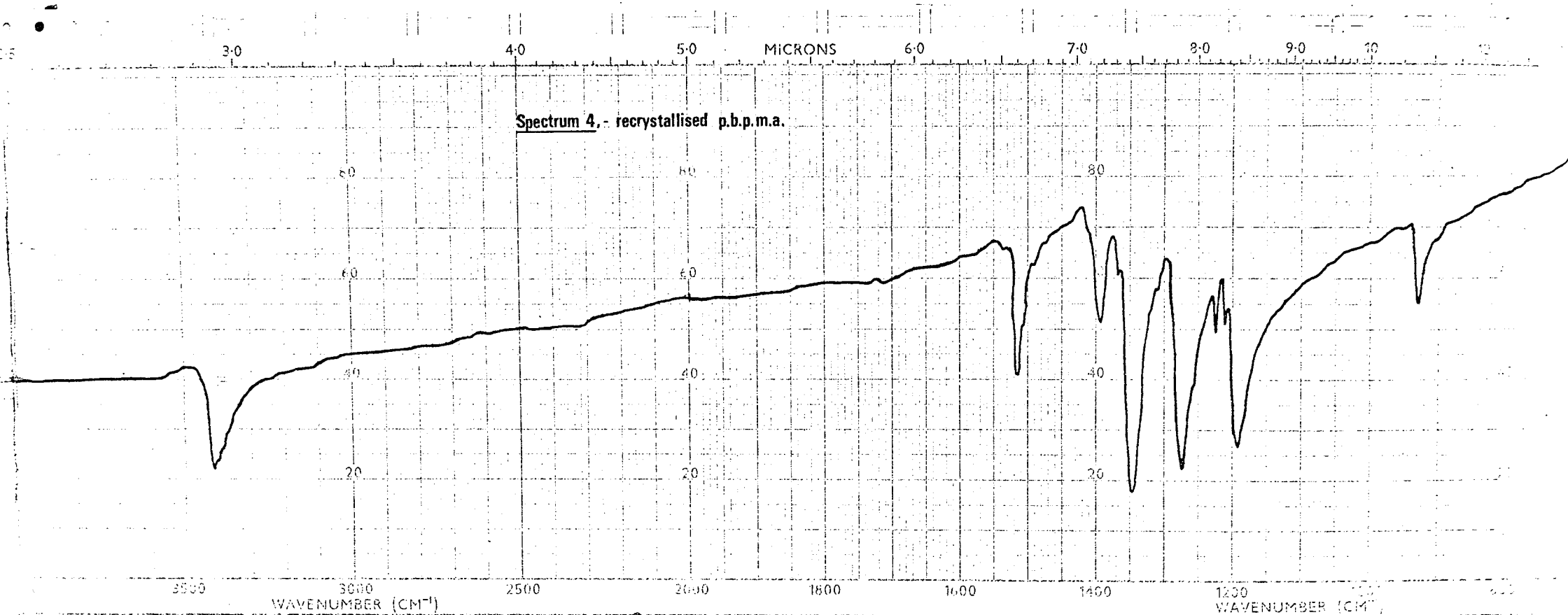
REMARKS

SCAN SPEED

SLIT

RPK/215/

Intek



1/ rest. pentabromophenylmethacrylate?

E.J. Quinnell

SOLVENT KBr Disc

CONCENTRATION -

CELL PATH

REFERENCE Air

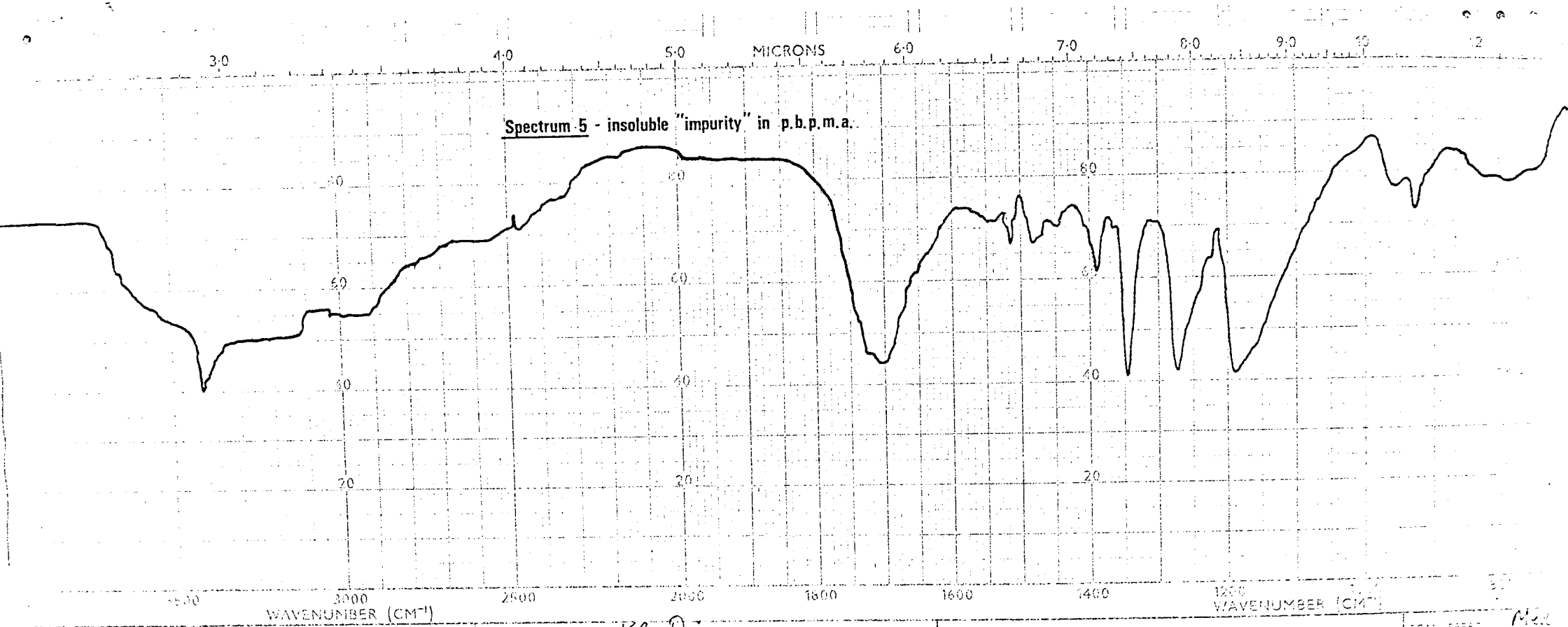
REMARKS

SCAN SPEED

SLIT

RPK/21[illegible]

Intek



3/ insol impurity in pbpma

G Simmons

SOLVENT KBr Disc

CONCENTRATION —

CELL PATH —

REFERENCE Air

REMARKS

Intek

5 respectively). The carbonyl absorption at 5.9 μ (1710 cm^{-1}) was very weak in the commercial material and totally absent after recrystallisation, only appearing strongly in the insoluble material. In addition a moderately strong absorption at 2.95 μ (3400 cm^{-1}) suggests a phenolic compound. The reported melting point of pentabromophenol is 229° - that of pure pbpma could not be found in the literature, that determined for the compound in question - 227°C.

Though specimen I R spectra for pbpma and pentabromophenol were not available, one of pentachlorophenol was obtained. Though obviously not identical, the similarity in the number of peaks, their relative intensities and approximate positions suggest the close similarity of the compounds. Further confirmation for this suspicion is provided by detection of a phenolic proton at 3.4 ppm by n m r spectroscopy in deuterated acetone (spectrum 6) (the band at 7.9 ppm on this spectrum is assigned to hydrogen impurity in the solvent - it was absent in deuterochloroform solution). Following up this spectroscopic analysis, a simple solubility test was performed:- a phenol would be expected to dissolve in methanolic sodium hydroxide whereas methacrylates are in general stable to alkaline hydrolysis. The sample of 'pbpma' dissolved to give a yellow solution, neutralisation with hydrochloric acid caused reprecipitation. Methanolic sodium hydroxide also extracted material from the powdered 'copolymer' to give the same yellow solution.

It was thus concluded that the material supplied by Polysciences Ltd was probably pentabromophenol and not pentabromophenyl methacrylate, though a trace of poly pentabromophenyl methacrylate may have been present as the insoluble 'impurity'. However these findings

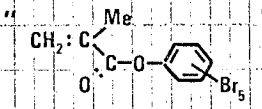
DATE	DEC. SHIFT	REF. STD.	R.F. FIELD	R.F. GAIN	REMARKS	SENSITIVITY	SWEEP RATE.	TIME CONST.	SCALE FACTOR	SPECTRUM
61173		TMS	$10^3 \times 1$	4/2	not very soluble – heated D$_6$ acetone below 40°	NORM: 8 INT :	32 128 UNITS PER TIME	0.05 SECS. 0.15 10 SECS.	10 C/S PER UNIT	No.

NUCLEUS 1H

SUBMITTED BY SIMMONS

COMPOUND

Spectrum 6



" " in deuterated acetone

SOLVENT Acetone

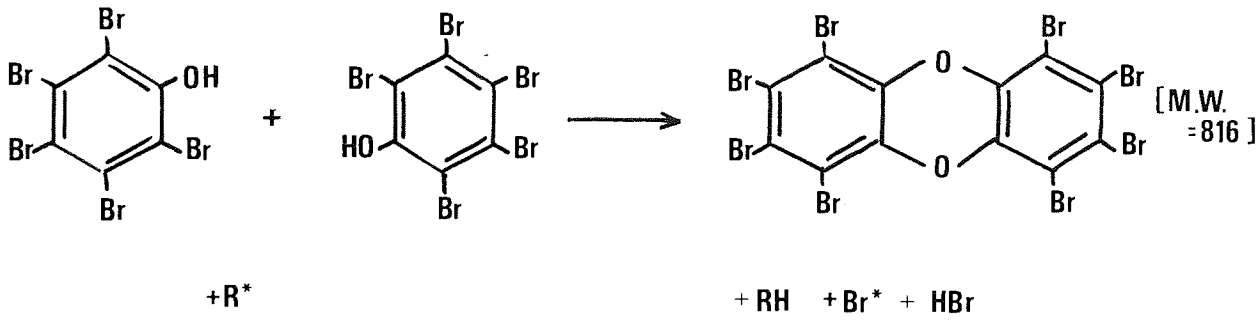
CONC.

OPERATOR HTH

0 1 2 3 4 5 6 7 8 9 10 PPM (SCALE 1)

0 10 20 30 40 50 60 70 80 90 100 CYCLES

do not help in assigning the gpc peaks at 400 and 740 as pentabromophenol has a molecular weight of 489. It is feasible though, that in the presence of free radicals in the polymerisation system the phenol could undergo a coupling reaction with itself:



Owing to the difficulty in accurately interpreting low molecular weights from the logarithmic scale of the gpc curve it is considered reasonable that these figures could be appropriate to the above scheme.

Confirmation or otherwise of the existence of such a dimer is beyond the scope of this investigation.

Unfortunately, owing to the long delays involved in obtaining this sample from the United States, and subsequently in its evaluation, there has not been time to obtain a new sample of the correct material. This study therefore had to be left incomplete and though this was obviously unsatisfactory from the point of academic interest an acceptable commercial product could not result. The price of the compound could never approach the £1 per pound specified even if large quantities were to be ordered.

Similarly, though their suitability was indicated by all testing, thus far completed, the bromostyrenes, especially at high levels of

bromination are prohibitively expensive.

In conclusion, it is felt that aromatically brominated comonomers are capable of satisfying the requirements for a radiopaque denture base material in all respects save that of economy. Owing to the essentially objective nature of this industrial project the long term toxicology and extractibility studies have thus been shelved and attention centred on the quest for an economic alternative.

CHAPTER 4

POLYMERS AND COPOLYMERS OF ZINC ACRYLATE

In earlier attempts to include a potentially interacting filler into a denture, the material was added as a powder at the doughing stage. Heavy metal salts are invariably insoluble in methyl methacrylate and this means that there is little chance of copolymerisation taking place except at the particle surface. The net result was that mouldings produced in this way were similar to those containing barium sulphate filler, with all the attendant problems of optical opacity and loss of strength. In addition unpolymerised zinc acrylate is readily soluble in water and would be rapidly extracted.

It is thus intended that zinc acrylate be first copolymerised with methyl methacrylate to form the polymer phase for dough moulding with further monomer. In this way it is hoped to achieve a high degree of interaction between the two phases and hence a homogeneous moulding.

The first step then is to devise a suitable system for this copolymerisation.

4.1 DEVELOPMENT OF A POLYMERISATION SYSTEM

To produce a copolymer it is essential that the monomers be in the same state, and thus of prime importance in the development of the system is the consideration of solubility data.

4.1.1 Methyl methacrylate: is miscible with most organic solvents,

immiscible with water. The polymer is soluble in solvents of solubility parameter δ = 8.5 - 10, eg acetone, chloroform, toluene, and methyl methacrylate monomer.

4.1.2 Zinc acrylate: is soluble in highly polar solvents, water, acetic acid, acrylic acid and methanol. A very slight solubility in acetone was also detected but none in methyl methacrylate.

Isolation of a polymer from a solution polymerisation invariably involves precipitation in a non solvent, it is thus difficult on an industrial scale to produce a fine powder free from residual solvent. If possible then a solvent free system is to be preferred. Ideally a suspension system would be desirable, but the solubility of zinc acrylate in water means that a non aqueous continuous phase would be required. Selection of a suspending medium in which neither monomer is soluble still does not solve the problem owing to their mutual insolubility.

It is thus apparent that a solvent based system is inescapable though a choice of solvents is available and the solution could subsequently form the suspended phase in a suspension polymerisation in a mutual non-solvent. To avoid the inclusion of volatile solvents in the copolymer preliminary studies were made on systems using acrylic acid as a polymerisable solvent in minimal concentrations.

4.1.3 Zinc acrylate/acrylic acid: It was found that up to 10% zinc acrylate dissolved quite readily in hot acrylic acid to give a clear solution. However, if solution was carried out in unstabilised acrylic acid violent polymerisation took place to give a hard white glassy polymer. A high degree of cross linking was indicated in this material by its insolubility in water. Swelling was

effected by boiling water or sodium hydroxide solution but no solvent was found, and the material was infusible by heat, it burned in air to zinc oxide without intermediate melting.

In a second experiment 10% zinc acrylate was dissolved in hot stabilised acrylic acid, on addition of an equal volume of methyl methacrylate a precipitate was formed. After filtration benzoyl peroxide was added (1% to overcome residual stabiliser) and polymerisation effected at 80°C under nitrogen. The polymer was produced as a clear hard gel soluble in methanol and THF. Analysis showed a zinc acrylate content of only 0.5%, the remaining zinc acrylate constituting the precipitate filtered off previously.

It was thus concluded that acrylic acid alone was not a sufficiently good solvent to provide a bridge between zinc acrylate and methyl methacrylate.

An assessment was therefore made of solvent systems containing alcohol which would subsequently be distilled out during polymerisation.

4.1.4 Zinc acrylate/acrylic acid/alcohol: Zinc acrylate was dissolved in a mixture of equal volumes of acrylic acid and ethanol to give a 5% w/v solution. A faint haziness was filtered off. Inhibitor free methyl methacrylate was then added (1 : 1 with the acrylic acid) followed by benzoyl peroxide (0.5% on monomers). Polymerisation was then commenced by heating under nitrogen, with the apparatus set up for distillation. As the temperature reached 80°C the viscosity of the solution was seen to rise, and ethanol began to distill out steadily. The transparency of the system was maintained throughout the polymerisation though the final solid polymer was a white foam. At the point of solidification some 65% of the ethanol had distilled out, together with a trace of

methyl methacrylate. The polymer produced was once more a highly cross linked infusible mass.

A similar polymerisation employed methanol rather than ethanol so as, hopefully, to achieve better separation from methyl methacrylate in the distillation due to the difference in their boiling points. However, after final drying of the polymer under vacuum at 90°C the resulting bulky white foam contained 16% zinc acrylate, implying that ~ 50% of the comonomers had been evaporated off. Methyl methacrylate being much more volatile than acrylic acid (bp 100°C against 142°C) it was to be expected that the copolymer would be largely acrylic acid.

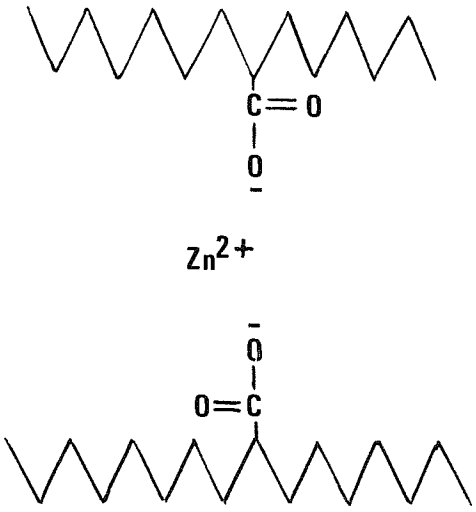
Analysis of this polymer was made by dissolution of a weighed sample in 10% sodium hydroxide solution. Water insoluble polymer was precipitated by neutralisation with dilute hydrochloric acid and filtered off, washed, dried, and weighed. The aqueous solution was then analysed for zinc by precipitation as the phosphate.

The results obtained were -

zinc poly acrylate	16.26%
water insoluble polymer	57.98%
Total	74.24%

There is thus some 25% of water soluble material in the copolymer. The drying conditions preclude the possibility of this being methanol, and residual monomer is unlikely owing to the reactivity of the materials involved. It was thus concluded that this 25% of water soluble material was linear polyacrylic acid. The water insoluble polymer was likewise concluded to be a copolymer of methyl methacrylate and acrylic acid. The complete solubility of the sample in dilute alkali proved the absence of homo polymethyl methacrylate and cross linked homopolyacrylic acid.

Cross linking in the polymer is largely due to the divalent zinc ions



(The zinc acrylate is represented in its ionised form, though the extent of ionisation in the system is not known.)

It is readily seen that sodium hydroxide will rapidly and totally break this type of cross links to yield the sodium polyacrylate and sodium zincate. Attack of the potential homopolyacrylic acid cross links would be less rapid and less efficient.

The high proportion of acrylic acid in this terpolymer system was confirmed by a further observation. A dough moulding was prepared using powder ground from the foamed polymer, and 'Stellon' monomer. On immersion in water this moulding rapidly became rubbery and sticky to the touch. It was not considered worth evaluating the physical properties of a material so fundamentally unsuited to the oral environment.

The use of acrylic acid in the polymerisation system as a vehicle for zinc acrylate inclusion thus appears to be unworkable. It is required at a high concentration to achieve compatibility, and at such a concentration it destabilises the final polymer in an aqueous environment.

It thus became necessary to consider an alternative solution

polymerisation system.

4.1.5 Zinc acrylate/methanol: It has already been established that zinc acrylate is very soluble in methanol (§ 2.2), and on heating the solution a fine precipitate of polymer is produced.

A copolymerisation system based on methanol as solvent was therefore used. Zinc acrylate (2 g) was dissolved in methanol (5 ml) and methyl methacrylate (20 ml), containing 0.5% benzoyl peroxide initiator, added. Polymerisation was effected in a current of nitrogen on a water bath at 80°C. The apparatus was arranged for methanol to distill out in the later stages of polymerisation. During polymerisation a white crust was seen to form around the liquid surface, though a clear solution of increasing viscosity was present in the bulk of the material. Heating was stopped before the mass solidified and the now rubbery liquid phase transferred to a Petri dish which was held at 100°C to cure off residual monomer for one hour before vacuum was applied. The zinc acrylate content of the dry polymer was determined to be 14.6%. This was estimated by gravimetric analysis, weighing zinc as the phosphate and was not detectably reduced by a 24 hour soak in water at room temperature. Consideration of the reactant weights, the loss of volatile material in the drying processes, and the fact that in a closed system the conversion with respect to non-volatile zinc acrylate is close to 100%, leads one to predict a zinc acrylate content of 36%. The lower figure determined (if reliable) means that the observed crust formed during polymerisation was almost pure zinc polyacrylate.

In order to attempt to maintain compatibility throughout the polymerisation the practice of distilling out solvent during polymerisation was dropped. Thus a repeat of the above polymerisation under reflux showed no precipitation during one hour's

reaction over which time a considerable rise in viscosity was observed. After this time, the solution, which by now was slightly hazy, was transferred to a beaker and the polymerisation completed in an oven at 80°C through which a current of nitrogen was passing. (This procedure was adopted to avoid solidification of the polymer within a narrow necked flask.) After a further hour, vacuum was applied to remove residual methanol, leaving 5.8 gm of hard translucent foam. During this drying process a large percentage of the methyl methacrylate monomer was lost. Thus a monomer feed of 1 : 10 zinc acrylate : methyl methacrylate produced a polymer containing 33% zinc acrylate (calculated from consideration of weights involved). This polymer was insoluble in monomer though somewhat swollen as it was in acetone. This polymer is designated 'C1'.

4.1.6 Zinc estimation techniques used on the various copolymers

With the increasing zinc content, and hence the higher degree of cross linking, the gravimetric technique for zinc estimation became less reliable. The method used to effect solution of the zinc up to this point had been a double digestion under reflux, first in acetone for three hours after which an equal volume of 10% methanolic sodium hydroxide solution was added and digestion continued for a further three hours. This treatment was sufficient to dissolve polymers containing less than 10% zinc acrylate and thus on subsequent neutralisation and precipitation with ammonium phosphate solution ($(NH_4)_2H\ PO_4$) it was safe to assume that zinc estimation was quantitative. Higher zinc contents in the polymer, as in the latest two polymerisations rendered the material insoluble, and even the rigorous conditions described produced only a swollen gel. It was thus apparent that a new analytical procedure was required for the reliable detection and estimation of zinc in

highly cross linked polymers. Pyrolysis under nitrogen in a thermogravimetric analyser was the technique arrived at. Initially nitrogen was the only carrier gas used but this was later modified to give more consistent results (Chapter 2) by burning off the residual char in oxygen. A calibration curve for the nitrogen pyrolysis was then constructed (Graph 4.1) from which zinc acrylate contents could be read. Graph 4.2 shows the TGA traces for the pre-C1 methanol solution polymer and it is immediately obvious that the zinc extraction system was not very effective. The zinc acrylate content determined by the extraction/precipitation method was 14.6% (see above) which correlates well with the difference observed in the results from the TGA before and after the digestion process:

Before digestion - 23% zinc acrylate

After digestion - 9% zinc acrylate

hence zinc acrylate extracted - 14%

TGA also detects a zinc loss after the water extraction which gravimetric analysis did not show

Before extraction - 23%

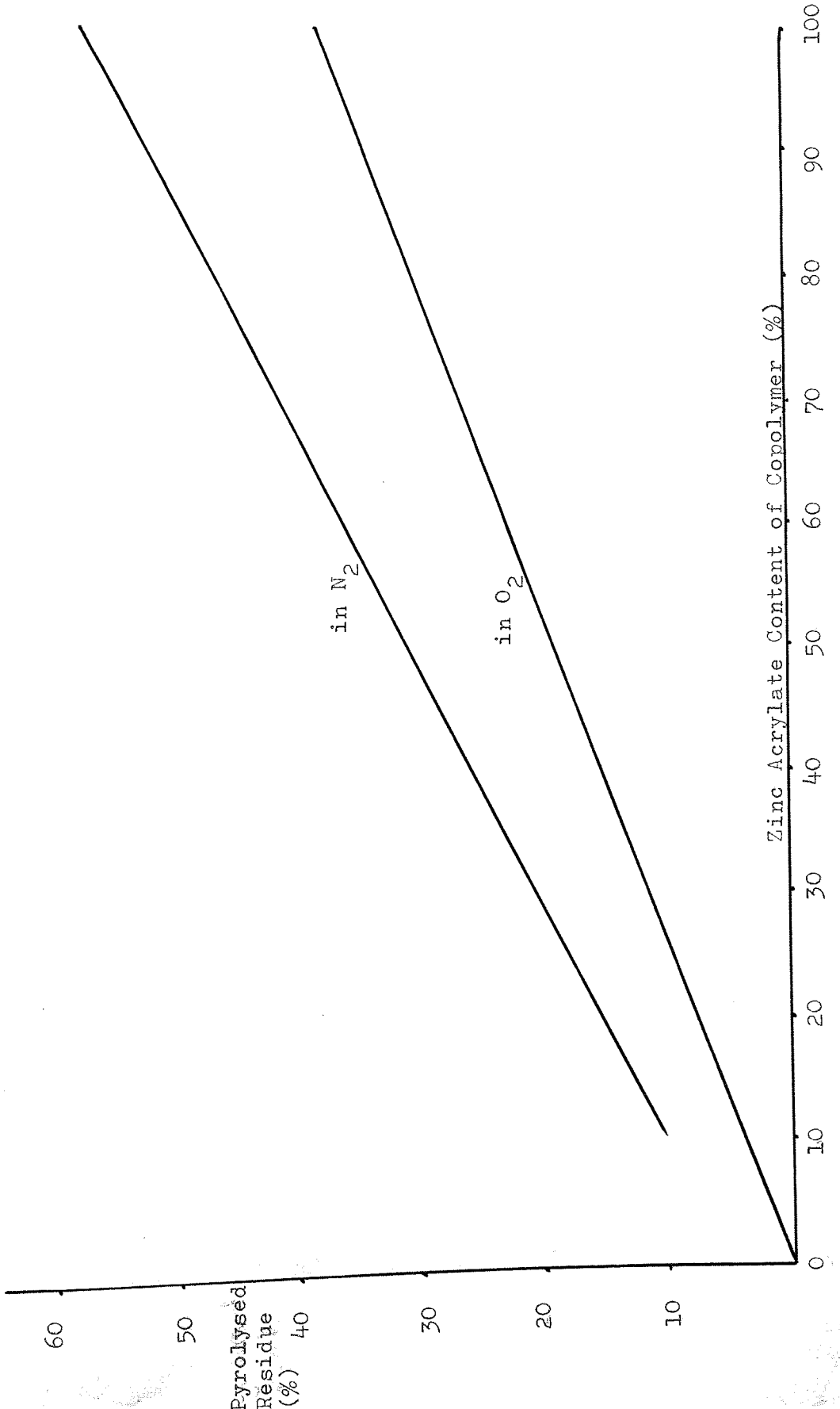
After extraction - 12%

Evaporation to dryness of the extractant solution yielded a white powder which analysed as zinc acrylate, and by its aqueous solubility must of necessity have been monomeric. The observed weight loss in the sample during extraction was 12% which again agrees well with the TGA result. (This figure seems to indicate the efficiency of the digestion system after the 24 hours aqueous soak, though the reason for this is not apparent.)

It was thus decided that future analyses should be by TGA pyrolysis and the gravimetric technique should be discontinued.

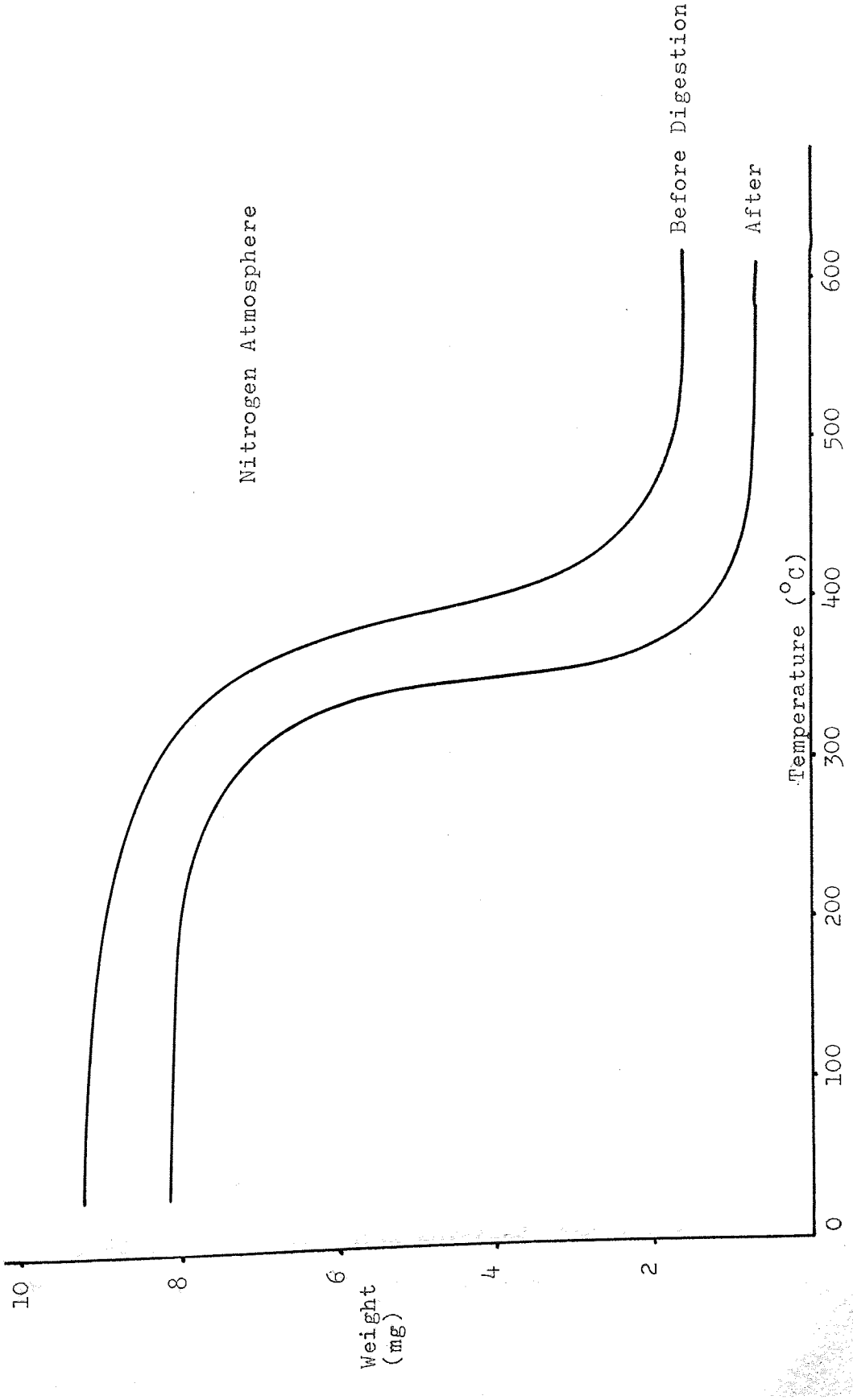
GRAPH 4.1

Calibration Curves for Thermogravimetric Analysis of Zinc Acrylate Copolymers



GRAPH 4.2

TGA Curves for the 'Pre Cl' Zinc Acrylate Copolymer
Before and After Digestion for Wet Analysis



TGA on the copolymer C1 gave a zinc acrylate content of 36%, in agreement with that estimated from consideration of the weights involved.

4.1.7 Further development of the polymerisation system

The translucency and degree of inhomogeneity in the cured polymer C1 was ascribed to the breakdown of compatibility in the latter stages of the polymerisation. As long as an appreciable concentration of methyl methacrylate monomer was present compatibility and clarity was maintained. When methanol took over as the predominant solvent, even homopolymethyl methacrylate would precipitate.

It appears that an ideal polymerisation system must contain solvents for as many of the chemical species possibly present as can be achieved -

Methanol is a solvent for zinc acrylate, and is miscible with methyl methacrylate.

Acetone is a (poor) solvent for zinc acrylate, is miscible with methyl methacrylate and is a solvent for polymethyl methacrylate.

As far as is known, no solvent is reported for homo zinc polyacrylate which does not cause its decomposition.

The system devised for copolymerisation 'C2' was therefore an acetone rich solution, though containing sufficient methanol to keep the zinc acrylate in solution:-

Zinc acrylate (1 g) was dissolved in methanol (2 ml) and acetone (5 ml) added, followed by uninhibited methyl methacrylate (10 ml) containing benzoyl peroxide initiator (0.1 g). Polymerisation was effected in an atmosphere of nitrogen under reflux (60°C). After two hours, polymerisation was well advanced, and a further 5 mls of acetone was added down the condenser to keep the polymerising

mass liquid. After a further hour, solidification appeared to be imminent so heating was stopped and the rubbery gel transferred to a polythene covered glass plate. There it was covered with a further layer of polythene and glass, and pressed into a plaque of 1-2 mm thickness. In order to allow slow evaporation of solvent from the polymer the gel was maintained at a temperature of 40°C for 4 days. The glass and polythene were then removed and the now-solid though flexible plaque finally dried at 80°C, applying vacuum in the final stages. Throughout these processes the transparency of the polymer was maintained, and though some bubbling was apparent in the final product the bulk of the material was quite clear.

The success of this system demonstrated that the cause of opacity in previous polymers had been correctly diagnosed as a breakdown in compatibility.

'C2' was a small scale trial system, and the same formulation was repeated in polymers 'C3' and 'C4'. 'C3' was not prepared in the plaque form, but was intentionally 'blown' into a foam by drying the swollen gel at 80°C under vacuum. In this way the polymer was obtained in an easily ground form and was readily rendered to an 80 mesh powder. The other copolymer 'C4' was pressed into a plaque as above, but a temperature of 30°C was employed in the drying for the first three days. The plaque was kept free of bubbles, and was indistinguishable from a pure polymethyl methacrylate sample.

This solvent system is now thought to be suitable for further study of the copolymerisation of zinc acrylate and methyl methacrylate. It will thus be employed as the standard system for preparation of a series of copolymers of widely ranging composition.

4.2 COPOLYMERISATIONS IN THE SYSTEM ZINC ACRYLATE/ METHYL METHACRYLATE

The polymers 'C1' - 'C4' were all prepared from a monomer system containing 9.1% zinc acrylate (ie 1 : 10) though the differing polymer isolation techniques led to differing zinc contents in the polymer: -

C1 - 36% zinc acrylate

C2 - 19% " "

C3 - 18.0% " "

C4 - 17.5% " "

Study of the series was extended to formulations containing increasing proportions of zinc acrylate. Thus 'C5' (13% zinc acrylate in monomers) and 'C6' (20%) copolymers were prepared in an identical fashion to C4 and were both obtained as transparent plaques. The zinc acrylate contents of the polymers were determined as:

C5 - 16.2%

C6 - 26.5%

The unexpectedly low figure for the C5 copolymer is ascribed to its physical form - This plaque was thicker than had previously been prepared (3 mm against 1.5 mm) and thus loss of residual monomer during the drying was retarded. As polymerisation and monomer evaporation were continuing in competition during all of the heating after removal from the reflux system, it is quite logical to assume that a retardation of the monomer loss would result in a higher degree of conversion with respect to methyl methacrylate. This is borne out by a comparison of the degree of conversion, calculated from observed compositions. (In each case conversion with respect to non volatile zinc acrylate is $\sim$ 100%).

Polymer	% conversion (methyl methacrylate)
C1	25
C2	48
C3	47
C4	47
C5	71
C6	66

When the concentration of zinc acrylate in the system was raised to 25% and above, it was no longer possible to prepare the polymer in the form of a plaque. In the system 'C7' (33% zinc acrylate) the onset of polymerisation was marked by a turbidity of the solution. As the reaction continued a bulky fine white powder precipitated. After a total polymerisation time of $3\frac{1}{2}$ hours under reflux this precipitate was filtered off, washed with clean methanol and dried for 30 minutes under vacuum at $75^{\circ}C$. The product was a very fine white free flowing powder. Analysis of this polymer showed a zinc acrylate content of 47% w/w. However, examination of the TGA curve reveals a large residual solvent which is volatile at $< 100^{\circ}C$ (Graph 4.3). Allowing for this, the corrected concentration was 62%.

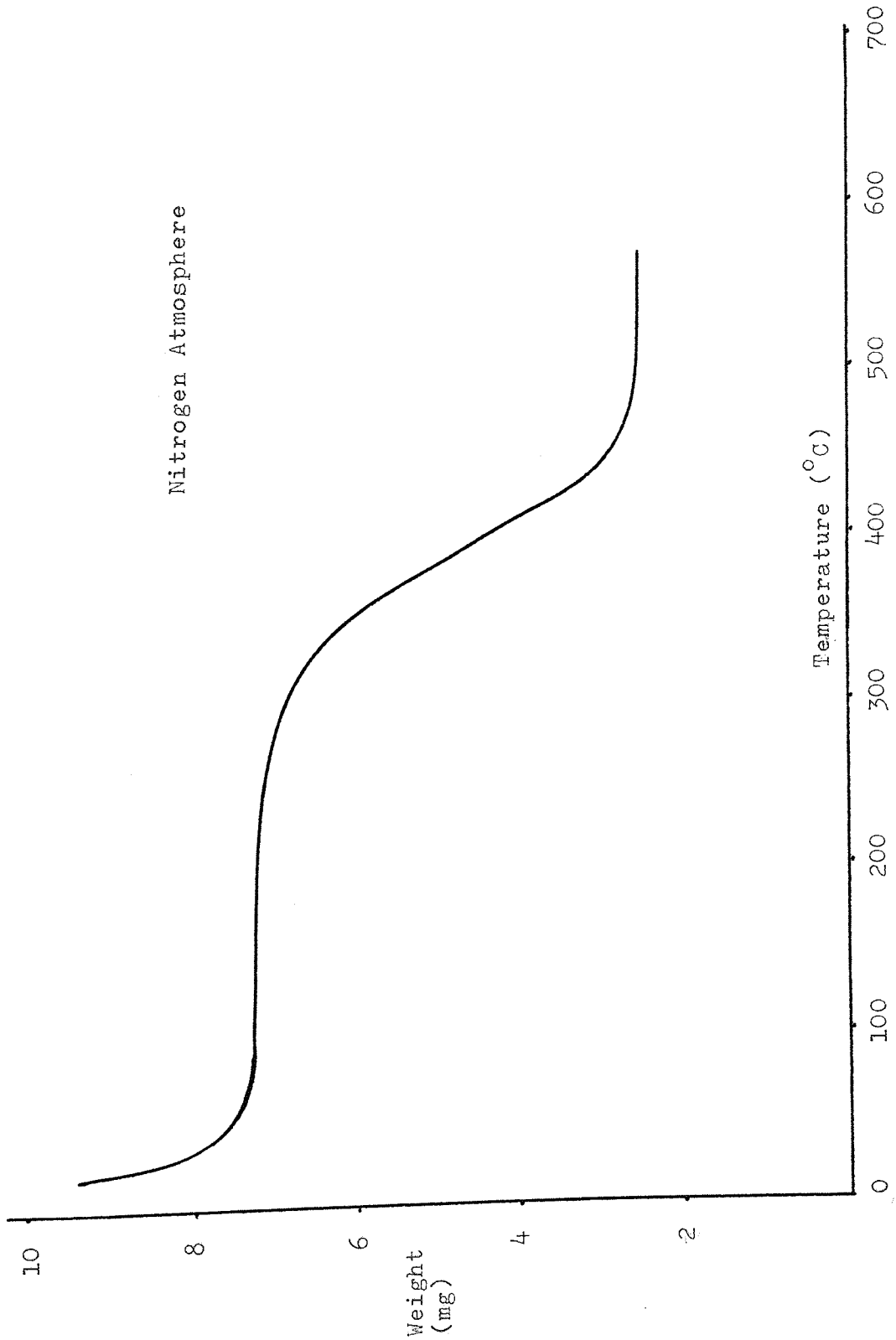
The series of copolymerisations was continued up to C13 (86% zinc acrylate in monomers) and the formulations and their corresponding copolymer compositions are summarised in Table 4.1.

The densities of all the copolymers were determined in a density gradient column, and are presented in graph 4.4. The overall linearity of the relationship between density and zinc content is apparent. It therefore appears that polymer density could provide a further method for zinc content determination.

Once again, under identical conditions of polymerisation the

GRAPH 4.3

TGA Curve for the C7 Copolymer Showing a High Solvent Content



GRAPH 4.4

The Density of Zinc Acrylate/Methylmethacrylate Copolymers as a Function of their Composition

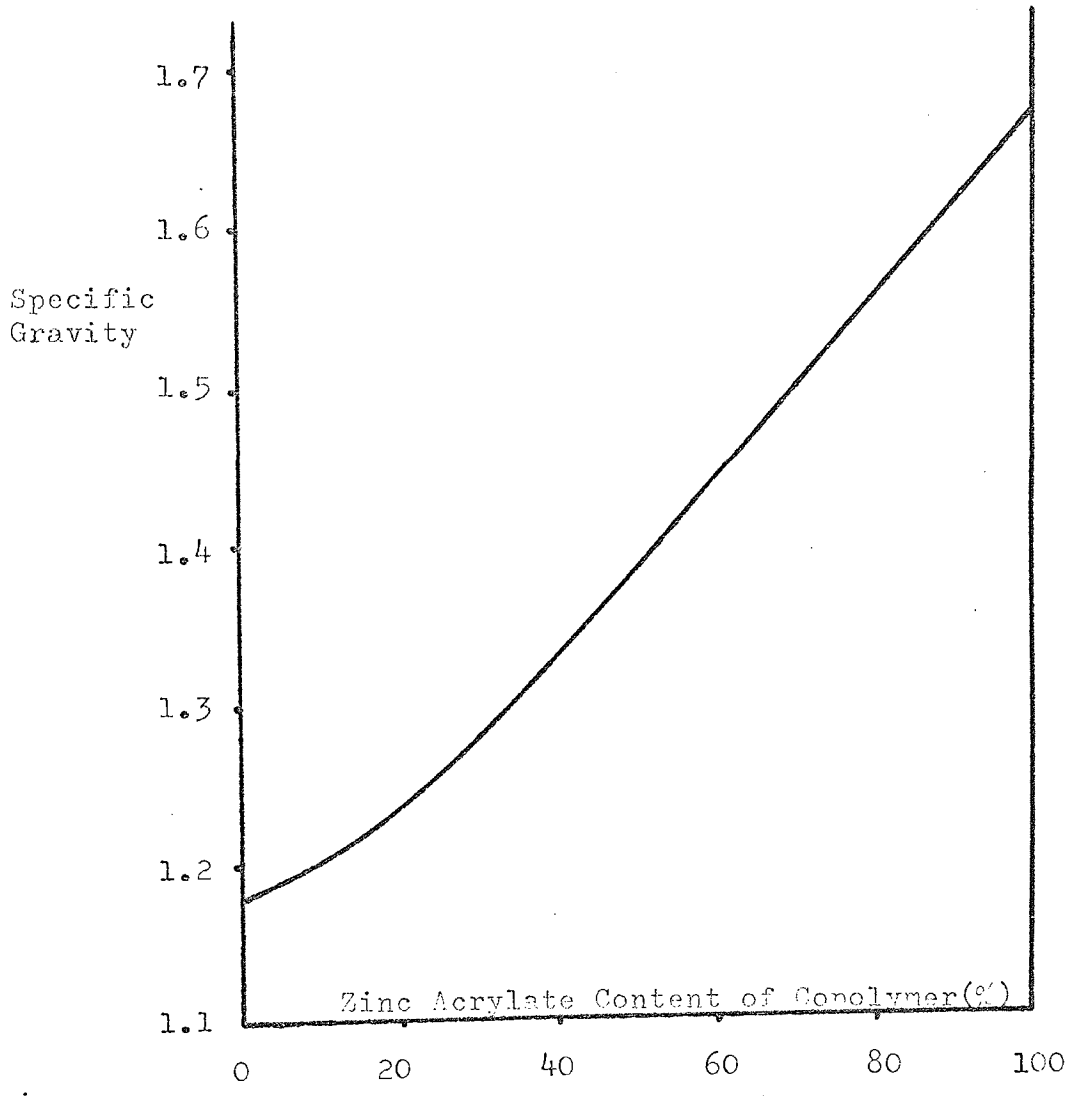


TABLE 4.1 A SUMMARY OF THE ZINC ACRYLATE/METHYLMETHACRYLATE COPOLYMER SERIES

Copolymer	Zinc Acrylate Content (%)			Solvent System (% on zinc acrylate)		Observations
	In Reactants	Calculated in Polymer	Estimated in Polymer	Methanol	Acetone	
C1	9.1	33	36	250	0	Hard white translucent foam
C2	9.1	13	19	200	500	Transparent brittle bubbly plaque
C3	9.1	17.5	18	200	500	Blown Foam
C4	9.1	17.5	17.5	200	500	Transparent brittle plaque
C5	13	17.5	16.2	200	500	Transparent tough plaque
C6	20	27	26.5	200	500	Transparent brittle plaque
C7(and C8)	33.3	-	62	200	500	Fine white powder
C9	25	-	54	200	500	Fine white powder or friable crumb
C10	30	-	63	200	500	Fine white powder
C11	50	-	71	200	500	Fine white powder
C12	67.5	-	75.2	200	500	Fine white powder
C13	86	-	100	200	500	Fine white powder

conversion with respect to methyl methacrylate was found to vary with the zinc acrylate content of the system (Graph 4.3). This would appear to indicate a high reactivity for zinc acrylate and/or its radical, compared to methyl methacrylate. This observation is reinforced by the rapid formation of a precipitate of polymer on warming a methanolic solution of pure zinc acrylate, and confirmed by the following observation:

4.2.1 Estimation of Reactivity Ratios

For the purposes of this project the determination of reaction parameters is superfluous, but a knowledge of the reactivity ratios may lead to improvements in the understanding of the system. Owing to the constantly changing composition of the monomer phase throughout a polymerisation, analyses for determination of the reactivity ratios had to be performed at effectively zero conversion. In order to comply with this requirement samples were extracted from the polymerisation system at the first sign of precipitation. This was achieved using a glass tube connected by a short flexible tube to a trap, and thence to a water-vacuum pump. In the trap was 100 ml of methanol cooled in ice to quench the reaction and ensure no polymer remained in solution. Only ca 5 ml of suspension was removed in this way, the precipitate was then filtered off washed with methanol and dried in vacuo at 70°C for 4 hours. Analysis was then made using the TGA technique.

Initial polymer produced in 'C9' polymerisation contained 69.5% w/w of zinc acrylate, or mole fraction 0.517. The equivalent figures for 'C12' were 79% w/w or 0.645.

Entering these figures in the copolymer composition equation

$$\frac{m_1}{m_2} = \frac{M_1 (r_1 M_1 + M_2)}{M_2 (r_2 M_2 + M_1)}$$

where M_i = mole fraction of 'i' in reactants

m_i = mole fraction of 'i' in polymer

r_i = reactivity ratio of 'i' in the system

produces a pair of simultaneous equations for r_1 and r_2. Solution of these equations yields

r_1 (zinc acrylate) = 0.81 r_2 (mma) =-0.019

The negative value for r_2 is surprising (in fact is is impossible as it implies depolymerisation) but the value is, within experimental error, zero.

Considering the propagation reactions:

ZA + ZA $\xrightarrow{k_{11}}$ ZA ZA (ZA zinc acrylate)

ZA + MMA $\xrightarrow{k_{12}}$ ZA MMA (MMA methyl methacrylate)

MMA + MMA $\xrightarrow{k_{22}}$ MMA MMA

MMA + ZA $\xrightarrow{k_{21}}$ MMA ZA

and $r_1 = \frac{k_{11}}{k_{12}}$ $r_2 = \frac{k_{22}}{k_{21}}$

the fact that $r_2 \backsimeq 0$ implies that zinc acrylate monomer units react with methyl methacrylate radicals very much more readily than do methyl methacrylate molecules. On the other hand the value of r_1 (0.81) shows a slight preference of zinc acrylate radicals for methyl methacrylate molecules though only 20% more than for its own kind (r = 1 implies random addition).

The difunctionality of the zinc acrylate probably means that this system is complicated by different reactivities of monomer, and half polymerised material. In an aqueous system this would be minimised by the extent of ionisation, and hence the lability of the zinc ion. In the solvent system used this effect cannot readily be evaluated without extensive study, considered beyond the scope

TABLE 4.2

INTERACTION OF SOLVENTS WITH C9 COPOLYMER

Solvent (solubility parameter = δ)	Observation
conc hydrochloric acid	50% swell at 1 month, opaque
30% " "	10% " " " " "
3% aqueous acetic acid	no effect
40% sodium hydroxide solution	50% swell, disintegration
saturated calcium hydroxide solution	250% swell rubbery
Water δ = 23	<1% swell
Formic acid δ = 13.5	COMPLETELY SOLUBLE
Methanol δ = 14.5	no effect
Acetic acid δ = 12.5	sample disintegrates
Cresol δ = 13.3	no effect
Dimethyl formamide δ = 12.1	<5% swell
Acetone δ = 10	no effect
Toluene δ = 8.9	<1% swell
Methyl methacrylate δ = 9.2	no effect
Carbon tetrachloride δ = 8.6	no effect

of the present investigation.

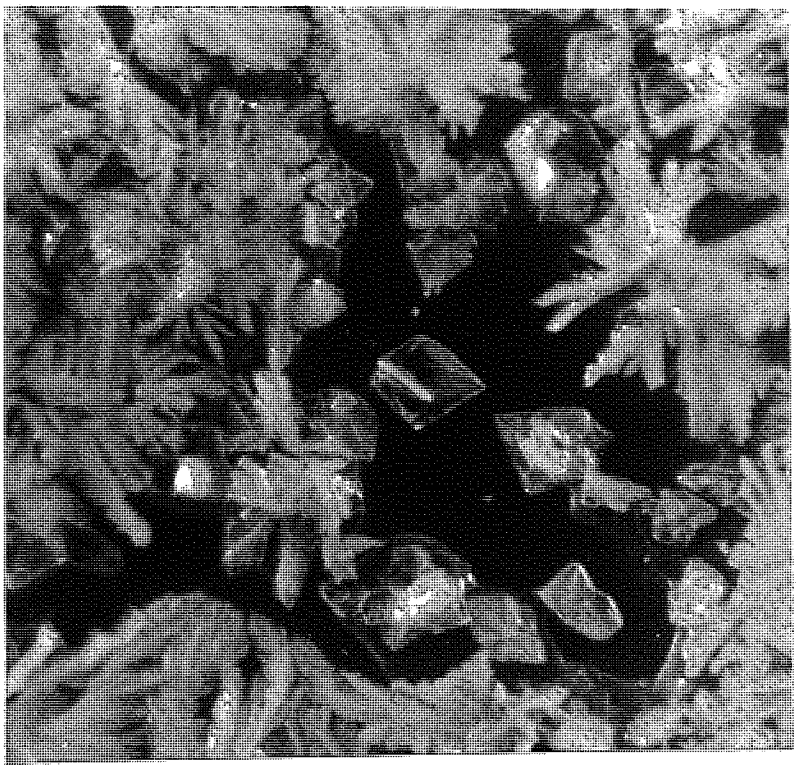
It is therefore accepted that these results cannot be regarded as absolute owing to the minimal number of estimations made, and more particularly the sampling technique necessitated by the nature of the polymerisation. The samples taken invariably contained both copolymer precipitate and a variable content of soluble material, and a representative sample could only be achieved if the powder suspension were completely uniform - a situation difficult to guarantee.

4.2.2 Molecular weight determination

Before an assessment of the properties of the copolymers was made, it was felt desirable to confirm that the molecular weights were comparable. Unfortunately the degree of cross linking derived from the difunctional zinc acrylate rendered all the copolymers insoluble in THF. However, a solubility screening performed on samples of sintered C9 (details of the sintering are included in Chapter 6) revealed a possible solvent - see Table 4.2.

Though some of the other systems show effects of interest, these will be discussed more fully later. At the moment the important factor is the complete solubility in formic acid. In fact this is not a true solution, as attempts to cast a film of C9 from formic acid, onto a polythene covered casting bed produced a film containing many crystals (plate 4.1). Immersion of this film in boiling water for a period of twelve hours, and subsequent drying resulted in a weight loss of 19% and a decrease in surface area of 30%. The film also became cloudy and more brittle, though at temperatures above 50°C in water it was rubbery and flexible (giving a rough estimate of the Tg). Working on the measured zinc

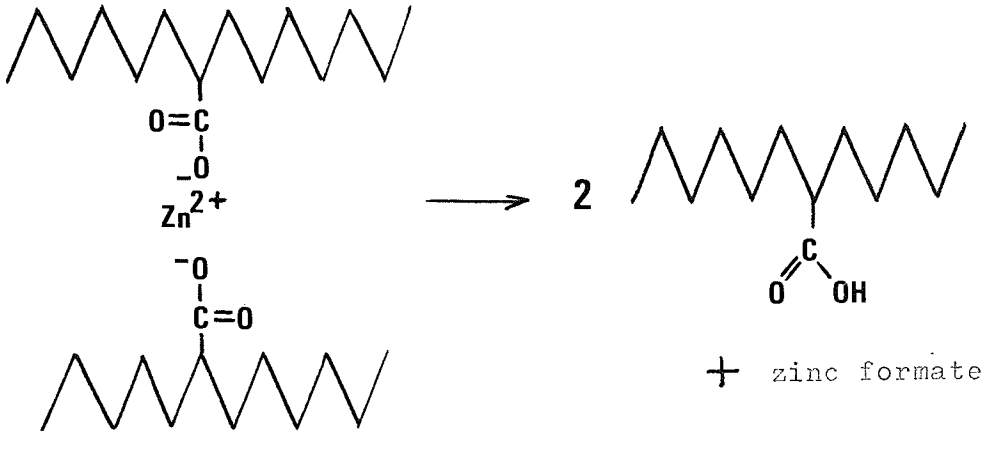
PLATE 4.1 CRYSTALLINE ZINC FORMATE EMBEDDED IN A COPOLYMER FILM CAST FROM A SOLUTION OF 'C9' IN FORMIC ACID



acrylate content of C9 of 54% w/w, a zinc content of 16.3% w/w was calculated. The observed weight loss of 19% on aqueous extraction would thus appear to be due to total loss of zinc plus 2.7% of residual formic acid in the film (though extraction of some polyacrylic acid derived from zinc acrylate homopolymer is also expected). In fact a TGA analysis on the extracted film showed a little residual zinc, equivalent to 4% zinc acrylate.

The extracted film was soluble in 50 : 50 acetone : methanol. It thus appears that formic acid is capable of breaking the ionic cross links in the copolymer, replacing zinc with hydrogen. The extracted zinc was obtained in the form of white crystals of zinc formate by evaporation to dryness of the extractant (the identity of the crystals was confirmed by IR spectra compared with commercial zinc formate).

So zinc acrylate/methyl methacrylate copolymer is converted to acrylic acid/methyl methacrylate copolymer



In this process the chain molecular weight should remain unchanged, though all the cross links will be removed.

The extracted sample was soluble in THF and could thus be submitted for gel permeation chromatography.

In fact, samples of the range of copolymers were not prepared in film form for extraction, but were precipitated in water from their formic acid solutions. Thus, a 10% solution of each copolymer was prepared in AnalaR formic acid. The powder copolymers dissolved readily at room temperature, but the plaques were less soluble, though solution was complete in all cases within twenty four hours. Precipitation was then effected by slowly dripping the solution into a large excess of vigorously stirred water. The hydrolysed polymer was filtered off and soaked in boiling distilled water for several minutes to remove residual formic acid and zinc formate. After a further filtration the polymer was dried in a vacuum oven at 60°C to constant weight and subjected to gel permeation chromatography. The results are presented in Table 4.3.

It is possible to gain further information from this hydrolysis from a consideration of the weights involved, and the knowledge of the zinc content of the polymer. Thus if the composition of the polymer before and after hydrolysis is considered:

BEFORE	AFTER
ZA/MMA copolymer plus ZA homopolymer plus MMA homopolymer	AA/MMA copolymer ppt plus aqueous solution of zinc formate and poly acrylic acid plus MMA homopolymer ppt

Where ZA = zinc acrylate; AA = acrylic acid; MMA = methyl methacrylate.

The weight loss on hydrolysis therefore represents the zinc extraction plus the polyacrylic acid derived from the homopolyzinc

acrylate. From the zinc contents measured by TGA the expected weight loss corresponding to total zinc extraction is readily calculable, and hence so too is the homopolyacrylic acid content. The presence of MMA homopolymer in the powder copolymers is strongly contra-indicated by the alcohol solubility of their hydrolysates. Thus the relative extents of true copolymerisation and production of zinc acrylate homopolymer can be assessed for the various formulations. This is included in Table 4.3 and is expressed in terms of the weight percentage of zinc acrylate present as homopolymer in the copolymer.

The following conclusions were drawn from these results:

4.2.2.1 Though not identical, the chain molecular weights of all the copolymers are comparable and similar to that of 'Stellon'.

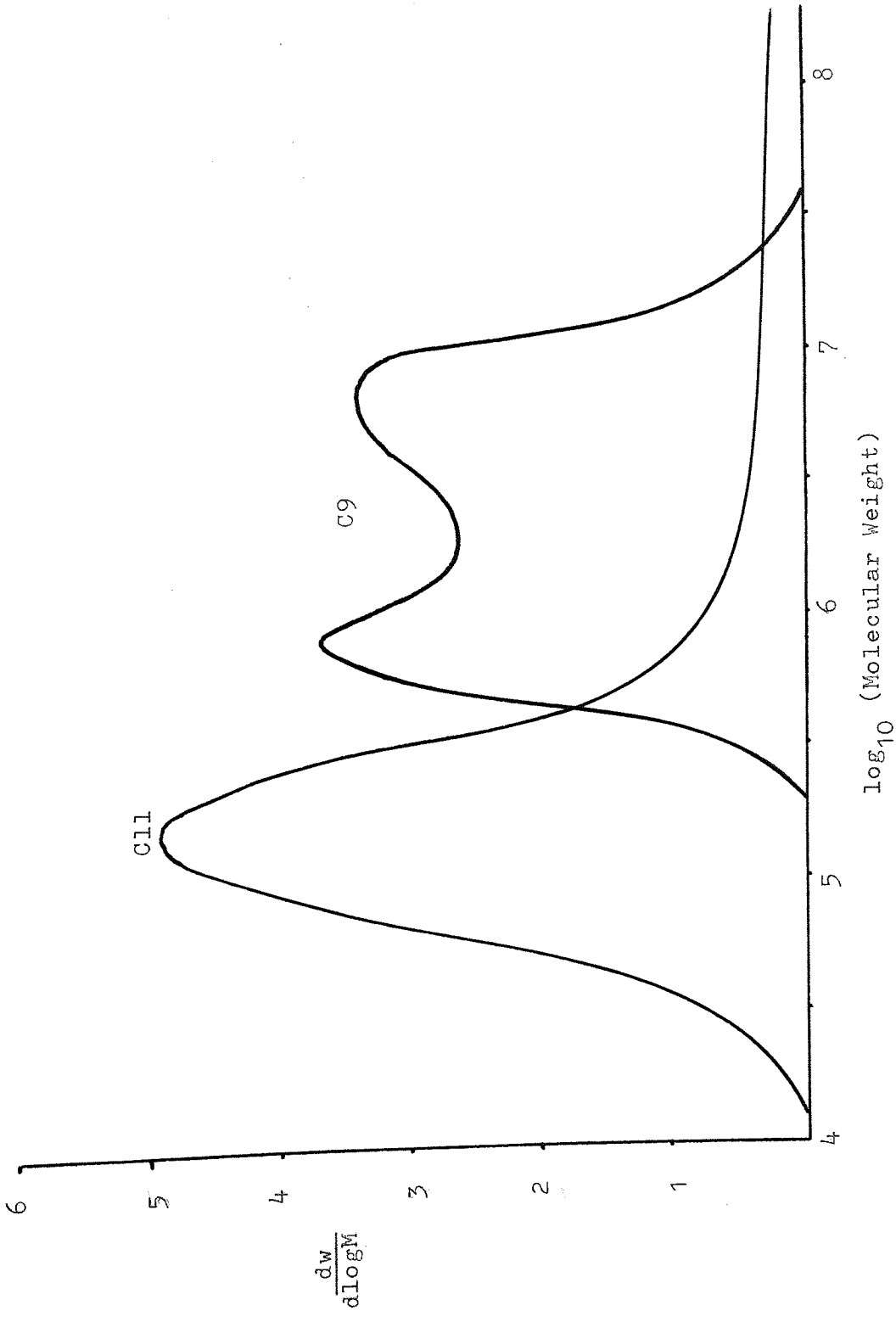
4.2.2.2 In general the molecular weight distributions, measured by $Mw/_{Mn}$ are relatively narrow though C5, C6, C7 and C11 are exceptions. This difference appears from the distribution curves (Graph 4.5) to be due to incomplete removal of cross links - C11 is seen to contain a small proportion of very high molecular weight material.

4.2.2.3 As more zinc acrylate is incorporated in the polymer, an increasing percentage is truly copolymerised, as seen by Graph 4.6. The experimental error on this curve is expected to be high as the determination is made by the difference of two other determinations. The slope of the curve, and its linearity are not therefore commented on. It is however surprising that this fall is observed, though the total content of homopolymer does increase as expected.

4.2.2.4 Copolymer 'C5' behaved exceptionally in all respects, and as its weight loss on hydrolysis corresponded to 210% homopolyzinc

GRAPH 4.5

Molecular Weight Distribution Curves for the Hydrolysates of Copolymers 'C9' and 'C11'



GRAPH 4.6

The Proportion of Zinc Acrylate Homopolymerising as a Function of the Total Zinc Acrylate Content of a Copolymer

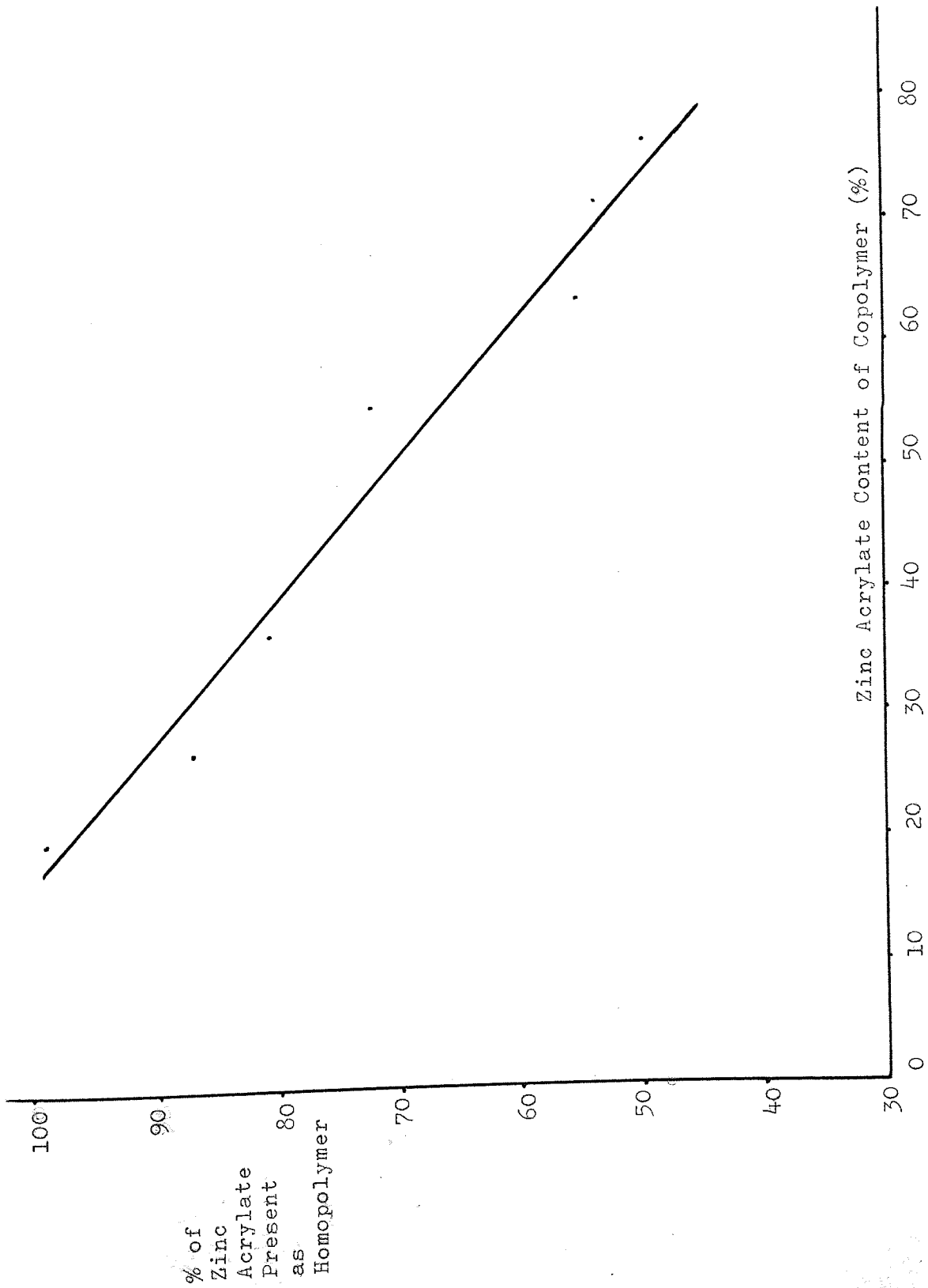


TABLE 4.3

MOLECULAR WEIGHT AND STRUCTURAL DATA ON THE COPOLYMER SERIES

	Polymer	Molecular Weight		Mw/Mn	w/w % ZA present as homopolymer
		Number Av Mn	Weight Av Mw		
	Stellon	2.49×10^5	1.07×10^6	4.3	-
Plaques	C1	3.27×10^5	8.12×10^5	3.39	80.5
Plaques	C2 (3,4)	2.08×10^5	8.12×10^5	3.90	62.0
Plaques	C5	2.05×10^5	4.15×10^6	20.19	100
Plaques	C6	6.5×10^5	1.0×10^7	16.47	87
Powders	C7 (8)	2.53×10^5	5.93×10^6	23.42	55
Powders	C9	1.39×10^6	4.15×10^6	2.96	72.5
Powders	C10	2.33×10^5	9.43×10^5	4.04	53.5
Powders	C11	1.15×10^5	3.10×10^6	27.01	53
Powders	C12	1.01×10^5	5.1×10^5	5.5	49.5
Powders	C13	No precipitate in water		-	100

acrylate it can only be concluded that there was a considerable quantity of residual solvents. The absence of any weight loss on the TGA trace identifiable as solvent would appear to indicate strong retention of solvent, or even bonding.

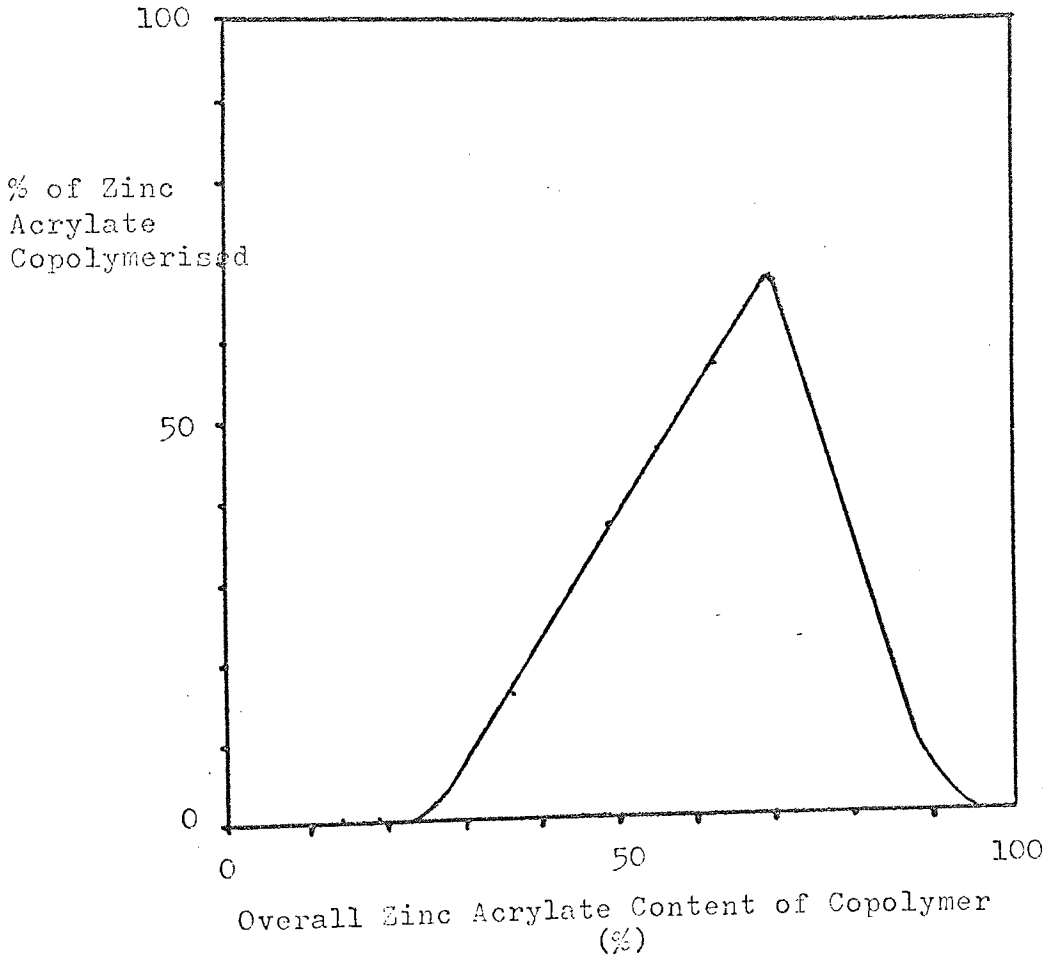
4.2.2.5 Obviously the various comments on the degree of true copolymerisation are only valid within the limits imposed by the separation technique. For instance a polymer chain composed of 90% + acrylic acid units and less than 10% methyl methacrylate will in all probability be water soluble and thus counted as homopoly acrylic acid. Errors arising from this effect are likely to be greatest at high zinc acrylate contents in the copolymer, resulting in excessive values for the homopolymer content of these copolymers. In addition the validity of these figures is dependent upon the complete hydrolysis of the zinc acrylate on dissolution in formic acid. This has in fact been shown not to be entirely correct by TGA on the hydrolysate which has shown up to 4% residual zinc acrylate. The figures are still thought to give useful information on the fundamental structure of the copolymers.

4.2.2.6 Graph 4.7 is interesting in showing a maximum in the curve of copolymerised zinc acrylate content against total zinc acrylate content. It is however felt that this is largely due to the effect described above, ie the water solubility of copolymers containing very low concentrations of methyl methacrylate. If indeed the measured values are correct the implication is that the zinc acrylate, being more reactive shows an increasing tendency to form homopolymer at high concentrations. The solvent content of the polymerisation system is governed by the zinc acrylate content, thus exaggerating the reduction in concentration of methyl methacrylate.

Further insight into the structure of the polymers was obtained

GRAPH 4.7

The Proportion of ZincAcrylate Truly Copolymerised as a Function of Copolymer Composition



from two sources:-

4.2.2.7 Reprecipitation of a zinc containing copolymer:-

A sample of the hydrolysate derived from C9 was dissolved in 50 : 50 acetone : methanol to produce a clear solution of the viscosity of glycerol. This was then dripped slowly from a funnel into a stirred methanolic solution of zinc acetate (containing a fourfold excess of zinc acetate on the calculated acrylic acid content of the polymer). A fine, almost gelatinous precipitate was at once produced. The mixture was left overnight, both to settle and to maximise reaction, and then filtered, washed with methanol and dried in vacuo at 60°C. This material was designated C90. As a check on the extent of reaction the filtrant was rotary evaporated to dryness. This yielded white crystals of zinc acetate smelling slightly of acetic acid, but no polymeric residue.

10.96 of hydrolysate yielded 12.41 g of precipitate corresponding to a zinc content in the product of 13.25% or a zinc acrylate content of 42%. This figure is almost double that expected on the basis of the calculated acrylic acid content but was confirmed by TGA.

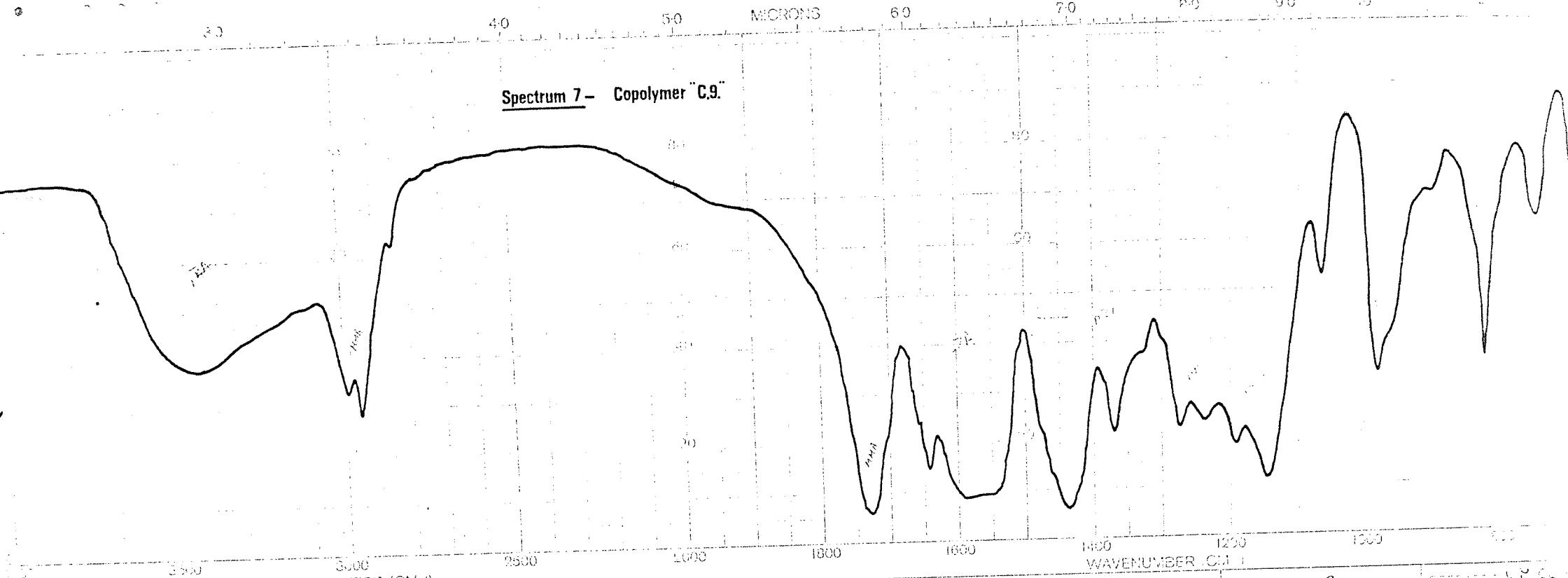
Spectroscopically C90 was identical in infra red absorption to C9 with an intense and broad carboxylate ion absorption at 1570 cm^{-1} (6.35 μ). (Spectra 7, 8, 9)

It thus appears that C90 has an essential point of difference from C9:

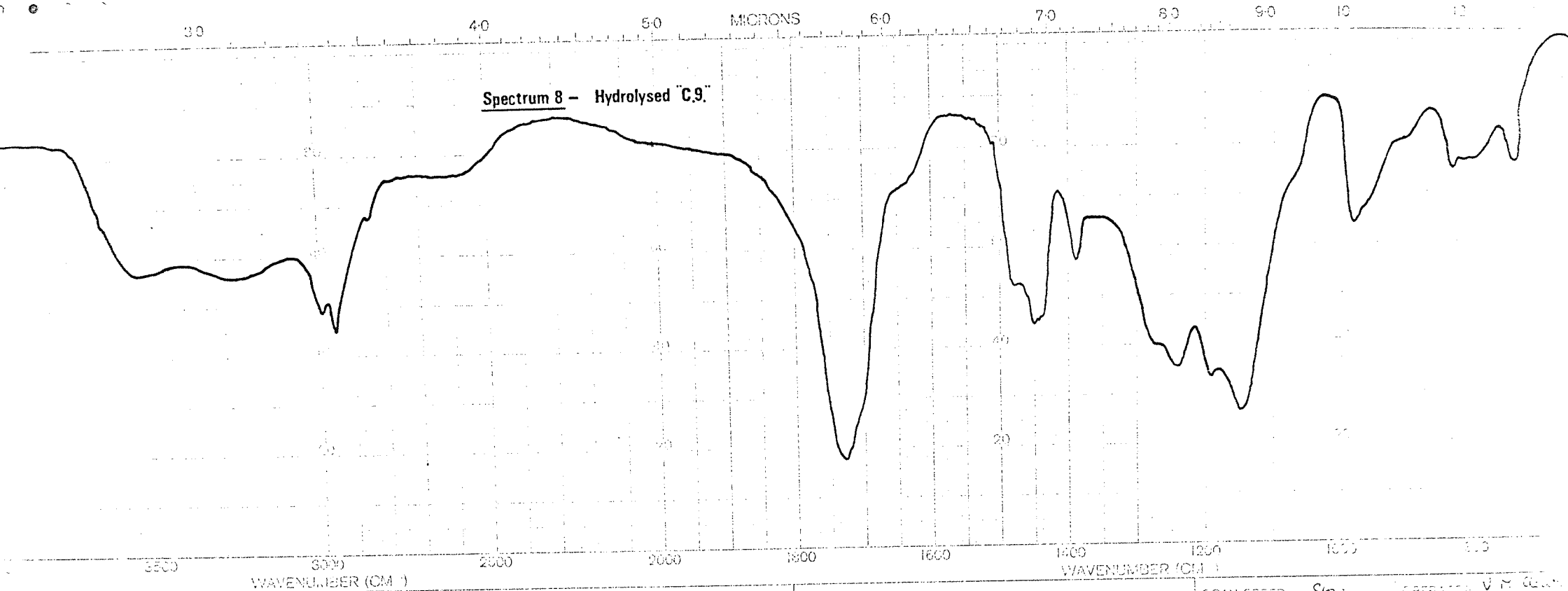
There are no pure zinc polyacrylate homopolymer chains, as the homopolyacrylic acid was removed in the aqueous precipitation. C90 is therefore a true copolymer.

The physical properties of C90 type polymers will be evaluated in the following chapter.

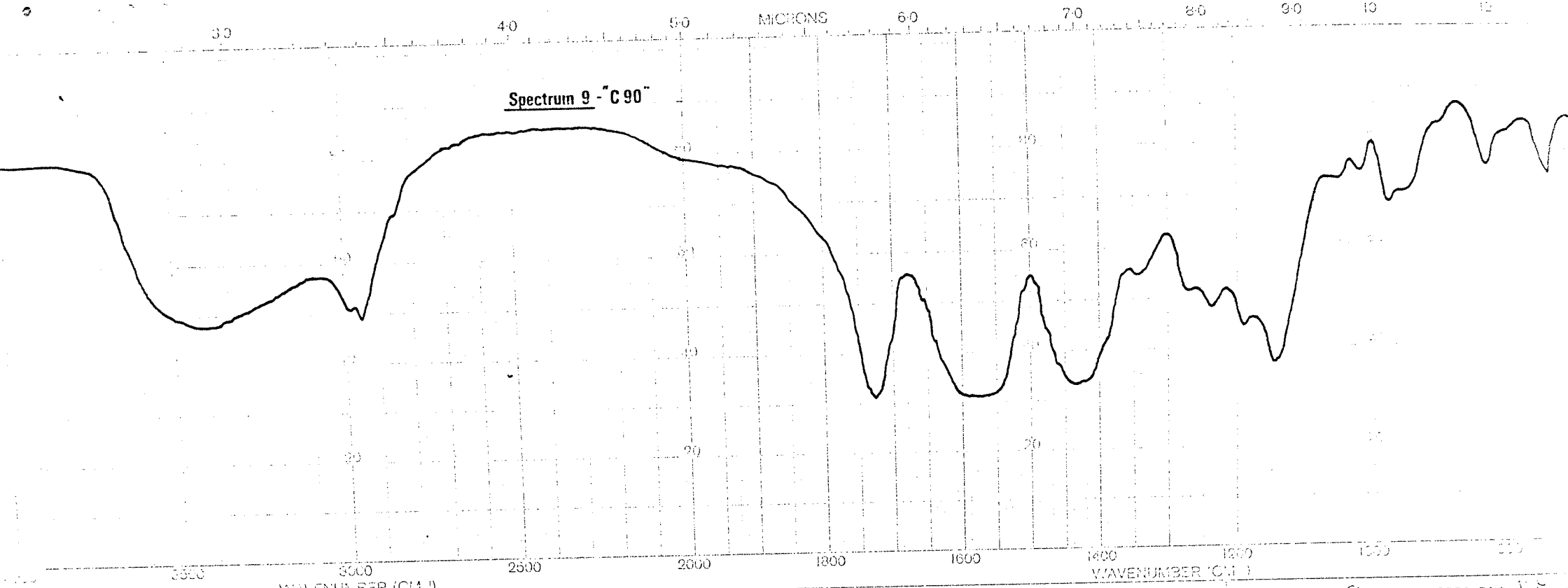
Spectrum 7 – Copolymer "C.9."



C.9.	SOLVENT CHCl₃	REMARKS	SCAN SPEED Slow SLIT Standard
C. Summers	CONCENTRATION approx 2-3%		PERKIN ELMER
	CELL PATH 13.0 m/m. dia. disc		PART NO 472-[illegible]
	REFERENCE Air		



C9D – formic acid sol² applied in water.	SOLVENT KBr.	REMARKS	SCAN SPEED Slow
G. Simmons	CONCENTRATION approx 2 - 3%		SLIT Standard
	CELL PATH 13.0 m/m dia. disc		PERKIN ELMER
	REFERENCE Air		PART NO 472 -



SAMPLE C 90 — C9 repptd then repptd with Zn^{2+}	SOLVENT KBr.	REMARKS	SCAN SPEED Slow
	CONCENTRATION approx. 2·0%		SLIT Standard
	CELL PATH 13·0 m/m. dia. disc		PERKIN ELMER
	REFERENCE Air.		PART NO 472-

C. Simmons.

4.3 FURTHER STUDIES ON THE C9 POLYMERISATION

It has been established that zinc acrylate is a more reactive monomer than methyl methacrylate. One would therefore expect the initially precipitated polymer to have a higher zinc content than that precipitated in the later stages of the reaction.

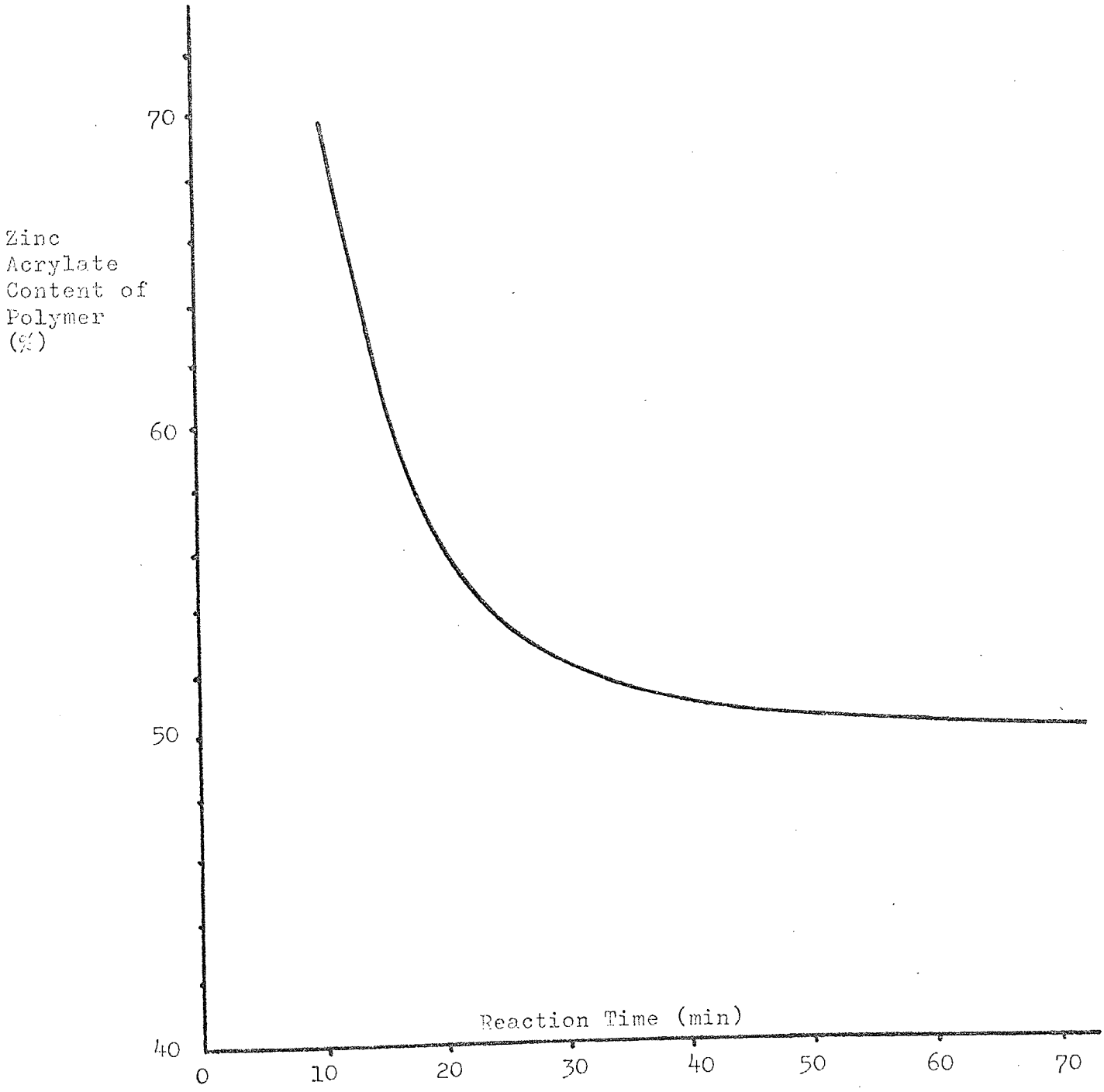
In order to assess the extent of this behaviour a C9 polymerisation was run, from which samples were removed at known times, from the first appearance of polymer to completion of reaction. Though it is theoretically possible, by a continuous filtration of the system, to isolate the polymer precipitated at a particular point in time, it is both more practicable and more relevant to allow the polymerisation to continue normally and take samples from the increasing bulk of polymer precipitate. Analysis of these samples will therefore yield the overall composition of polymer formed at times $\leqslant t$.

The results of this experiment are presented as Graph 4.8.

When it is considered that the monomer phase originally contained only 25% w/w zinc acrylate, the fact that the initially precipitated polymer contained nearly 70% w/w zinc polyacrylate is testimony to the reactivity of the monomer. Over the first 30 minutes of polymerisation the overall zinc acrylate content in the polymer fell from 69.5% to 51.5%. As this figure includes all of the earlier precipitated polymer, it follows that the curve for polymer produced at a point in time would fall more steeply still. The rapid levelling off of the curve, and hence the little influence exerted by the zinc-rich early polymer is to be expected as the bulk of the precipitate was formed between 30 minutes and 1 hour into the reaction. Similarly it is expected that small quantities of methyl methacrylate-rich material produced in the late stages of

GRAPH 4.8

The Zinc Acrylate Content of Material Precipitated in a C9 Polymerisation as a Function of Polymerisation Time



reaction should have little effect on the weighted curve. (In order to ensure that methyl methacrylate-rich material was not lost in solution, each sample was added to excess cold methanol on withdrawal from the reactor as described earlier.)

4.4 A PRELIMINARY ASSESSMENT OF THE STABILITY OF ZINC ACRYLATE CONTAINING POLYMERS TO AQUEOUS EXTRACTION

Small specimens (approx 1 g weighed accurately) of dough moulded 'Stellon' control, and 'C4' copolymer plaque were immersed in distilled water at 37°C. Similar samples were immersed in buffered solutions at pH4 and 9. The extractant solutions were changed after known time intervals up to 3 weeks and the extracted zinc estimated by complexiметric titration as described in Chapter 2. At the end of this time the samples were weighed and then dried to constant weight.

TABLE 4.4

PRELIMINARY ZINC EXTRACTION STUDIES IN AQUEOUS SYSTEMS

Sample	Zinc Loss (mg)	Weight Change (%)	
		Wet	Redry
Stellon (w)	-	1.08	-0.1
C4 (w)	$\leqslant$ 0.32 (0.5%)	8.8	0
Dough Moulded C3 (w)	Blank	2.2	-0.15
Stellon (4)	-	2.5	-0.15
C4 (4)	$\leqslant$ 0.32 (0.6%)	7.5	-1.2
Stellon (9)	-	1.33	-0.1
C4 (9)	$\leqslant$ 0.65 (1.1%)	5.6	-1.7

Where (w) represents aqueous extraction, (4) pH4, and (9) pH9.

The vagueness in the zinc extraction figures arose from the fact that in no instance was a titre of more than two drops recorded. The maximum error in such cases is therefore plus zero but minus up to 50%. However at this stage of the investigation the overall significance of these results is the low figure for zinc extraction. After three weeks in more hostile environments than that found in the mouth a ceiling figure of 1.1% of the zinc present was extracted. It appears that in this respect at least the zinc acrylate copolymers show a potential for denture materials. However the precise extent of extraction under more varied conditions will be evaluated in the following chapter. A rather more worrying result for zinc extraction was found when a sample of C9 powder copolymer was immersed in distilled water for one week at 37°C. After filtration of the powder from the extractant, titration showed that 12% of the zinc had been extracted. (The quantities used were 1 g polymer : 100 ml water and the flask was shaken daily.) Though this figure is high, it is felt that the very high surface area of the material is to blame. When incorporated in a dough-moulding the reduced exposure to the extractant is expected to render this value more acceptable. As stated above this will be evaluated later.

4.5 ASSESSMENT OF THE OPTIMUM SOLVENT SYSTEM FOR THE POLYMERISATION SYSTEM

Thus far it had been assumed that the solvent system in use, arrived at somewhat intuitively was ideal. In order to test this assumption a series of C9-type polymerisations was carried out, using solvent systems varying from pure methanol to 11% methanol in acetone (the minimum methanol required to dissolve the zinc acrylate).

The following comments apply to these extreme cases.

$C9_2$ (100% methanol) - the copolymer was produced in the form of a rubbery opaque white gel, very difficult to remove from the stirrer. Vacuum drying at 60°C yielded a brittle translucent material.

$C9_3$ (11% methanol) - In this system a fine white polymer precipitate was formed but due to the extremely small particle size and somewhat viscous solution, filtration proved extremely difficult. Ultimately the slurry remaining in the filter paper solidified and was finally dried to a hard glassy white solid.

Polymerisations intermediate between these compositions showed a steady gradation in characteristics, and, somewhat fortuitously the easiest system to control and isolate polymer powder from, was that used previously (viz 33% methanol in acetone, 2 : 1 methanol : zinc acrylate).

Gel permeation chromatography on these polymer hydrolysates yielded molecular weights comparable with the series discussed earlier

	Mn	Mw	Mw/Mn
$C9_2$	4.05×10^5	2.51×10^6	6.19
$C9_3$	2.66×10^5	4.14×10^6	15.5
(C9	1.39×10^6	4.15×10^6	2.96)

However the zinc content of the resultant copolymer varied quite considerably with the solvents employed:

$C9_2$ - 40.02% zinc acrylate

C9 - 53% " "

$C9_3$ - 40.53% " "

On consideration these results are quite consistent with the observed behaviour of the polymerisations. It is to be expected that the higher the zinc content of a copolymer, the less interaction will it have with the solvent system, and therefore the more easily will it be isolated from the solvents. The higher zinc content has been shown not to be due to exclusion of homopolymethyl methacrylate which was present in the other polymers by the absence of polymeric residue on evaporation to dryness of the residual solvents after polymer isolation.

It should be pointed out that the copolymer 'C9' was taken as a typical formulation for all these tests. It is the powder polymer of lowest zinc content, and therefore would be expected to be most affected by solvents. Extending this hypothesis C9 is expected to be the most suitable copolymer for incorporation in 'Stellon' at the dough-moulding stage, and hence the most strongly bound into the final composite. Because of its position at the bottom of the powder-polymer series, the C9 polymerisation was the most difficult to control. Thus slight variations in temperature and stirrer speed led on occasion to the production of a friable crumb rather than a powder (though still readily rendered to a powder when dry).

'C9' was thus selected for more intensive investigation in both chemical and physical behaviour.

CHAPTER 5

ASSESSMENT OF ZINC ACRYLATE COPOLYMERS FOR INCORPORATION IN DENTAL MOULDING MATERIALS

It has already been suggested that a successful radiopaque dental material requires two main properties not specified in the appropriate standards, those of dough mouldability by standard techniques, and cheapness. The latter requirement is readily complied with by the zinc acrylate based formulations, as the raw materials, zinc oxide and acrylic acid are available at low cost, and the subsequent copolymerisation requires no specialised techniques. However, where the polymer is produced as a plaque, moulding is not possible by accepted procedures without grinding to a powder which is an expensive process on an industrial scale. (Alternative thermoforming techniques will be considered later in this chapter and in Chapter 6.) It appears then that for commercial acceptability study should be concentrated on the powder copolymers. For the reasons specified in the previous chapter attention is to be focussed on the C9 copolymer powder containing 54% w/w zinc acrylate, though not to the exclusion of all others. It was not found possible to dough mould the powder polymer under normal conditions using the standard quantity of monomer.

5.1 AN ASSESSMENT OF THE DOUGH MOULDING PROPERTIES OF FORMULATIONS CONTAINING C9 COPOLYMER

The parameters involved in moulding are largely subjective being concerned with the 'feel' and handling properties of the dough. A degree of quantification may be obtained by timing the onset of

TABLE 5.1

MOULDING PROPERTIES OF SYSTEMS CONTAINING C9 COPOLYMER

Formulation	Composition (%)			Doughing Time (mins)	Observations
	C9	P*	M*		
Stellon Control	0	10	4	9	Easily worked dough - good flow
A1	10	0	4.5	-	No dough - moulded as moist powder
A2	8	2	4.5	-	
A3	5	5	4.5	12	Very stiff dough, little flow
A4	3	7	4.5	10	Stiff dough, reasonable flow
B1	10	0	6	-	Moist powder as A1,A2
B2	8	2	6	-	
B3	5	5	6	16	Stiff dough, reasonable flow
B4	3	7	6	18	Good dough, easily worked quite good flow
B5	6.5	3.5	6	15	
C1	10	0	8	-	Moist powder
C2	8	2	8	30	Stiff powdery dough, no flow
C3	5	5	8	50	Very wet dough, little flow, pressure squeezed out monomer
C4	3	7	8	50	

* 'P' ≡ 'Stellon' polymer

'M' ≡ Methyl methacrylate monomer

doughing, and this measurement together with the more abstract qualities were used in evaluating a series of formulations. All of these systems were subjected to the standard moulding procedure. The two solid components were lightly ground together in a pestle and mortar prior to their addition to the monomer. The results are summarised in Table 5.1.

The most important fact obtained from these results is that C9 alone is not doughed by methyl methacrylate monomer in any proportions. Incorporation of 'Stellon' polymer in the system to act as a binder improved the moulding properties. The most satisfactory material compromising high zinc content with doughing properties appeared to be close to 'B3'. A further formulation 'B5' intermediate between 'B2' and 'B3' was prepared which doughed in 15 minutes to a reasonably workable dough with moderately good flow properties. As described earlier the dough mouldings were produced in the form of a plaque and a wedge. All of the specimens were subjected to a full physical property screening:-

Appearance/transparency

Radiography

Flexural Strength and Modulus

Impact Strength and Modulus

UV light stability

Microscopy

Extractibility

5.1.1 Appearance - The transparency of the samples was assessed on the wedges, and the possibility of reading through them. Plate 5.1 shows all of these specimens and a summary of the observations made is presented in Table 5.2

PLATE 5.1 WEDGE SPECIMENS DOUGH MOULDED FROM STELLON CONTAINING VARYING PROPORTIONS OF 'C9' COPOLYMER

A1	A2		A3	A4
B1	B2	B5	B3	B4
	STELLON CONTROL			
C1	C2		C3	C4

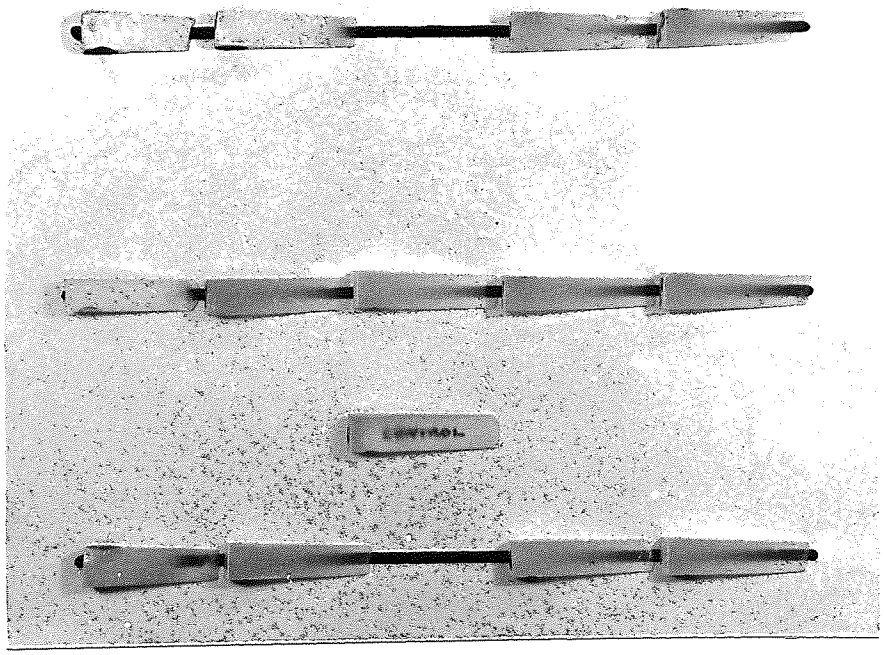


TABLE 5.2

VISUAL ASSESSMENT OF THE SERIES OF DOUGH MOULDINGS

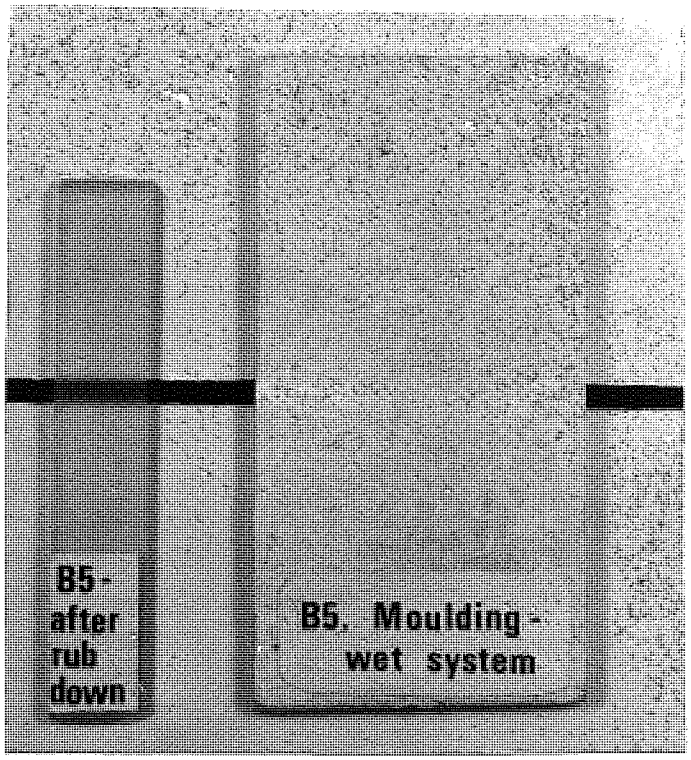
Sample	Observations
Control	Completely transparent, free of any defects either in the surface or in thick or thin sections
A1	White opaque porous, verging on friable
A2	Similar to A1 but less extreme, transparent in very thin sections
A3	Surface whitening otherwise fairly homogeneous no bubbles or voids. Bulk of material translucent verging on transparency at $\leqslant$ 2 mm thickness
A4	Very similar to A3 possibly a little more transparent surface whitening still exhibited.
B1	Thick whitening on the surface but transparent homogeneous areas in the bulk, alongside areas of porosity. The material was very brittle, and a marked tendency to spontaneous shattering from moulded in stresses was apparent.
B2-B5	Similar to A3, A4.
C1	Similar to B1 but the bulk of the material was transparent and the tendency to shattering was greater.
C2-C4	Similar to A3-A4 and B2-B5

In addition a sample of the gel/plaque copolymer C5 (16% zinc acrylate) was included throughout the physical testing. In appearance this material was indistinguishable from the 'Stellon' control.

If one accepts the fact that interaction between C9 and methyl methacrylate monomer is minimal then the observed results, at least in the 'A' series are wholly as expected. The only unexpected effect noticed was the total transparency in the bulk of samples B1 and C1 which would have been predicted to be similar to A1. The spontaneous shattering of these samples was also rather unexpected as no such behaviour had been encountered before. It would appear that a differential contraction in cooling after moulding had resulted in a high degree of stress in the plaque. The inherent brittleness of the composite meant that the stresses were not dissipated by creep which would have produced a deformed product, but instead resulted in the shattering.

The surface whitening of the mouldings was found to extend to a depth of up to 0.2 mm into the material. Similar mouldings produced using dry polythene separating sheets in place of the aqueous alginate solution did not show this effect. The C9 powder polymer has already been shown (4.2.9) to be water sensitive to some extent in the finely divided form. Thus, on contact of the surface layer with an aqueous separating medium at the moulding temperature of 80°C it is not surprising that a degree of hydrolysis occurs. However, even using this separating system the extent of the whitening is such that it is wholly removed by the standard sample preparation techniques of rubbing down on fine emery paper (Plate 5.2).

PLATE 5.2 WHITENING OF MOULDINGS CONTAINING 'C9' COPOLYMER DUE TO INTERACTION WITH AQUEOUS SODIUM ALGINATE SOLUTION - BULK TRANSPARENCY IS SHOWN AFTER RUBBING DOWN ON EMERY PAPER



5.2 RADIOGRAPHY

The calculated and measured (for 10 mm samples) values of the mass attenuation coefficient for all samples are summarised in Graph 5.1 (at 0.329Å). As had been observed before (Chapter 2) on barium sulphate composites the curves were found to coincide exactly at low concentrations of radiopacifier, but to deviate increasingly as the loading was increased. This deviation will be considered more fully in Chapter 7. At 100% C9 the observed value was 8% lower than the calculated, but in an area where previously no quantitative measurements were made this agreement is considered reasonable.

5.3 FLEXURAL STRENGTH PROPERTIES

With the exception of formulations B1 and C1 which were too brittle to form into test specimens, the results of these tests are presented in Graphs 5.2-5.7. The immediately apparent indication of these results is that C9 was behaving as a non reinforcing or non interacting filler. All three experimental parameters, viz breaking load, initial modulus and deflection at break, are consistent with this behaviour -

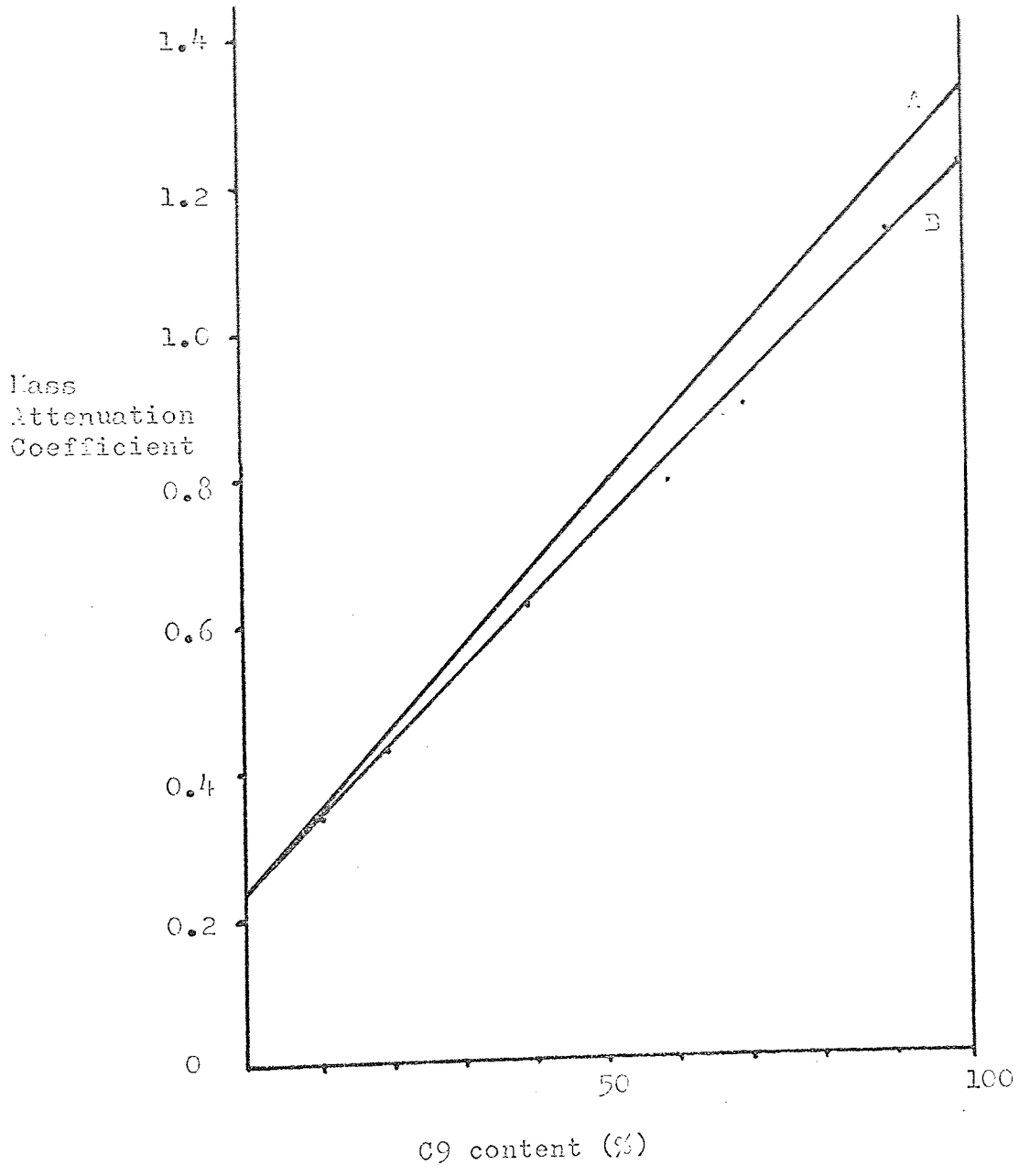
Ultimate breaking load (Graphs 5.2, 5.3) - Increasing the content of C9 results in a steady decline in the breaking load. (The high incidence of off-line points on the graph was attributed to the single specimen testing procedure, adopted because of the time factor in sample preparation and testing.)

Initial modulus (Graphs 5.4, 5.5) - A marked increase in modulus was observed as the C9 content of the composite was increased.

GRAPH 5.1

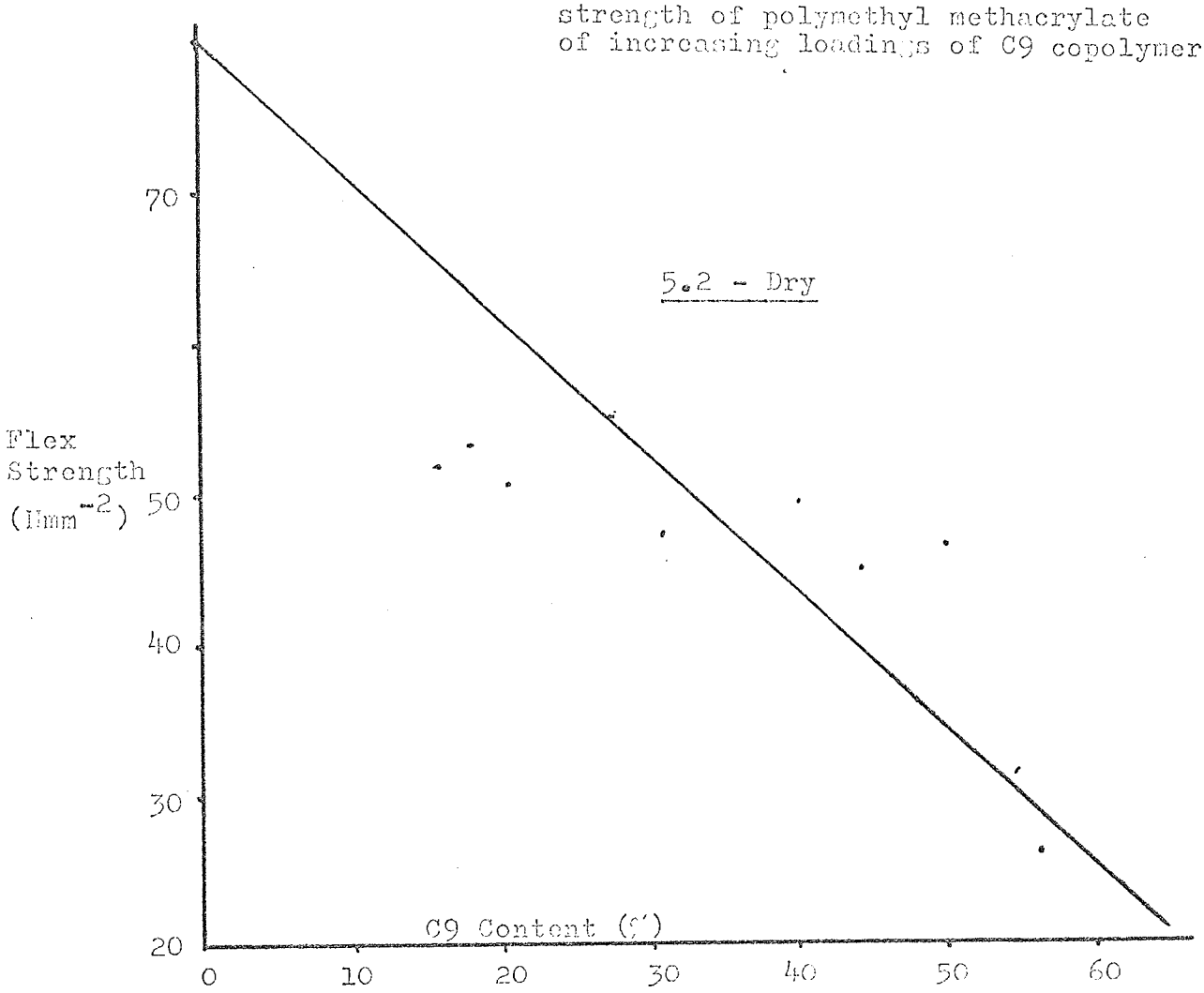
Calculated and measured mass attenuation coefficients of composites containing C9 copolymer (54% zinc acrylate)

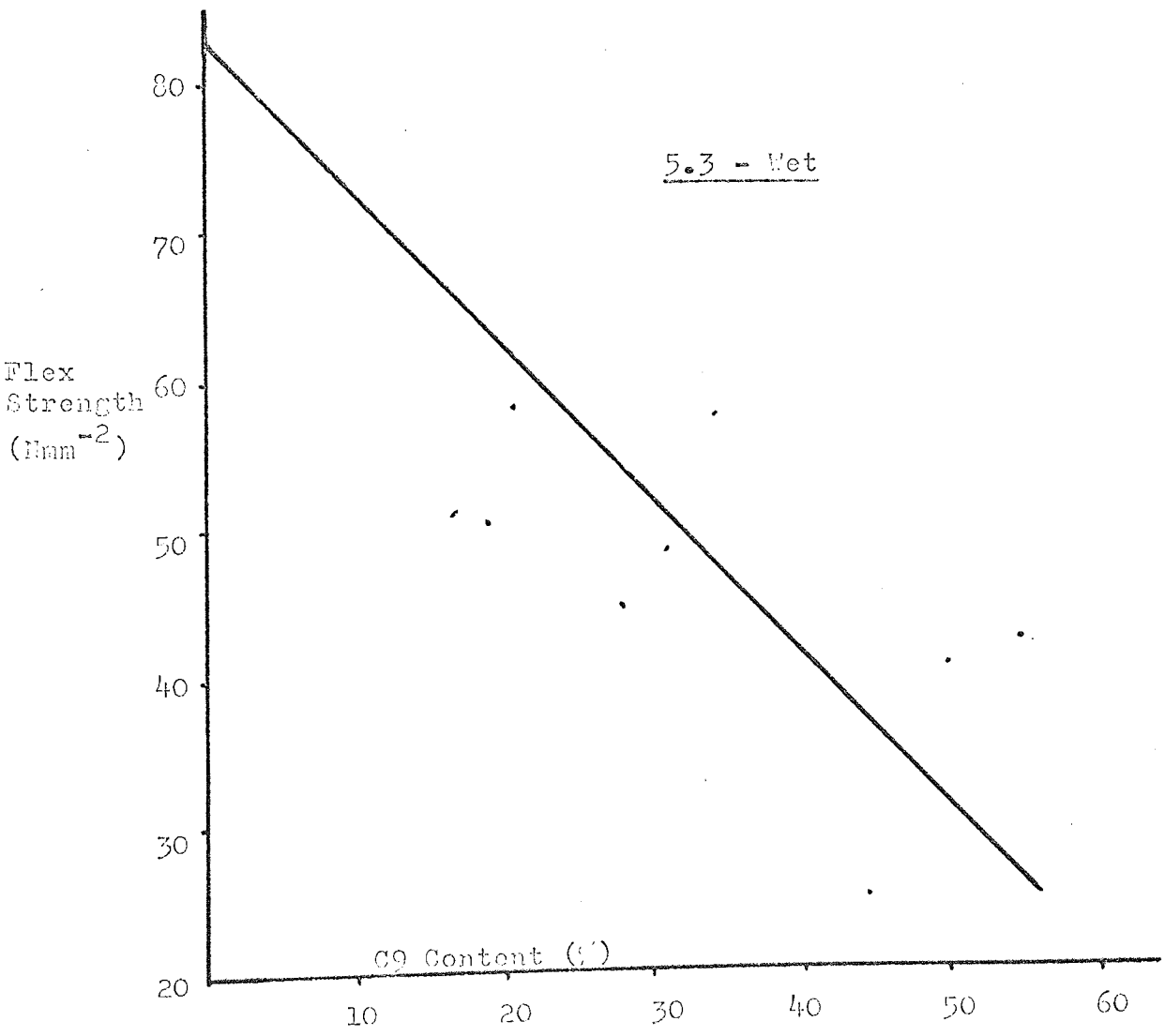
A - calculated values
B - experimental values



GRAPHS 5.2, 5.3

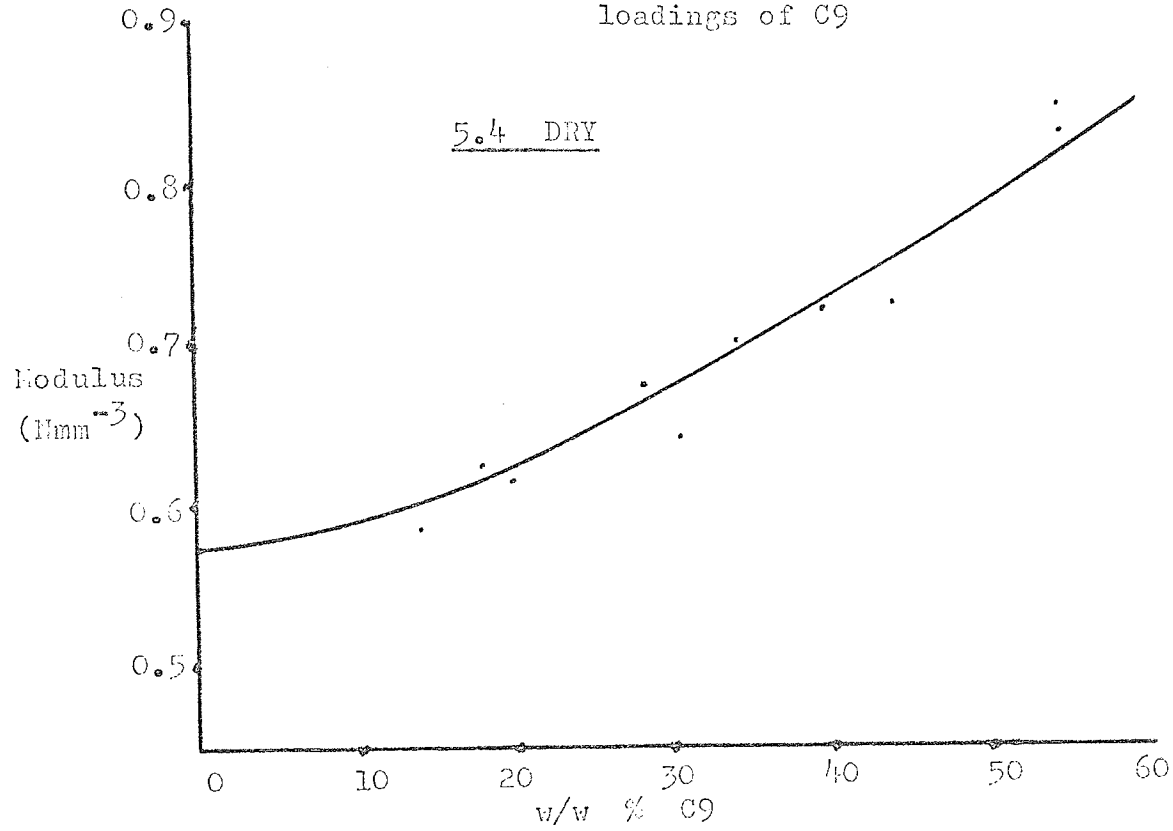
The effect on the ultimate flexural strength of polymethyl methacrylate of increasing loadings of C9 copolymer

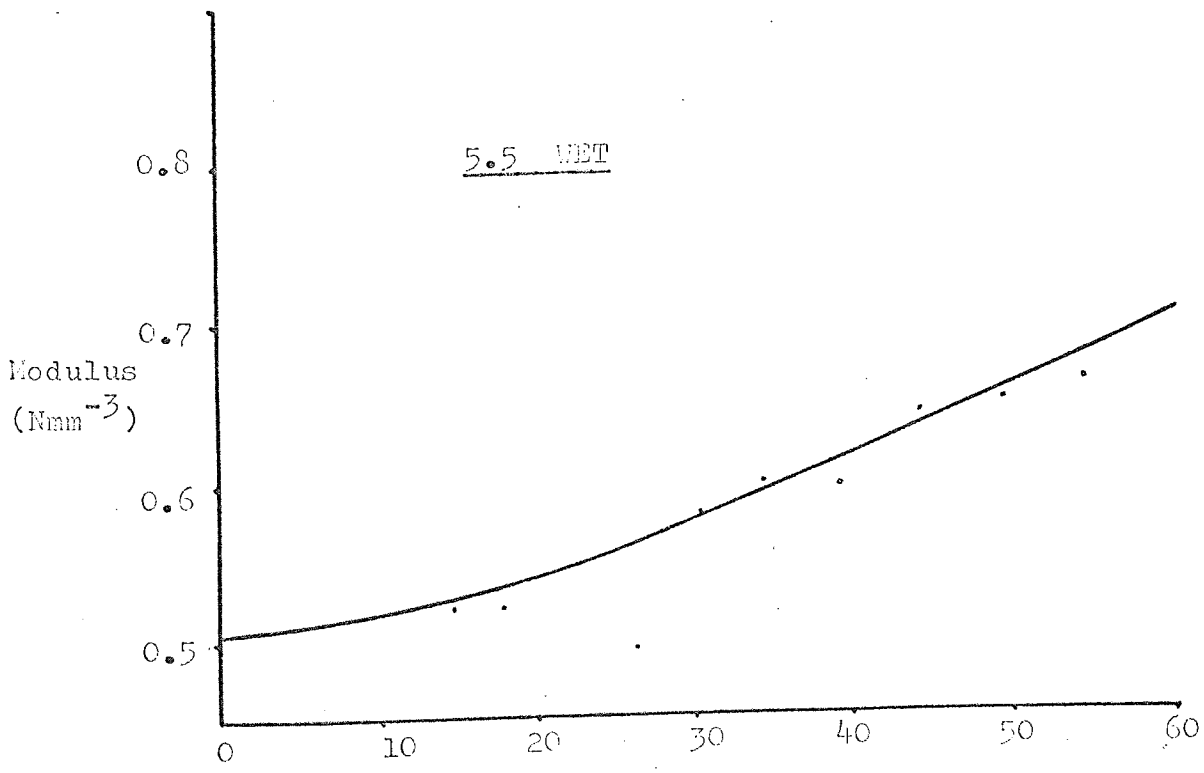




GRAPHS 5.4, 5.5

The effect on the flexural modulus of a composite of increasing loadings of C9





Deflection at break (Graphs 5.6, 5.7) - The degree of deformation decreased markedly with C9 content.

These three parameters indicated a steady increase in brittleness with increasing C9 content. This effect is shown qualitatively in the stress strain curves for the test (Graph 5.8). The curve for Stellon control was typical of a tough low modulus material. That for sample A2 (55% C9 w/w) had the triangular form characteristic of brittle failure. Samples of lower C9 content produced curves intermediate between these two extremes.

5.4 IMPACT STRENGTH PROPERTIES

The results of the impact testing are shown in Graphs 5.9-5.12. In addition a typical family of stress/strain curves is shown in Graph 5.13.

As was predicted from the similarity in the mode of deformation, the results from flexural and impact strength testing showed similar behaviour.

Thus the overall conclusion to be drawn from physical strength evaluation is that the copolymer C9 behaved in a manner typical of an inert filler, and no monomer-copolymer interaction was apparent.

5.5 UV LIGHT STABILITY

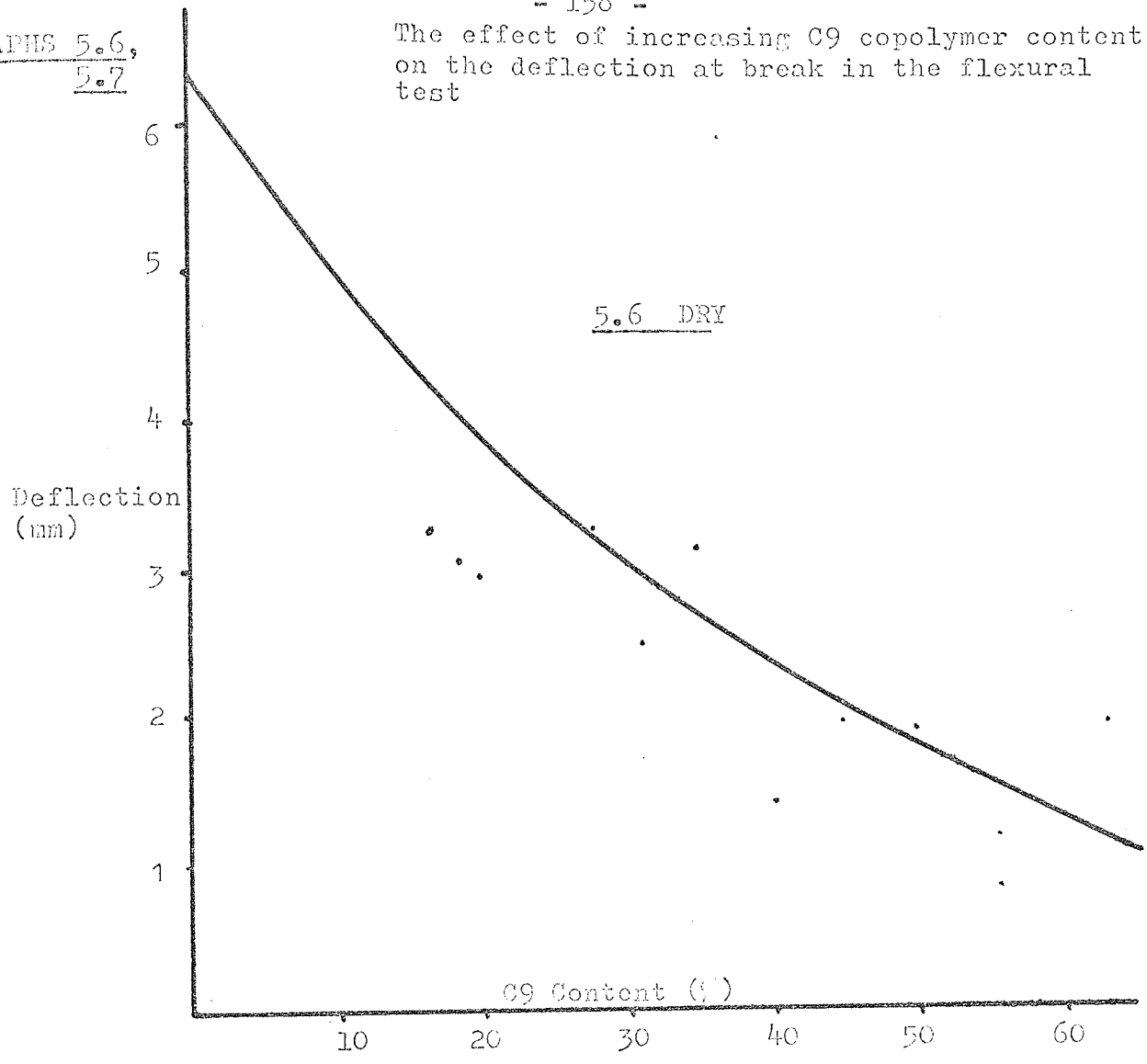
All samples were acceptable after 24 hours exposure - no colour change was detectable.

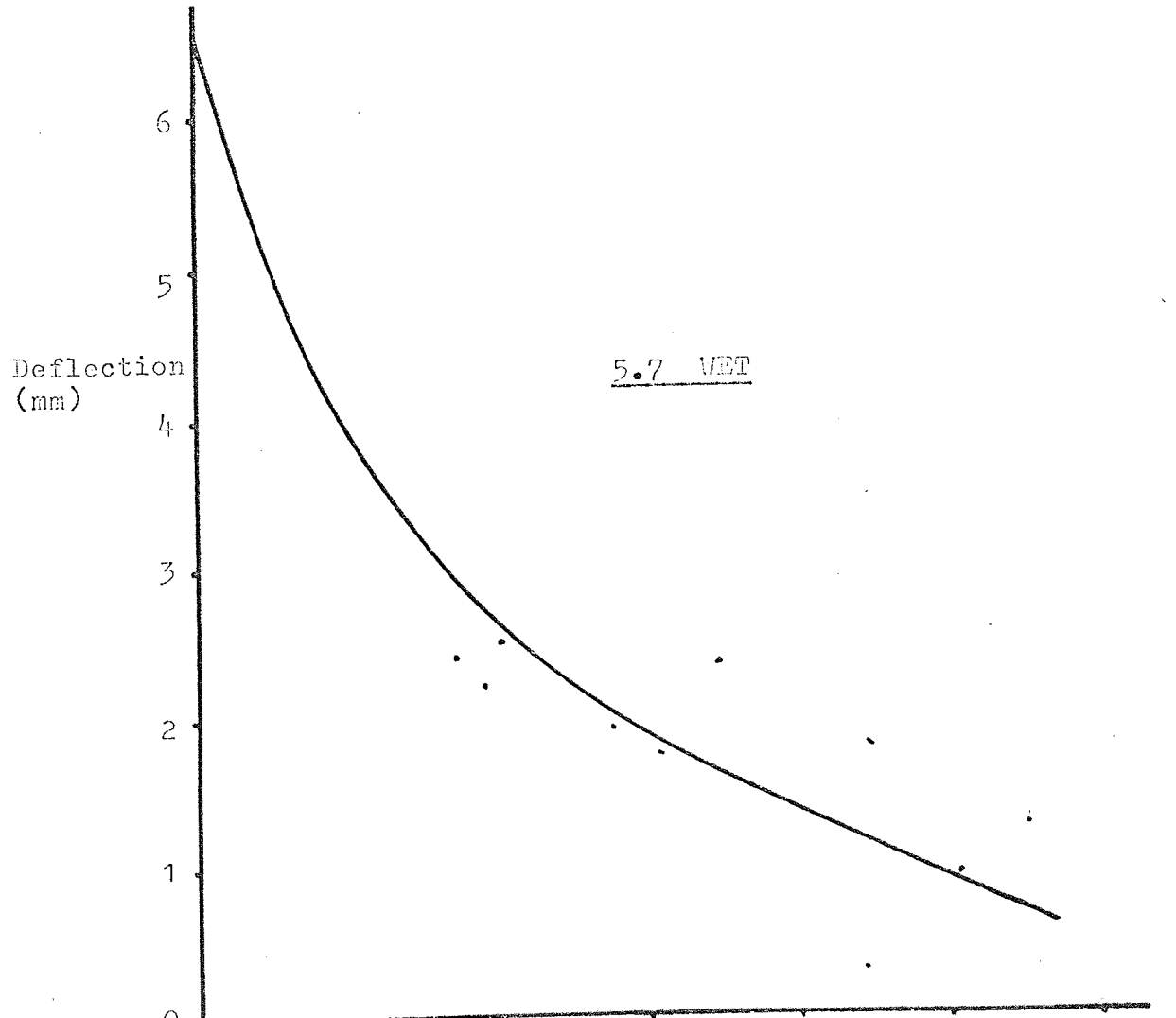
5.6 MICROSCOPY

Owing to the increased brittleness of the high C9 content materials it was not possible to cut thin sections on the microtome. However, the value of optical microscopy on samples approaching

GRAPHS 5.6, 5.7

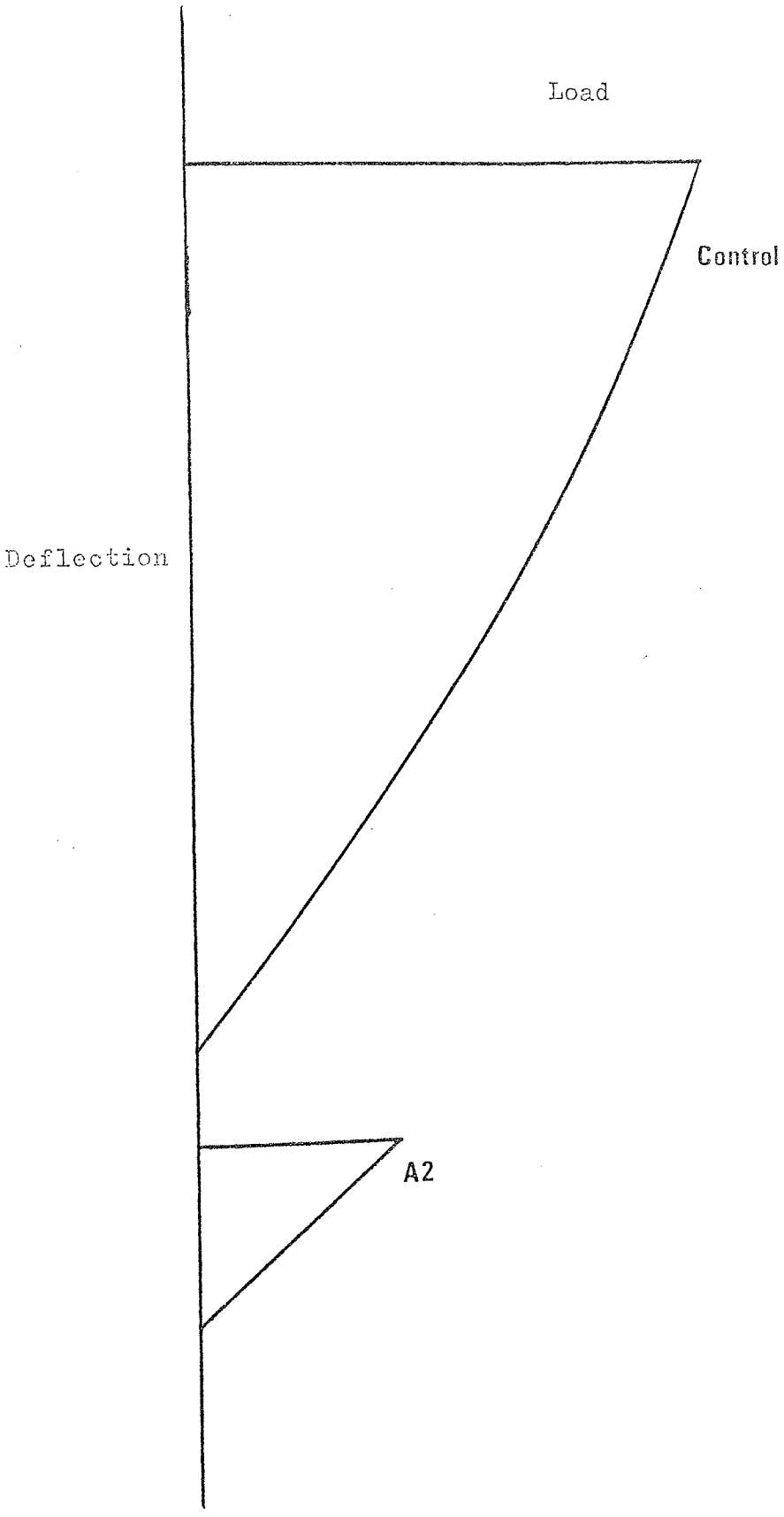
The effect of increasing C9 copolymer content on the deflection at break in the flexural test





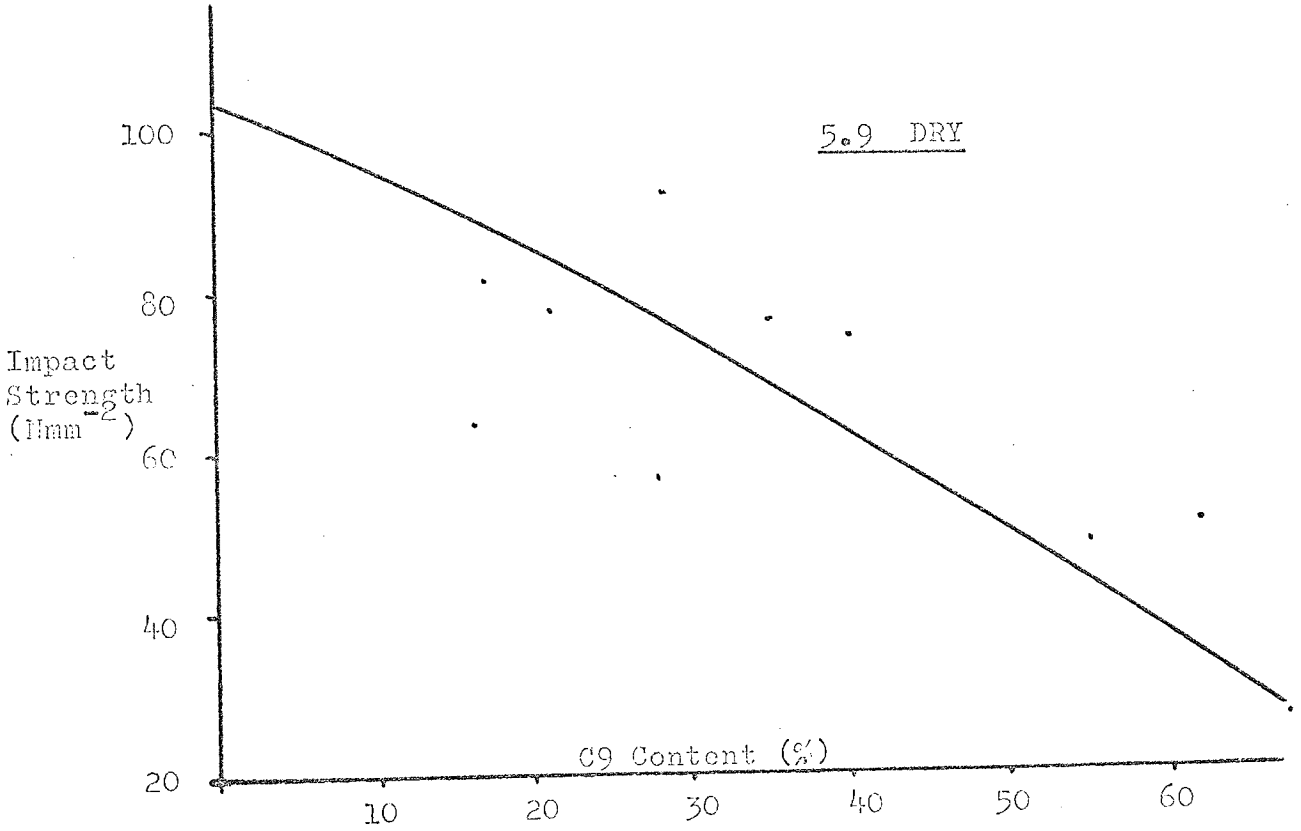
GRAPH 5.8

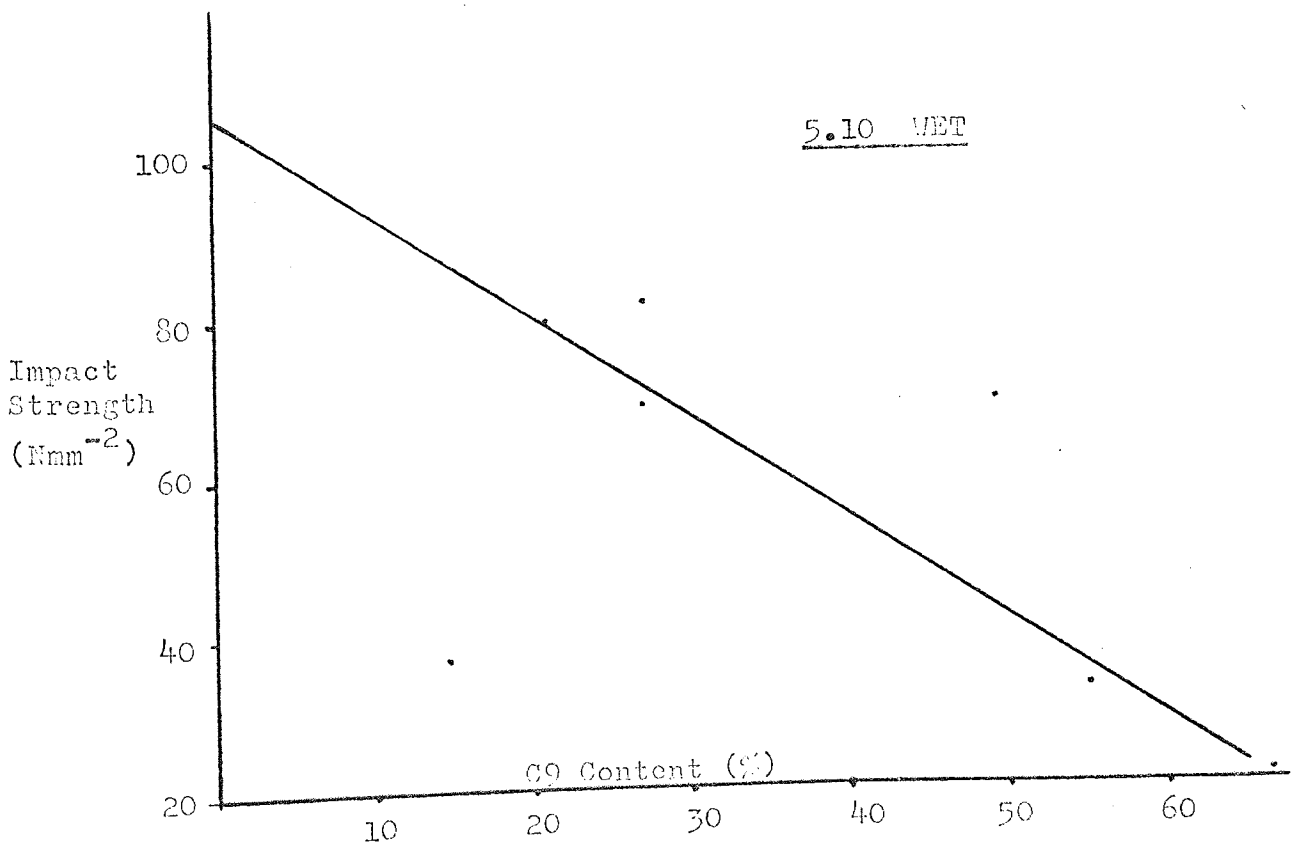
Typical flexural stress/strain curves for 'Stellon' control and a brittle high C9-content material



GRAPHS 5.9, 5.10

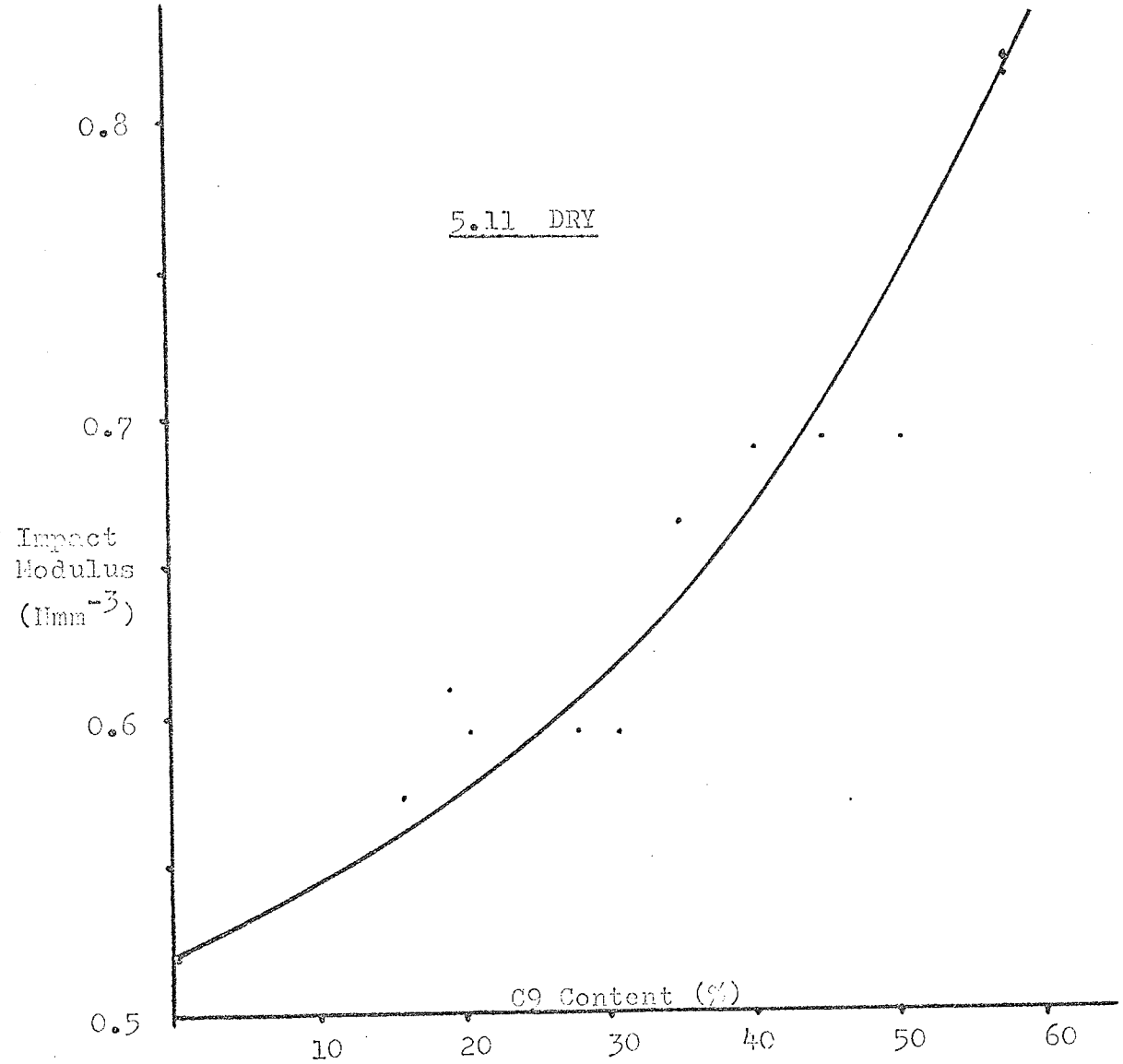
The effect on the impact strength of increasing loadings of C9 copolymer

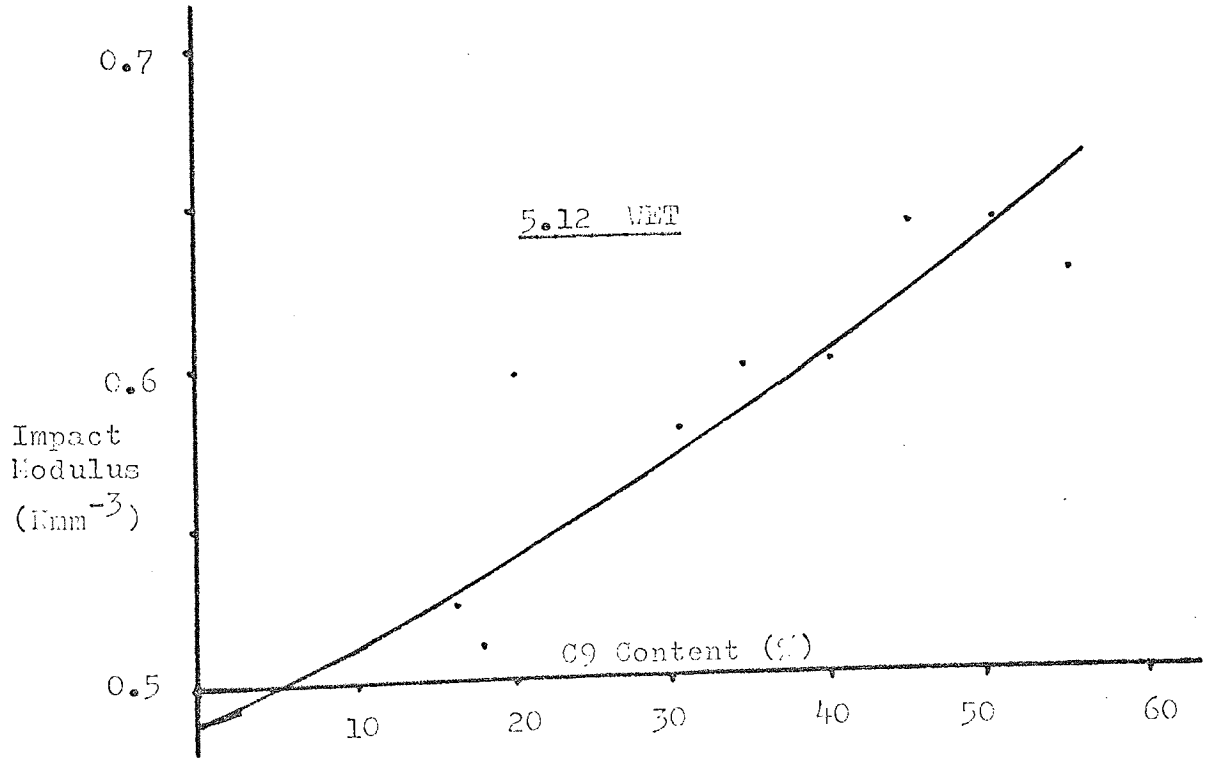




GRAPHS 5.11, 5.12

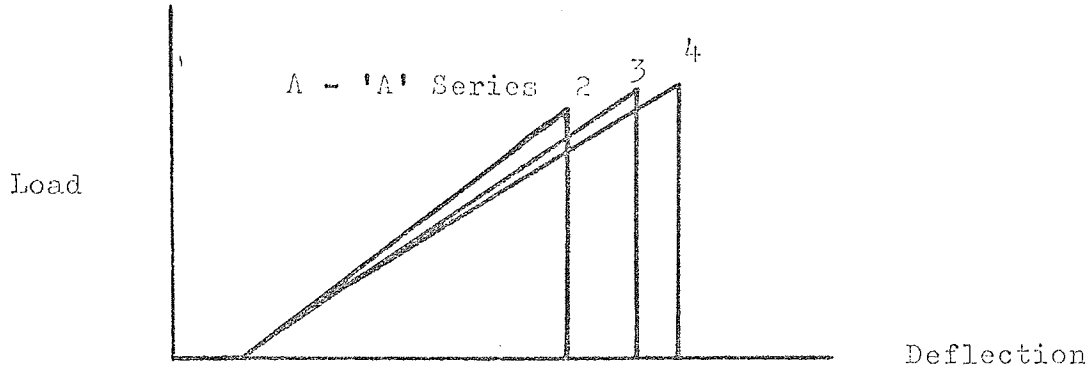
The effect on the impact modulus of increasing loadings of C9 copolymer

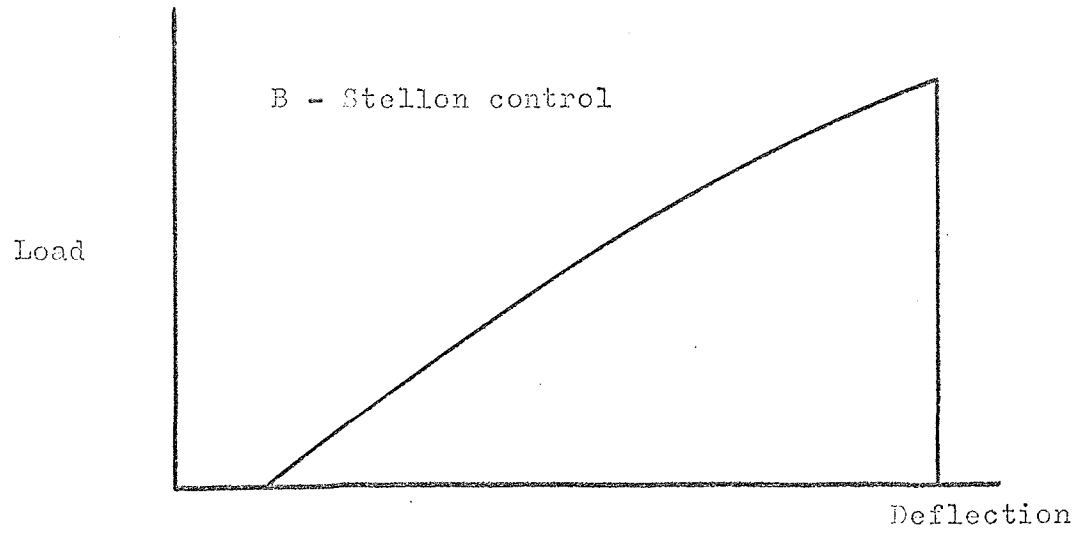


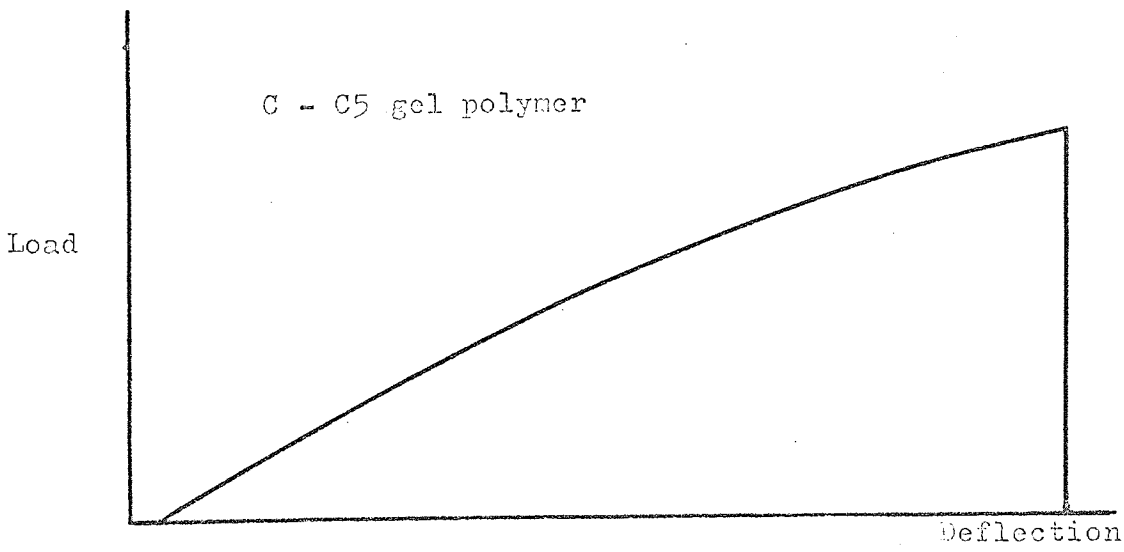


GRAPH 5.13

Typical impact stress/strain curves







transparency is thought to be questionable owing to the low contrast between the two phases present. Stereoscan electron microscopy of fracture surfaces was found much more satisfactory (Plates 5.3 - 5.11). For comparison a photograph of 'Stellon' polymer powder is included (Plate 5.4).

The following observations were made from these plates:

5.6.1 The spheres of 'Stellon' polymer were no longer visible on the fracture surface of a dough moulding without any filler present (Plate 5.3). A conchoidal fracture typical of a glassy material was observed with large numbers of microscopic cracks and flakes.

5.6.2 Plate 5.5, an optical transmission micrograph of a thin section of 'Stellon' moulding does show sphere boundaries. As no filler was present the intersphere darkening can only be due to dust traces which in this case serve a useful purpose as the size of the spheres can be estimated. If a truly homogeneous dough were realised it would be expected that flow in the moulding process would eliminate any evidence of the original spheres. However, not only was the sphere boundary clearly visible, but the estimated size of the particle was similar to the dry polymer. It was only possible to estimate the change in size on dough moulding as the polymer is a polydisperse material and the estimate was made on an average of several spheres in each case.

5.6.3 The visibly opaque high C9 content mouldings have a porous spongey structure containing multiple voids up to 0.5 mm across (Plate 5.6). As these materials were moulded from an incompletely wetted powder this structure was expected.

5.6.4 The fracture surface topography of the optically translucent

PLATE 5.3 STEREOSCAN ELECTRON MICROGRAPH (SEM) OF A FRACTURE SURFACE IN PURE 'STELLON' X 250

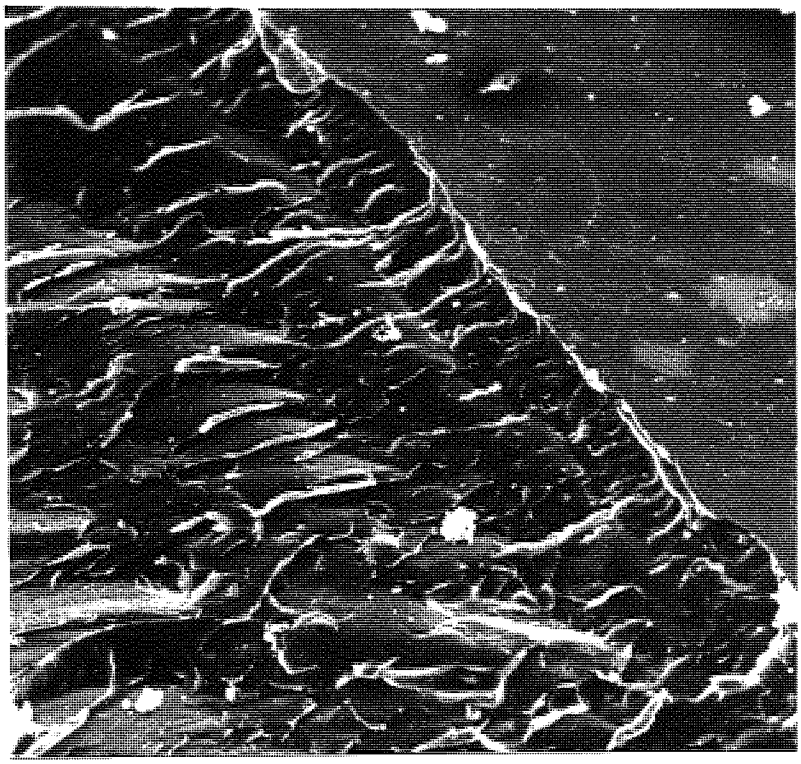


PLATE 5.4 COMMERCIAL 'STELLON' BEADS X 250

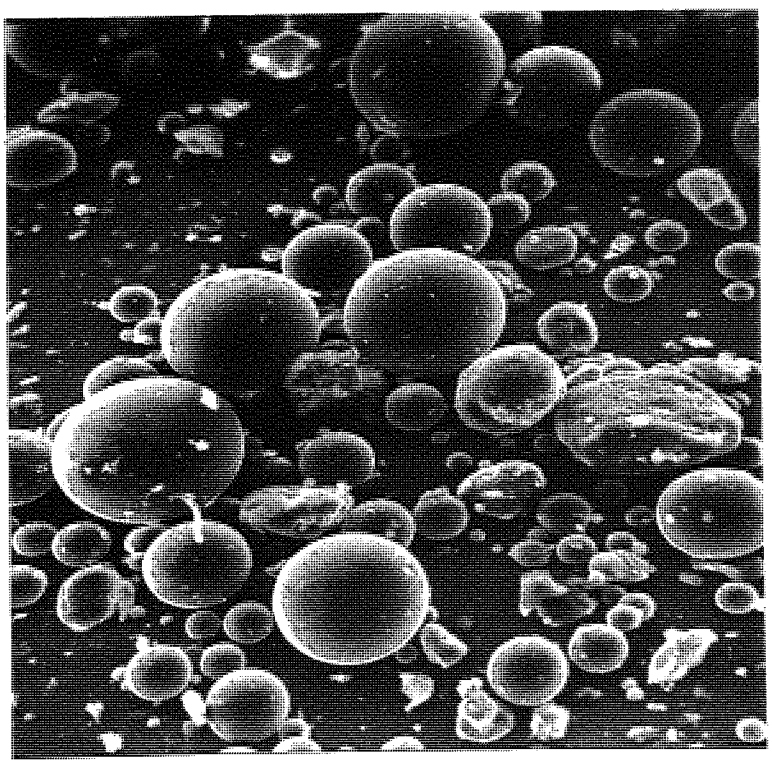


PLATE 5.5 OPTICAL MICROGRAPH OF A THIN SECTION OF A 'STELLON' DOUGH MOULDING X 250

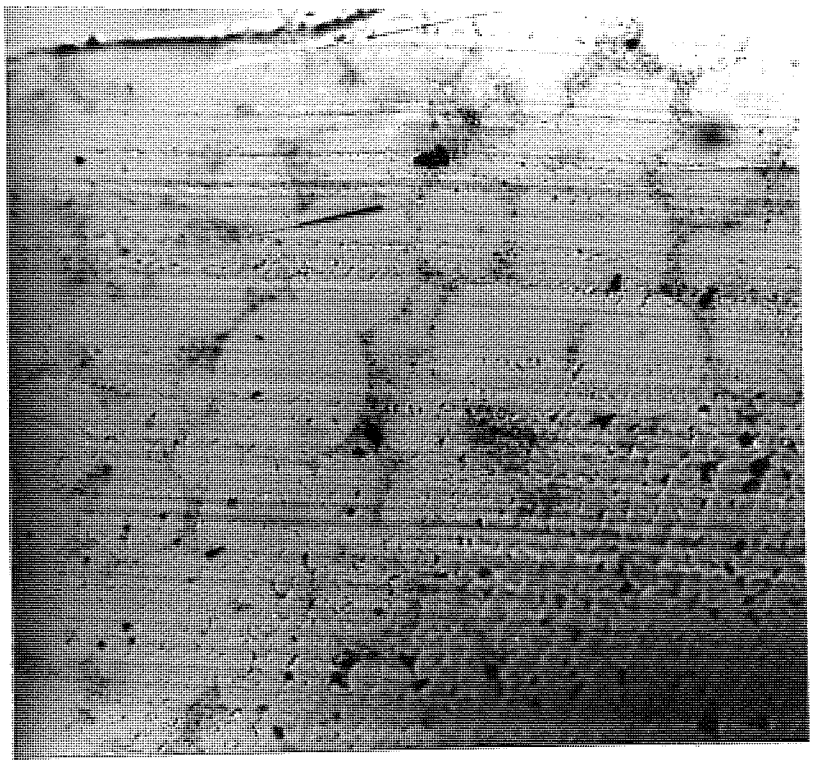
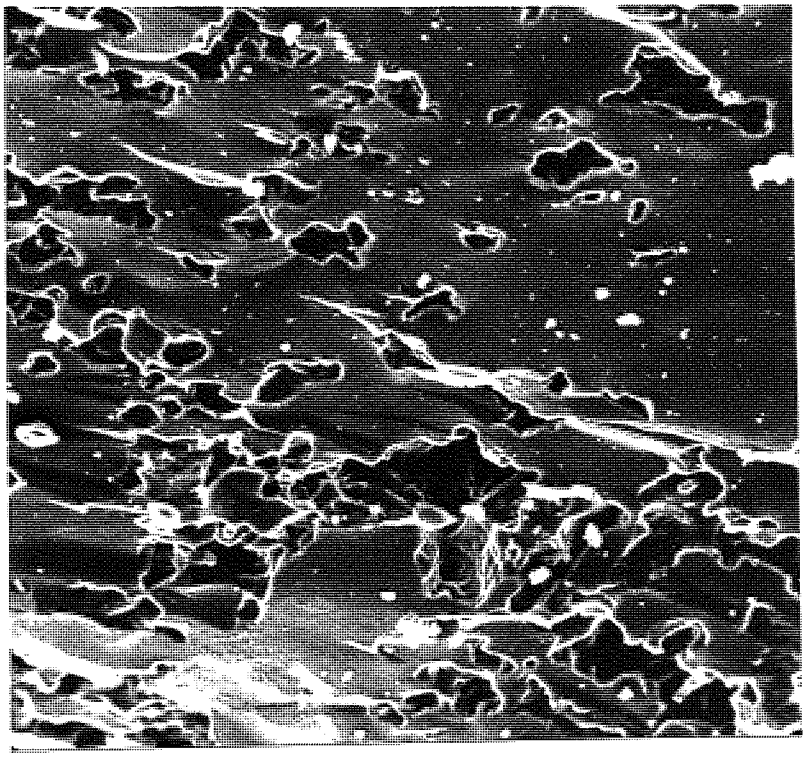


PLATE 5.6 SEM OF A FRACTURE SURFACE OF THE POROUS ZINC-RICH DOUGH MOULDING 'B1' X 250



mouldings typified by formulation B5 (Plate 5.7) was very similar to the control material. There was no sign of any heterogeneities at magnifications up to 2000 x. B5 contained 40% of C9, thus in the interspherular material the loading must be assumed to be much higher, in the region of 62%. The absence of any obvious filler particles in the surface implied that bonding between the two phases was achieved and fracture was through the particles rather than round them. Fracture by this mechanism would yield a featureless surface.

5.6.5 In contrast to the above, a dough moulding containing only 10% w/w (3% v/v) barium sulphate (Plate 5.8) clearly showed filler particles at only 200 x magnification. Barium sulphate is known to behave as an inert, non bonding filler. This result is thus an indication of bonding in the case of C9.

5.6.6 An interesting effect was noted on the sample of gel copolymer C5. The material was tough and difficult to chip (it was unbroken in the flexural strength test). The fracture surface was typified by a high density of minute cracks (Plate 5.9) in some areas. Presumably the toughness is at least partially due to stress dissipation by the abundance of cracks. Over the majority of the fracture surface the cracks seem similar to those exhibited in previous samples (Plate 5.10). However, an unusual compacted ribbon-like structure was shown in certain areas (Plate 5.11). On closer examination it appeared that the ribbon-like structure was exhibited mainly in lateral surfaces, and the more normal structure in vertical fractures. This anisotropy is not surprising when it is considered that the polymer plaque was prepared by pressing a gel between glass plates, and thus subjected to a unidirectional stress.

PLATE 5.7 SEM OF A FRACTURE SURFACE OF THE HOMOGENEOUS TRANSLUCENT DOUGH MOULDING 'B5' X 250

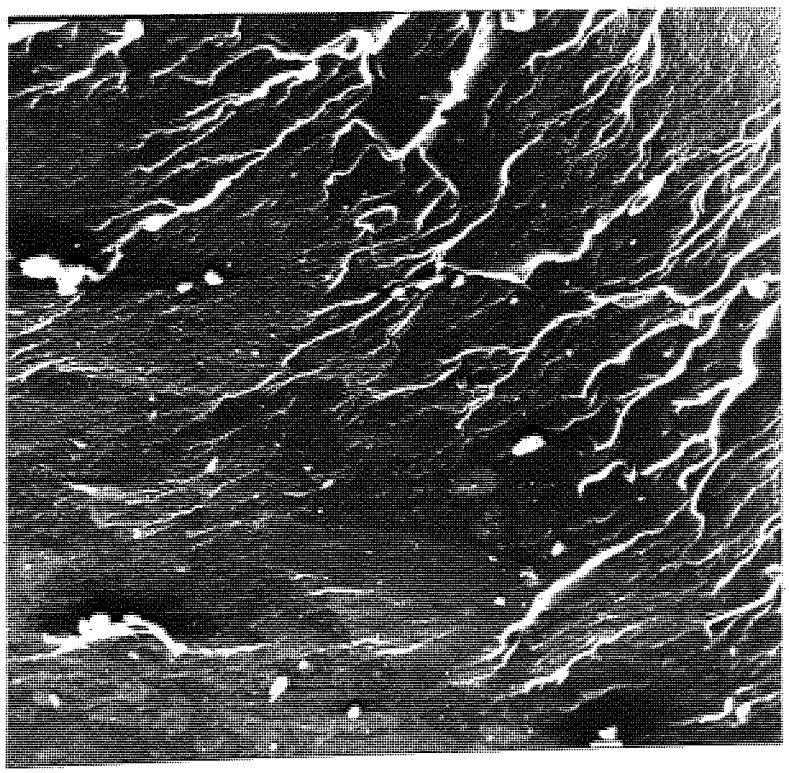


PLATE 5.8 FILLER PARTICLES VISIBLE IN THE FRACTURE SURFACE SEM OF A 'STELLON' DOUGH MOULDING CONTAINING 10% BARIUM SULPHATE X 250

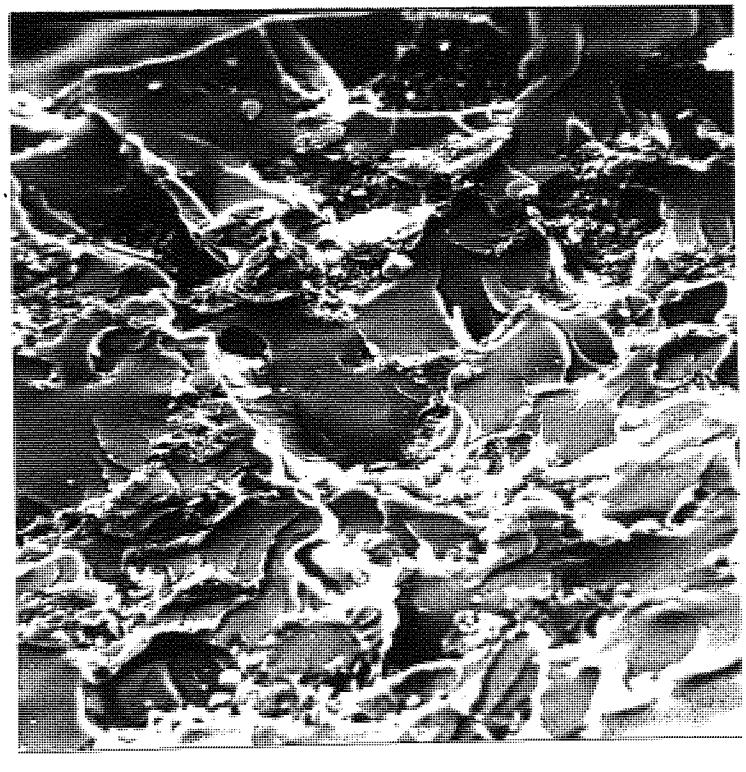
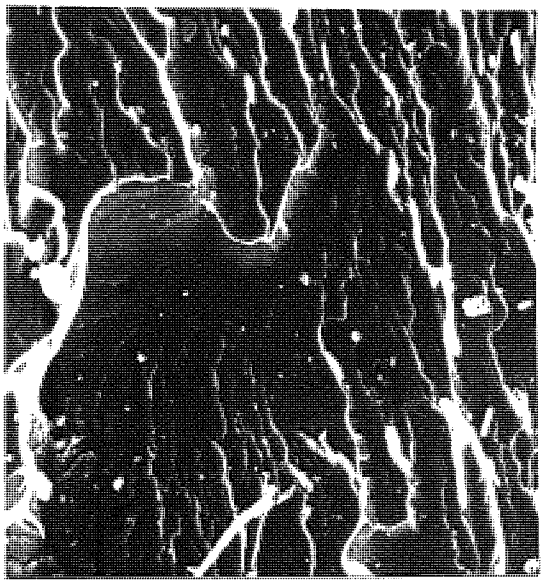


PLATE 5.10
'STELLON' LIKE CRACKING
PERPENDICULAR TO THE
PLANE OF THE PLAQUE
SEM X 500



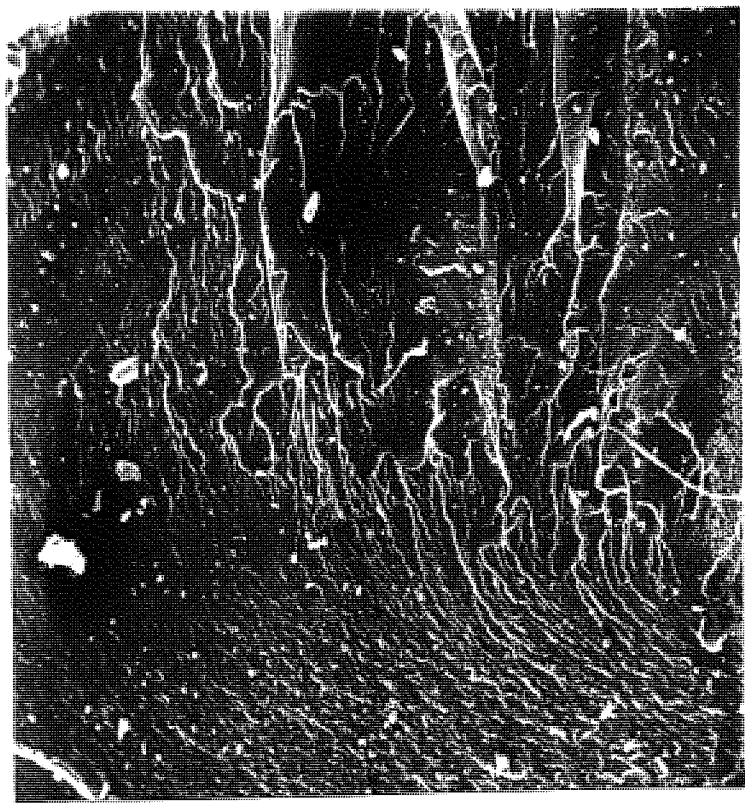
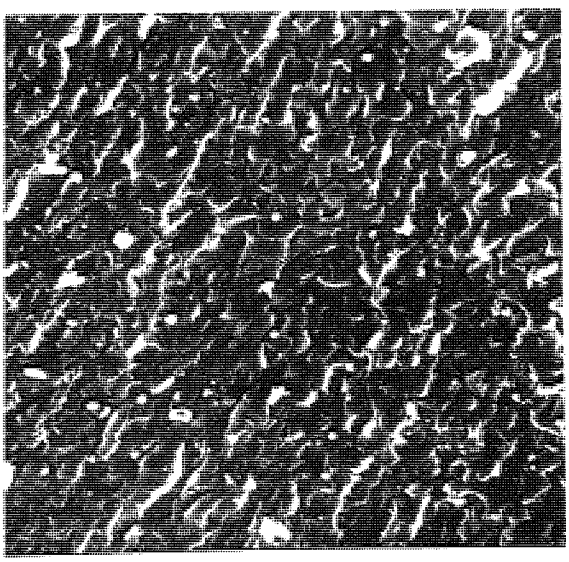


PLATE 5.9
THE TWO FRACTURE TYPES
TYPICAL OF 'C5' GEL
COPOLYMER SEM X65

PLATE 5.11
'RIBBON' CRACKING IN
THE PLANE OF THE PLAQUE
SEM X 500



5.7 ZINC EXTRACTION

Immersion of flex test samples of the series of mouldings in distilled water at 37°C for 7 days yielded the results in Table 5.3 (Analysis was by dithizone colourimetry).

These results are also presented as Graph 5.14.

The extent of zinc lost over one week appears to be very much a function of the original zinc content. However, the very high results for samples A1, A2, B1, C1 cannot be interpreted as simply as this for the samples were not in the same physical state. All other samples were homogeneous and translucent but these high zinc content materials were opaque, white, and more important, porous. Graph 5.14 shows quite clearly the discontinuity between the porous and homogeneous samples. Excluding these atypical materials the zinc extraction figures were promising as it is anticipated that a levelling off, or at least a reduction of rate of extraction will occur at extended times.

5.8 INTERIM SUMMARY

Testing has indicated that incorporation of C9 copolymer into a Stellon dough moulding has the following effects:

5.8.1 - Lengthening of doughing time and reduction in flow of the moulding.

5.8.2 - Mouldings of less than 55% C9 w/w were translucent (acceptably so) those of greater loading were opaque and porous.

5.8.3 - The brittleness of the composite, both in slow and high speed deformation in three point bending became progressively worse as more C9 was incorporated.

5.8.4 - UV stability of all specimens was acceptable.

5.8.5 - Stereoscan microscopy indicated good bonding of C9 into

GRAPH 5.14

The relationship between C9 content and zinc extraction by water at 37°C over 1 week.

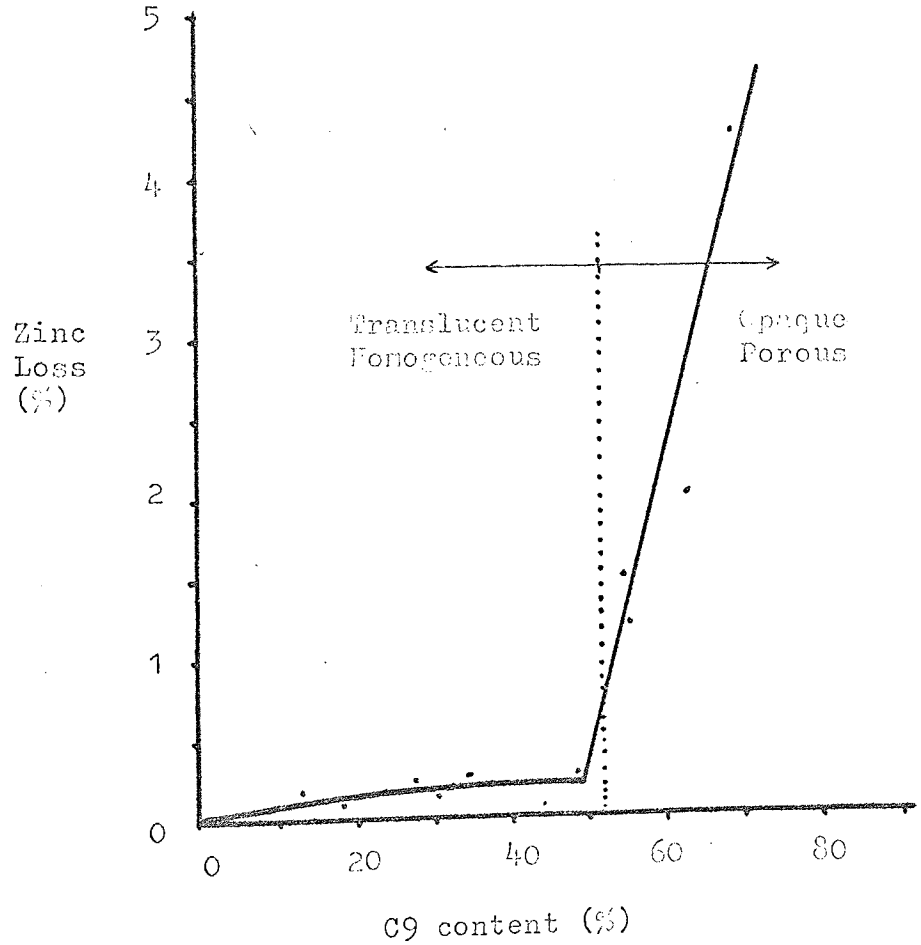


TABLE 5.3

ZINC EXTRACTION IN WATER - A PRELIMINARY STUDY

Sample	Total Zinc Extracted (µg/g sample)	% of Zinc Present Extracted
Control	0	-
A1	9.200	4.30
A2	2,660	1.5
A3	300	0.28
A4	335	0.52
B1	3,900	2.0
B2	240	0.15
B3	140	0.14
B4	31.4	0.053
B5	30	0.024
C1	2,100	1.2
C2	138	0.1
C3	190	0.21
C4	76	0.14
C5 gel polymer	3.9	0.007

the polymer matrix in formulation B5. By contrast a sample filled with barium sulphate to only a quarter of the extent clearly showed non-bonded filler particles.

5.8.6 - The extent of zinc extraction in water at 37°C was minimal for the translucent mouldings. Only the porous materials were unstable to extraction.

Consideration of these observations led logically to further investigations.

5.9 EXTENDED EXTRACTION STUDIES

The extraction results over a period of one week were promising. In order to evaluate the potential suitability of a material for dental applications much more extensive testing was needed. Thus distilled water extraction was extended to samples of different surface areas, and for time periods up to one year with a weekly change of extractant. Parallel extractions were carried out in solutions of pH 2.9, 4, 9, and 12.5. A further sample was immersed in stagnant distilled water from which small samples were taken for analysis.

These analyses were carried out on formulation B5 taken as a typical translucent moulding of high zinc content.

The results of these extractions are shown in Graphs 5.15 - 5.18. The samples represented in Graph 5.15 are:

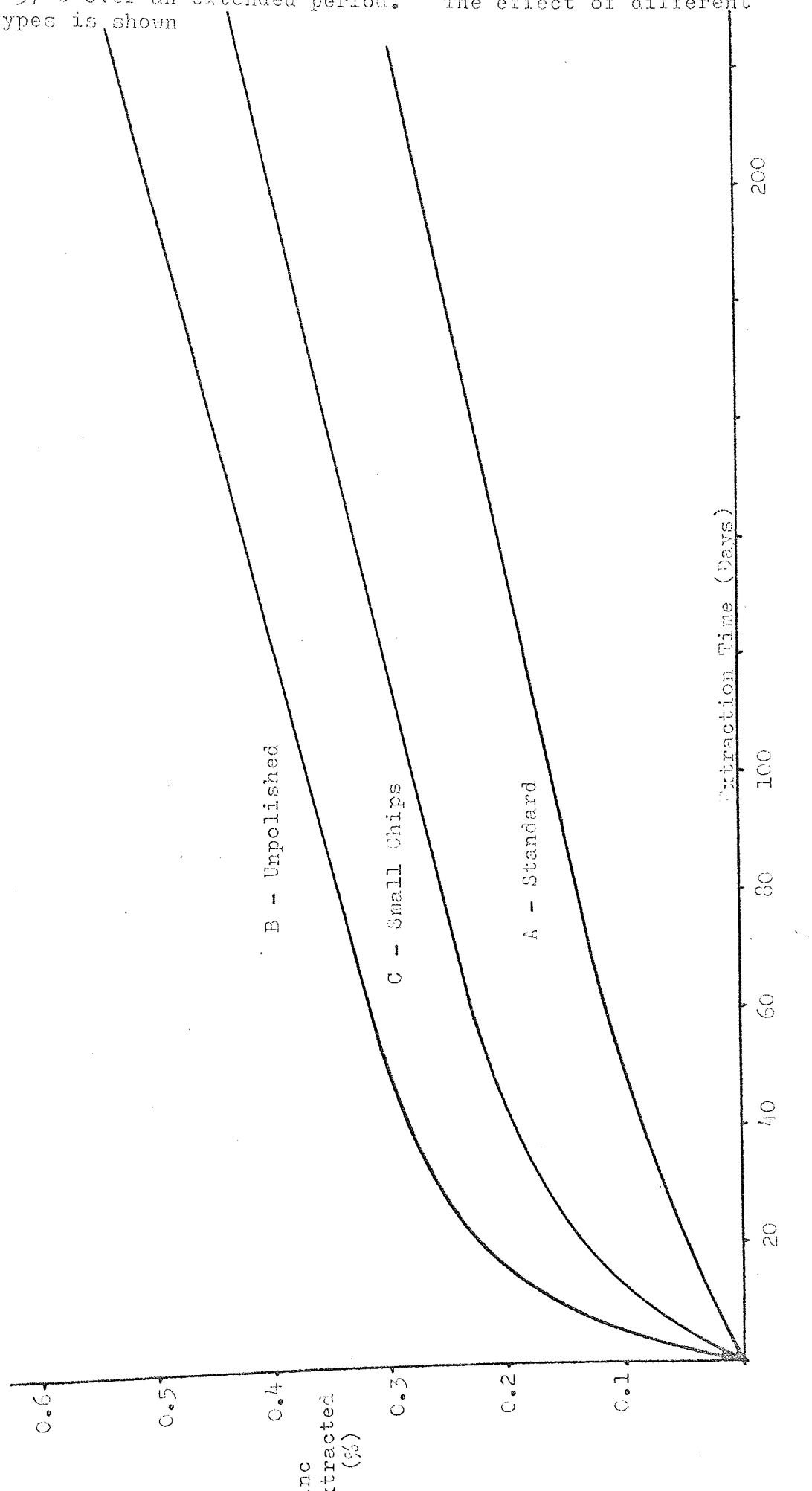
A) Standard sample 10 mm x 2.5 mm x 60 mm surface rubbed down on 600 grade emery ($\sim$ = 1550 mm^2)

B) Dough moulded sample with surface whitening left undisturbed 10 mm x 2.5 mm x 60 mm ($\sim$ = 1550 mm^2)

C) Fifteen small samples 2.5 mm x 4 mm x 10 mm with surface rubbed down on 600 grade emery ($\sim$ = 2250 mm^2)

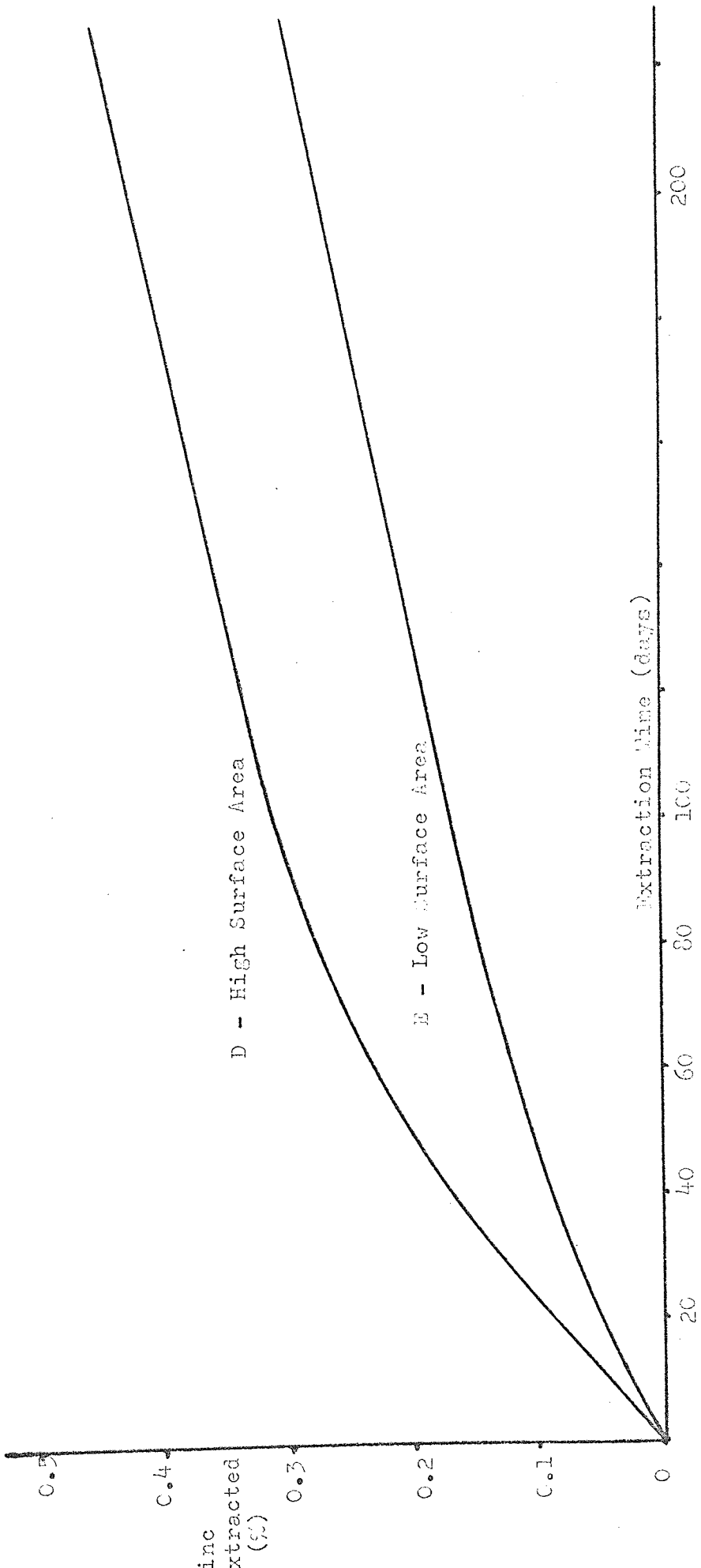
GRAPH 5.15

Showing the extraction of zinc from a B5 moulding immersed in water at 37°C over an extended period. The effect of different sample types is shown



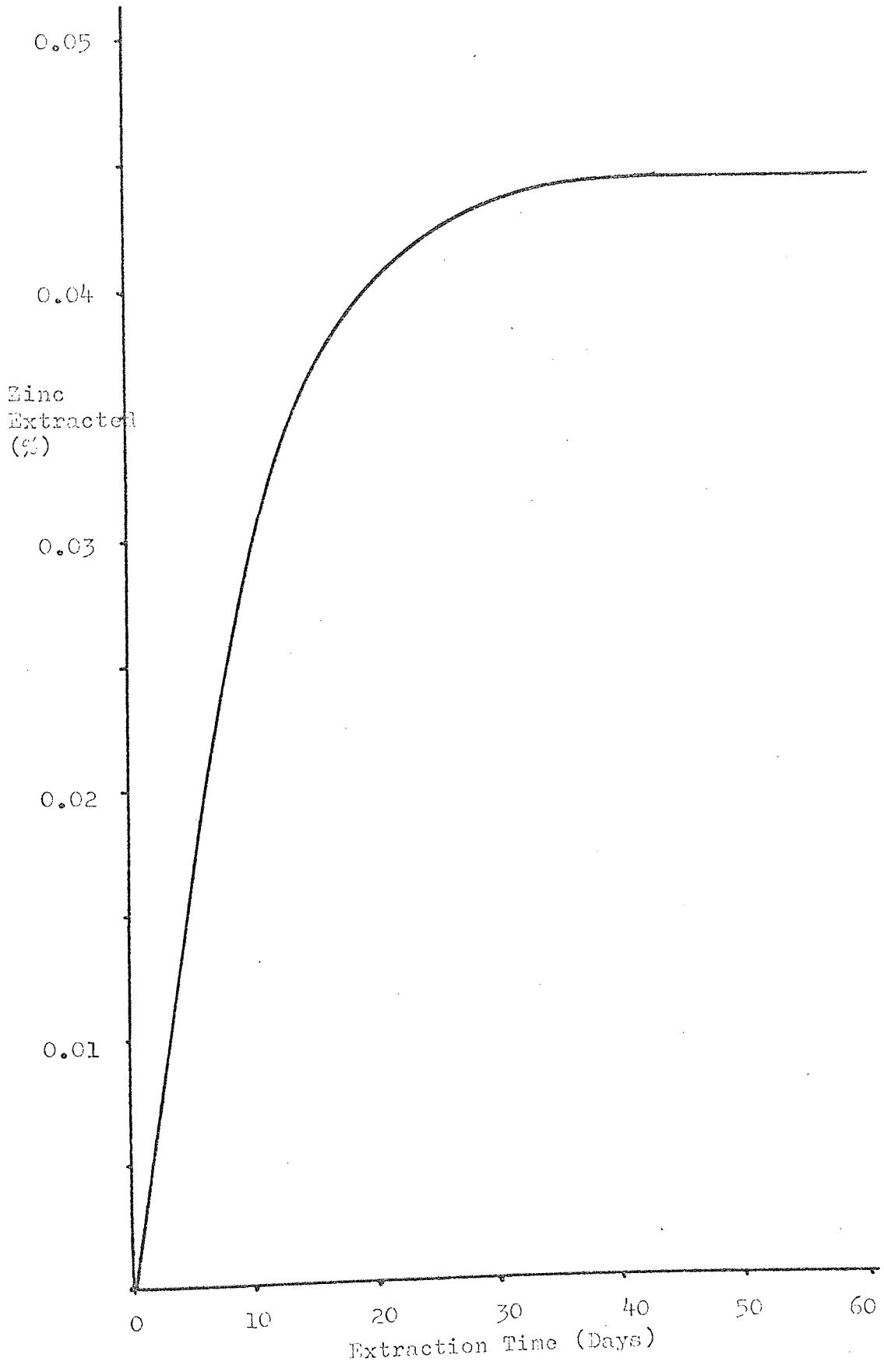
GRAPH 5.16

The effect of surface area (measured macroscopically) on long term zinc extraction



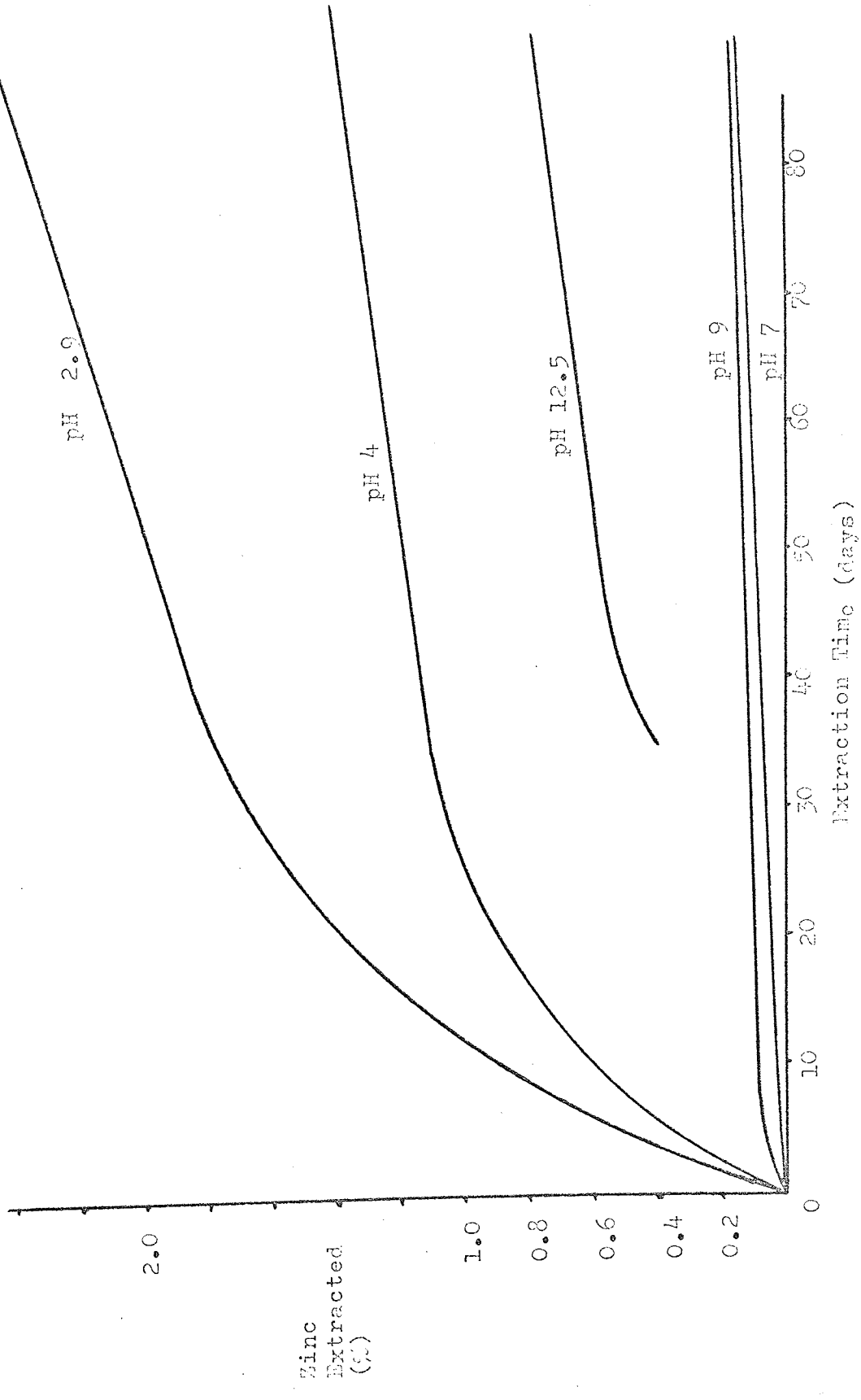
GRAPH 5.17

The zinc extraction from a B5 moulding into stagnant water at 37°C



GRAPH 5.18

The effect of pH on the rate of extraction of zinc from B5 mouldings immersed at 37°C



Where α represents the macroscopic surface area.

All of the above samples were cut from B5 dough mouldings in which sodium alginate solution was employed as the separating medium. The samples involved in the extractions of Graph 5.16 were moulded using polythene separating sheets. These samples were rubbed down on 600 grade emery.

D) 20 mm x 1 mm x 60 mm (α = 2640 mm^2)

E) 20 mm x 7 mm x 10 mm (α = 960 mm^2)

In Graph 5.18 the samples used were all identical to the alginate moulded (A) above, and the quoted pH's of the extractants were achieved using the following solutions:

pH 2.9 - 0.01 M Acetic acid solution

pH 4 - saturated potassium hydrogen tartrate solution

pH 7 - distilled water

pH 9 - 0.01 M borax solution

pH 12.5 - saturated calcium hydroxide solution.

In all of these systems analysis was begun weekly by dithizone colourimetry. After four weeks parallel analysis was performed by atomic absorption spectroscopy and continued for a further three weeks. The colourimetry was then discontinued and atomic absorption alone employed for the remaining estimations.

A complication arose in the case of the pH 12.5 solution as it was found that neither of the above techniques was sensitive to zinc at this pH. Whether this was due to the presence of the zinc as a precipitate of hydroxide or as the zincate is unknown. It was found that neutralisation with dilute hydrochloric acid prior to analysis prevented this interference so that the zinc analyses could be made. Unfortunately this phenomenon was discovered retrospectively, and the appropriate curve on Graph 5.18 is begun

at 35 days extraction at an arbitrary position.

The following observations were made on the graphs:

5.9.1 Increased surface area of a sample results in a greater rate of zinc extraction, at least in the initial stages of the test.

5.9.2 Removal of the surface whitening of the alginate-moulded material resulted in a drastic reduction in the initial rate of extraction.

5.9.3 Extraction in a stagnant system followed the curve for the constantly changing system up to three weeks into the test (0.04% w/w extracted). Beyond this point the stagnant extraction levelled out to a constant figure.

5.9.4 With the exception of the stagnant system, no equilibrium was reached with any sample. In all cases linearity of the curve was approached after approximately forty days though not necessarily of similar gradients.

5.9.5 The equilibrium gradients of all the extraction curves for samples immersed in water were very similar.

TABLE 5.4

EQUILIBRIUM EXTRACTION RATES IN WATER

Sample	Gradient
A (α = 1550 mm^2)	1.01×10^{-3} %/day
B (rough surface)	1.15×10^{-3} %/day
C (α = 2550 mm^2)	1.2×10^{-3} %/day
D (α = 960 mm^2)	1.12×10^{-3} %/day
E (α = 2640 mm^2)	1.01×10^{-3} %/day

Though the lack of a plateau in the above systems was a cause of concern, continued extraction at the steady rates observed would only result in a loss of 8-10% of the zinc over a period of 25 years. This period is longer than the recommended life of a denture, and it may safely be assumed that more than 90% of the initial radiopacity will be retained throughout the useful life of the material.

5.9.6 Extraction in systems other than distilled water invariably resulted in increased rates of extraction throughout the test (Graph 5.18). The curves were similar in form to those obtained in water, showing a reduction in gradient with time, until a steady gradient was reached. These steady gradients were not similar to those for the neutral system.

TABLE 5.5

EQUILIBRIUM EXTRACTION RATES IN SYSTEMS OTHER THAN WATER

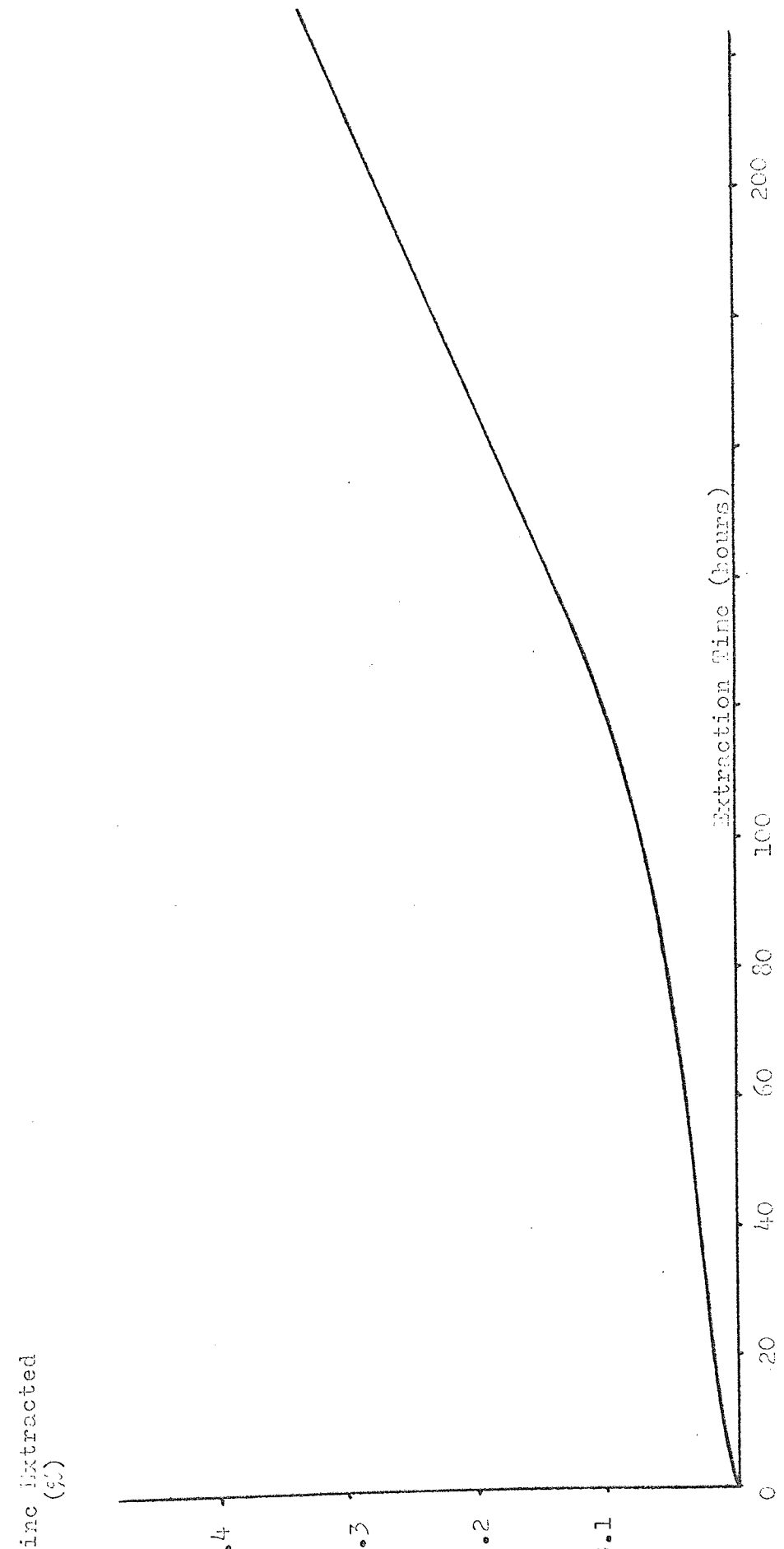
pH of extractant	gradient (%/day)
2.9	1.31×10^{-2}
4	5.1×10^{-3}
(7	1.01×10^{-3})
9	1.00×10^{-3}
12.5	5.2×10^{-3}

These gradients are all seen to lie on a smooth curve when plotted against the pH of the extractant (Graph 5.20).

The extremes of environment expected in the mouth correspond to pH4 and 9 though for the majority of the time a more neutral system is normal. At these extremes of pH the useful radiopaque life of a B5 moulding is still expected to exceed fifteen years, (by which time the zinc content may have fallen by up to 25%).

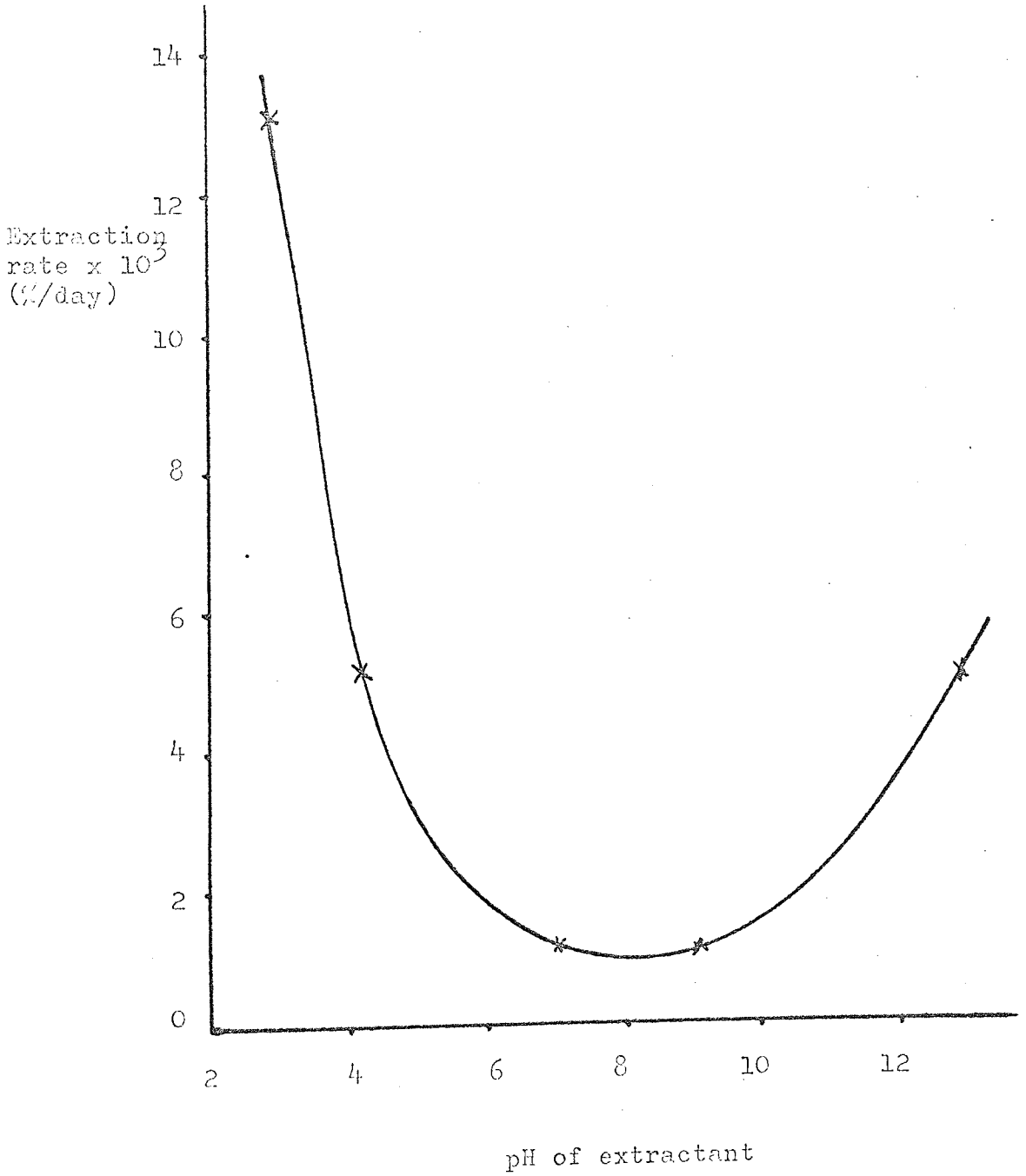
GRAPH 5.19

Zinc extraction from a B5 moulding at 100°C in a soxhlet extractor



GRAPH 5.20

Equilibrium zinc extraction rates at 37°C as a function of the pH of the extractant



5.9.7 An attempt to simulate long term performance extraction at elevated temperatures in a soxhlet extractor at 100°C did not produce a comparable extraction curve to those at 37°C (Graph 5.19). In this case an accelerating extraction was observed, though once again attaining a steady gradient in the later stages corresponding to a rate of extraction of 0.55%/day. The sample in this test was similar to sample E (α = 2640 mm^2). During the high temperature extraction the sample 'warped' considerably and showed a degree of roughening of the surface. The warping is considered to be due to relaxation of moulded-in stresses above the glass transition temperature of polymethyl methacrylate. The surface roughening was assumed to be due either to this same relaxation effect or to swelling of the copolymer particles in the surface by water.

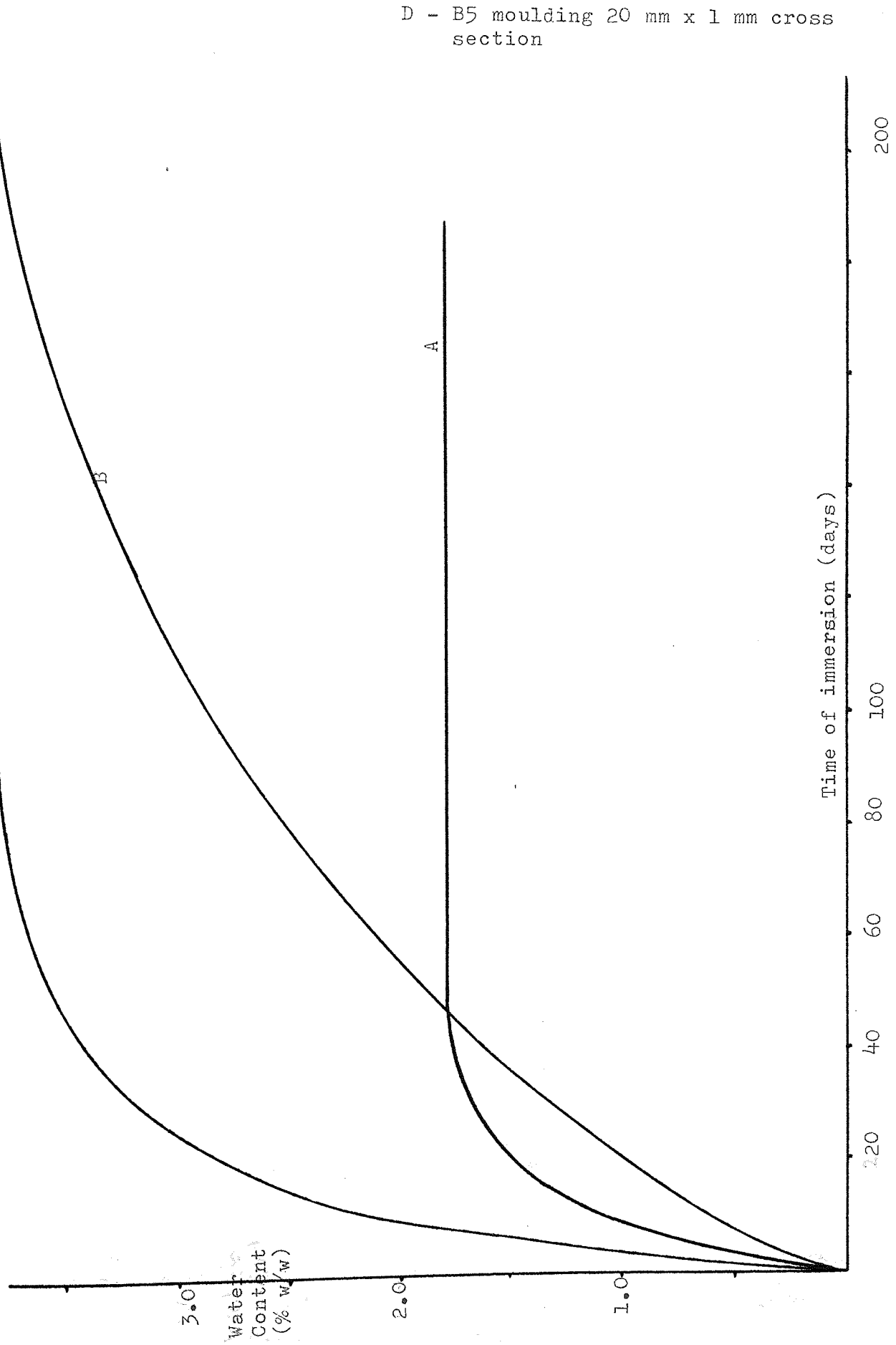
In the context of long term extraction studies it is considered worthwhile, in an attempt to assign the various parts of the curves to a definite physical process, to evaluate the long term water-sorption behaviour. The weight percentage of absorbed water for the various sample configurations is shown as a function of time in Graph 5.21. It has been reported (50) that denture base material in general absorbs its equilibrium water content within 40-60 days. The curves of Graph 5.21 confirm this observation for thin specimens of 'Stellon' and 'B5 composite'. However, the low surface area, 7 mm thick B5 sample took over six months to achieve equilibrium. It was surprising to note the identical similarity of the curves for 1 mm and 2.5 mm thick specimens of B5. This behaviour is not readily explained and is considered to be a problem of diffusion properties, and as such, outside the scope of this study.

In the extraction studies on standard samples (Graph 5.15) the

GRAPH 5.21

Water sorption behaviour of:

A - Stellon control
B - B5 moulding 7 mm x 7 mm cross section
C - B5 moulding 10 mm x 2.5 mm cross section
D - B5 moulding 20 mm x 1 mm cross section



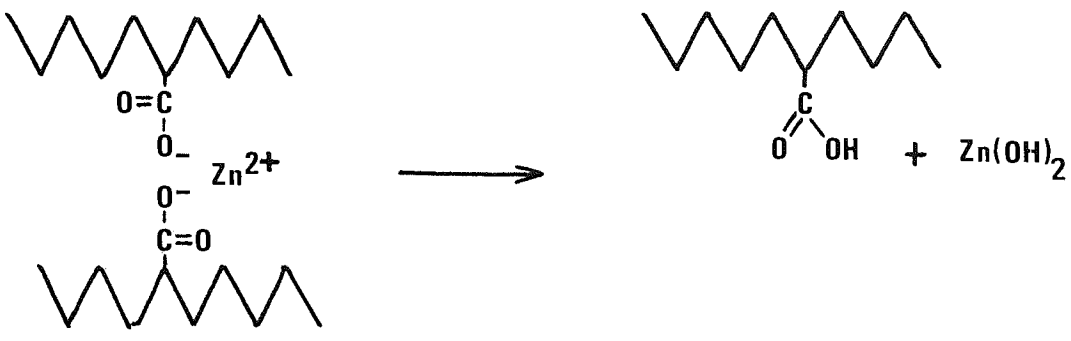
onset of linearity of the curves occurs at about 35 days - the time for equilibrium water sorption. Unfortunately this relationship was not born out in the high and low surface area samples of Graph 5.16. The greatest discrepancy was observed in the sample of low surface area, extraction became linear after 40-60 days, whereas some 200 days was needed for equilibrium absorption. However, due to the low initial extraction rate of this sample and hence the absence of a pronounced curve the onset of linearity could easily be confused with experimental error in the extraction analysis.

It appears then that extraction occurs by two mechanisms:-

a) Preliminary dissolution of any soluble zinc compound remaining in the composite during initial water absorption. This effect is dependent on the surface area of the sample.

b) Steady extraction of zinc from the saturated sample - proportional to time, independent of surface area.

An explanation of the mechanism of b) above is suggested by consideration of the stagnant system. An equilibrium extraction level in a stagnant system suggests that the process is controlled by the solubility of the species extracted. The saturation concentration measured was 155 μg Zn/100 ml solution or 0.000155%. This figure corresponds to the reported solubility of zinc hydroxide at a similar temperature (equivalent to 0.00013 - 16% with respect to zinc). It is thus suggested that the mechanism of zinc extraction is primarily one of hydrolysis rather than a purely solution effect.



It is known that the reverse reaction occurs at high temperatures and pressures (74) and it is not surprising that in an aqueous system the zinc salt should be hydrolysed. Zinc hydroxide is soluble in dilute acids and strong bases and thus an increased rate of hydrolysis is to be expected at pH's differing from neutrality. This behaviour was observed.

It appears that the linear gradients correspond to the rate constants of the hydrolysis reaction in the various solutions. The high rate of extraction at 100°C in the soxhlet is also understandable. This rate of 0.54% per day is ca 450 times greater than at 37°C, a not unreasonable increase over a temperature difference of 63°C. Over and above the temperature effect on the hydrolysis is the fact that soxhlet extraction implies the constant redistillation of the extractant and thus prevents any inhibition of the reaction by a build-up of zinc hydroxide. It is not considered worth investigating the extraction at other intermediate temperatures, though obviously this could provide a course of study in itself to evaluate the reaction parameters.

5.10 MODIFICATION OF THE ZINC CONTAINING COPOLYMER

Consideration of all the test results from the series of mouldings containing C9 polymer suggested an inherent brittleness or lack of bonding within the copolymer particles. The validity of the brittleness theory was tested by modification of the comonomers used to produce the solid phase. Internal plasticisation of the copolymer was attempted by incorporating flexibilising monomers such as lauryl methacrylate. The formulations were as follows, in each case the zinc acrylate (or methacrylate content was maintained at the level used in the C9 polymerisation).

Zinc Acrylate / lauryl methacrylate (ZALMA)

Zinc Acrylate / methyl acrylate (ZAMA)

Zinc Acrylate / ethyl acrylate (ZAEA)

Zinc Methacrylate / lauryl methacrylate (ZMALMA)

Zinc Methacrylate / methyl methacrylate (ZMAMMA)

The liquid monomers were purified by distillation at reduced pressure and their purity confirmed by gas/liquid chromatography. Polymerisation was then carried out under the conditions described previously for the zinc acrylate/methyl methacrylate system. Precipitation of the copolymers occurred as in the earlier system to yield a series of white friable crumbs. After vacuum drying at 100°C these materials were easily ground to fine white powders to pass through a 200 mesh sieve.

Analysis of these copolymers by TGA showed the zinc contents to be as follows (at ~ 100% conversion with respect to zinc acrylate).

TABLE 5.6

COMPOSITION OF MODIFIED COPOLYMERS

Copolymer	w/w % zinc (meth) acrylate
ZALMA	30.5
ZAMA	48.4
ZAEA	54.2
ZMALMA	42.8
ZMAMMA	47.9

In all of these systems the monomer phase contained 25% of zinc (meth) acrylate and it is therefore interesting to note the variation in zinc content of the copolymers at similar degrees of conversion.

Dissolution in formic acid and reprecipitation in water was used once more to remove the zinc and homopoly acids. This yielded the following figures for the comparative effectiveness of copolymerisation and homopolymerisation.

Copolymer	w/w % of zinc salt homopolymerised
C9	54
ZALMA	58
ZAEA	47
ZAMA	57
ZMAMMA	66
ZMALMA	69

As was expected any increase in the bulk of the monomer molecules resulted in a reduced tendency to form a copolymer. Little significant difference was observed in the simple acrylates.

All of these copolymers were dough moulded with Stellon polymer and monomer according to the B5 formulation, copolymers C9 and C11 (71% zinc acrylate) were included for comparison.

The improved properties of the copolymer 'ZALMA' are not regarded as of great significance due to its lower zinc content (30.5% against the>50% of C9). It appears that little or no improvement was observed in the moulding process for any of the formulations. However, if the lack of interaction with monomer is to be ascribed to the cross linking effect of the divalent zinc atom it is not expected that variation of the comonomer should affect the moulding properties.

The object of this experiment was to modify the physical properties of the dough moulding, hopefully to comply with the British

TABLE 5.7

DOUGH MOULDING PROPERTIES OF MODIFIED COPOLYMERS

Copolymer	Observations
C9 (standard B5)	Stiff workable dough, moderate flow - translucent product
C11	Stiff dough, good flow, moulding was white, opaque.
ZMAMMA	Similar to C11
ZAMA	Similar to C9
ZAEA	Greyish watery dough, required heating to become mouldable - product was translucent.
ZALMA	Slightly 'gritty' dough, good flow product verged on transparency.
ZMALMA	Very 'thirsty' powder requiring almost double the standard quantity of monomer to produce a dough. Product was yellowish and translucent.

Standard. The results of flexural strength testing were as follows:

TABLE 5.8

FLEXURAL STRENGTH PROPERTIES OF THE MODIFIED MOULDINGS

Sample	Breaking Load (Nmm^{-2})		Initial Modulus (Nmm^{-3})		Deflection at Break (mm)	
	Dry	Wet	Dry	Wet	Dry	Wet
B5(C9)	50	61	0.725	0.683	2.25	2.3
C11	56	51	0.806	0.721	2.4	2.5
ZMAMMA	55.8	51.7	0.670	0.590	2.8	2.9
ZAMA	48	42.5*	0.690	0.500	2.4	4.1
ZAEA	39.8	40.7	0.650	0.571	2.1	2.5
ZALMA	22.9	24	0.205	0.206	3.8	4.1
ZMALMA	32.6	33.9	0.363	0.364	3.1	3.2

*The wet ZAMA sample was considerably swollen accounting for the depression of the breaking load which is a function of the cross sectional area.

From this table it is readily apparent that though the modulus is dependent on the composition of the copolymer the deflection at break is not. By variation of the copolymerisation system it would seem to be possible to achieve any value of initial modulus in the range 0.20 - 0.80 Nmm^{-3}. However, this increased flexibility did not lead to a reduction in brittleness. The reason for this apparently contradictory behaviour lies in the virtually unaltered deflection at break. Standard 'Stellon' polymer breaks, on average, at a deflection of 6.5 - 7.5 mm - Except in the case of the low zinc content 'ZALMA' none of the novel copolymers exceeded half of this value and 2.5 mm was more normal. The reason for this behaviour could be one or more of the following:

1) The inherent brittleness of heavy metal polyacrylates.

2) The high level of cross linking in the copolymer.

3) A physical weakness within the copolymer powder particles.

4) Lack of interaction between the copolymer and the matrix.

5) Low chain molecular weight.

(Possibilities 4) and 5) are contra-indicated by previous results on C9).

The first of these possibilities was examined by preparing a copolymer of potassium acrylate and methyl methacrylate of similar composition to C9. Polymerisation was readily effected, though the polymer remained in solution and the product was obtained in the form of a viscous solution in methanol/acetone. The polymer was precipitated in vigorously agitated distilled water and dried under vacuum at 100°C. After grinding this material was dough moulded without the addition of any 'Stellon' polymer. DOUGHING AND SUBSEQUENT MOULDING PROPERTIES WERE SIMILAR TO STELLON CONTROL.

The molecular weight of the copolymer was determined as

Mn	$= 1.78 \times 10^5$	(Stellon Mn	$= 2.5 \times 10^5$)
Mw	$= 3.26 \times 10^5$	(Mw	$= 1.07 \times 10^6$)
Mw/Mn	= 1.84	(Mw/Mn	= 4.3)

and is seen to be similar to 'Stellon'.

The physical properties of the moulded material were also similar to Stellon, though predictably more affected by water.

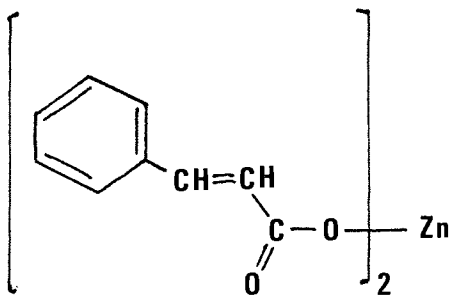
Sample	Breaking Load (Nmm^{-2})		Initial Modulus (Nmm^{-3})		Deflection at Break (mm)	
	Dry	Wet	Dry	Wet	Dry	Wet
Potassium Copolymer	64.4	68.3	0.471	0.404	5.6	11*
Stellon	80	83	0.580	0.506	6.5	7.5

* Unbroken

These results appear to prove that the presence of metal ions in a copolymer of this nature do not necessarily cause brittleness. Obviously it cannot be concluded with certainty that a zinc containing system would behave similarly, but it is indicated that the mere presence of the metal ion would not cause such brittleness.

It is difficult to test theory 2, that the brittleness is due to cross linking through divalent zinc ions because of the difficulty of preparing a zinc salt with only one polymerisable group. Attempts to produce a basic acrylate $Zn(OH)C_3H_3O_2$ or an acetate/acrylate resulted in mixtures of the two parent compounds rather than true mixed salts. This was shown when a sample prepared as a basic acrylate was dissolved in methanol - a suspension of zinc hydroxide remained.

However it is reported (74) that when prepared under conditions of high temperature and pressure a zinc acrylate/ethyl hexyl methacrylate copolymer was a tough material. Also, at a late stage in this investigation a report was found of the homopolymerisation in the melt state of zinc cinnamate.



(116)

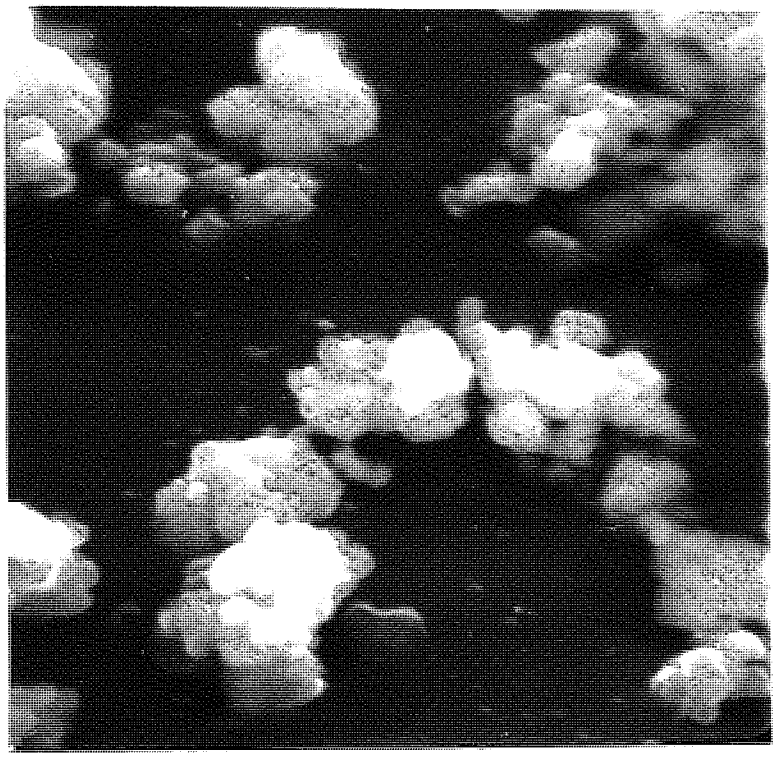
The very fact that polymerisation occurred at high temperature to give a polymer melt is contradictory to the theory of embrittlement by cross linking.

It would thus appear that the most likely cause of the observed weakness is that of fundamentally weak copolymer particles. As the polymer powder was precipitated in the polymerisation it is quite conceivable that the particles be porous or otherwise weak. No physical deficiency was visible under the optical microscope even at 1000x magnification - indeed the fine powder particles of homopolyzinc acrylate produced when a methanolic solution was heated were not even resolved at this magnification. When viewed at 11,000x magnification (Plate 5.12) with the stereoscan electron microscope the polyzinc acrylate powder is resolved and a degree of aggregation is evident even within these particles. The aggregates appear to be composed of a series of irregular platelets built on top of one another. Even at this magnification the detail is not very clear, but at higher magnifications the energy of the electron beam caused rapid degradation of the polymer. A more clearly defined picture was obtained on a powder sample ground from a friable solid C9 copolymer (Plate 5.13). In this photograph the anisotropic structure of the polymer is more distinct and the laminar agglomeration is clearly visible.

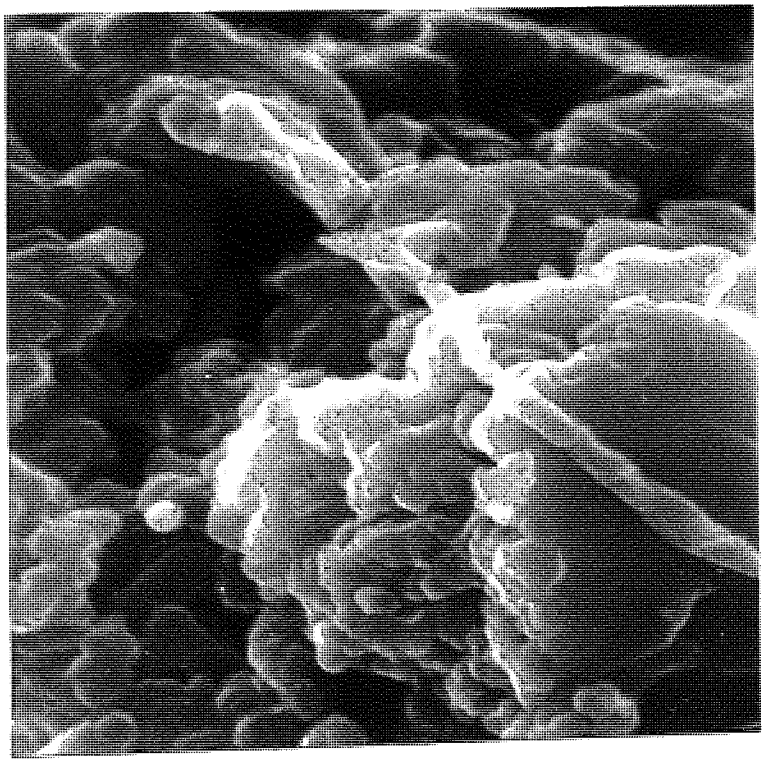
It is thus not surprising that a polymer composite, containing such a material as a filler, should be weakened. It seems that in the composite fracture takes place through the copolymer particles rather than around them, and the agglomerated nature of the particles would facilitate this process. If indeed delamination of the agglomerates is responsible for the weakness it is predictable that, regardless of the chemical nature of the copolymer, failure should occur at similar strain levels. This constancy of deflection at break has been observed and is recorded earlier.

It appears then that the physical structure of the copolymer

PLATES 5.12, 5.13 LAMINAR STRUCTURE OF POLYMER POWDERS CONTAINING ZINC ACRYLATE



5.12 ZINC POLYACRYLATE
SEM X 11,000



5.13 'C9' COPOLYMER
(54% ZINC ACRYLATE)
SEM X 11,000

particles is probably responsible for the weakness observed in the dough mouldings. Further evidence for this observation was provided by the retention of the poor physical strength even when dough moulded with monomer containing 50% nhexyl methacrylate. Normally one would expect the inclusion of such an internal plasticiser at this stage to produce a tough material too flexible for use as a denture base.

Sample	Breaking Load (Nmm^{-2})		Initial Modulus (Nmm^{-3})		Deflection at Break (mm)	
	Dry	Wet	Dry	Wet	Dry	Wet
n hexyl methacrylate moulding	28.6	26.5	0.57	0.475	1.6	1.85
Stellon	80	83	1.22	1.20	6.5	7.5

A test of the validity of the theory developed above would be provided if a polymer of the composition of C9 but in a different physical form were synthesized and incorporated into a dough moulding. This problem was approached in two ways.

5.10.1 Preparation of a zinc acrylate polymer by ion-exchange. As an alternative to the copolymerisation of zinc acrylate and methyl methacrylate, with its attendant problems of cross linking, zinc ions were introduced into a copolymer of acrylic acid and methyl methacrylate. It was not possible to buy suitable ion exchange resins for this process as commercial materials invariably have a high level of cross linking to provide stable granules. Polymers were therefore prepared as required:-

5.10.1.1 Vacuum distilled acrylic acid (18 g) and methyl methacrylate (32 g) were mixed in a large test tube. Azobisisobutyronitrile

(0.05 g) was added and dissolved by agitation with nitrogen bubbles from a capillary gas bleed. The tube was then stoppered and polymerisation carried out in a water bath at 50°C for several days. The glass tube was then broken away and the polymer rod cut into pieces and dissolved in 50 : 50 methanol : acetone. Solution was effected after about eight hours on a magnetic stirrer, though some gels (presumably cross-linked) remained. This solution was then filtered under pressure through a nylon cloth/wadding/cloth pad, and finally through a coarse filter paper to remove all of the gels. A small sample (of known volume) of the solution was then dropped into agitated distilled water to precipitate the polymer. This sample was filtered off, washed, dried (under vacuum at 100°C) and weighed, thus evaluating the concentration of the parent solution. The solid sample was submitted for gel permeation chromatography giving - $Mn = 4.86 \times 10^4$ $Mw = 1.33 \times 10^6$ $Mw/Mn = 27.4$ (C9 derivative $Mn = 1.3 \times 10^6$ $Mw = 4.1 \times 10^6$ $Mw/Mn = 2.96$)

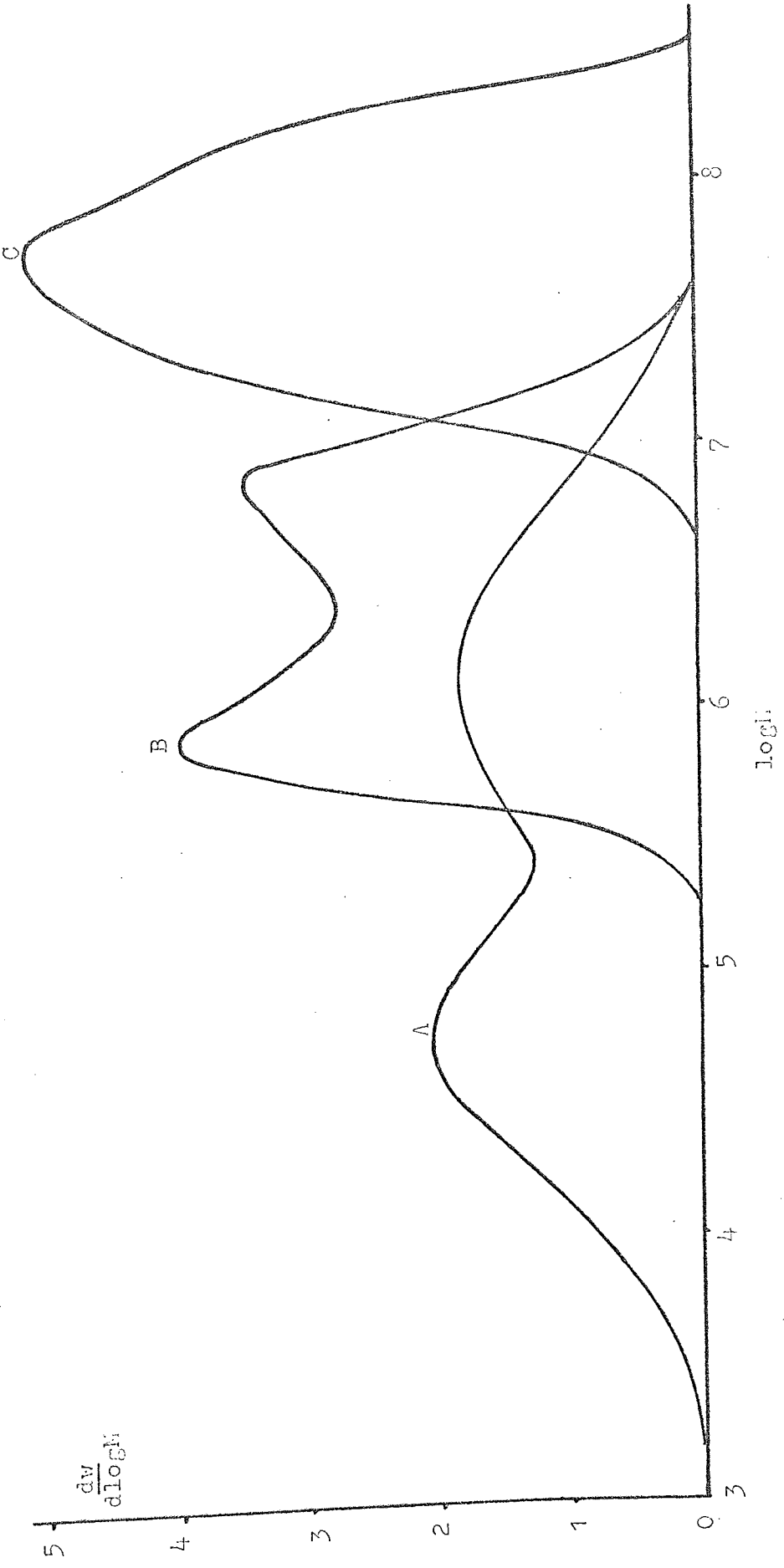
The very high value of Mw/Mn for the bulk copolymer is seen from Graph 5.22 to be due to a bimodal distribution. The reason for this behaviour is not known as the absence of homopolymers is proved by the solubility of the material in alcohols. A 50 : 50 copolymer prepared in similar fashion did not show this behaviour.

The quantity of zinc acetate required to react completely with the copolymer remaining in solution was calculated, and a methanolic solution made up containing a 50% excess. The polymer solution was then dripped slowly into the zinc solution with constant vigorous stirring. The zinc-containing polymer precipitated as heavy white curds. It was left in contact with the solution overnight to maximise the interaction, and then filtered, washed and dried. The dry polymer was obtained in the form of a hard white solid, grindable

GRAPH 5.22

Molecular Weight Distribution Curves of Acrylic Acid/Methyl methacrylate Copolymers:

A - Bulk polymerised 45% acrylic acid (w/w)
B - C9 hydrolysate
C - Bulk polymerised 50% acrylic acid (w/w)



with difficulty to a fine powder. The zinc content of this polymer was determined by TGA at 42% w/w as zinc acrylate. Some of the acrylic acid groups had not reacted. This was assumed to be due to steric factors operating in the already-precipitated material once sufficient groups had reacted to render the polymer insoluble. A 50 : 50 copolymer was required to give a zinc derivative containing 52% zinc acrylate. On dough moulding (in B5 formulation again) these materials behaved, if anything, worse than C9. The hard gritty powder formed a very wet dough and moulded into a plaque more opaque than a standard B5 moulding. It had previously been found impossible to produce a satisfactory moulding with either the acrylic acid copolymer, or its zinc derivative with monomer alone (ie using no 'Stellon' polymer).

A similar dough moulding was made from the C9 hydrolysate with the zinc reapplied (designated C90) described in the previous chapter, this too behaved poorly in the doughing process, and gave a rather opaque moulding.

TABLE 5.9

PHYSICAL PROPERTIES OF MOULDINGS MADE FROM ION EXCHANGED COPOLYMERS

Polymer in dough moulding	Ultimate Flex Strength (Nmm^{-2})		Initial Modulus (Nmm^{-3})		Deflection (mm)	
	Dry	Wet	Dry	Wet	Dry	Wet
52% zinc polyacrylate No Stellon polymer	34.5	34.2	1.36	0.85	0.85	3.3
52% zinc polyacrylate B5 type	32.41	31.58	0.596	0.448	1.7	2.93
42% zinc polyacrylate No Stellon polymer	8.9	23.02	0.374	0.159	1.1	7
C90 - B5 type	50.31	48.76	0.58	0.492	2.2	3.7

From these results it is clear that this approach to the problem has not been successful. The macrostructure of the copolymer was modified as intended and the particles could be seen under low power magnification to be solid and glassy, but there now appears to be no bonding to the methyl methacrylate matrix of the moulding. This appeared to be due to a solubility effect rather than the physical structure because the acrylic acid copolymer behaved equally badly in the moulding process and this material was not cross-linked. An attempt to introduce a similarly prepared strontium-containing polymer had the same disappointing results.

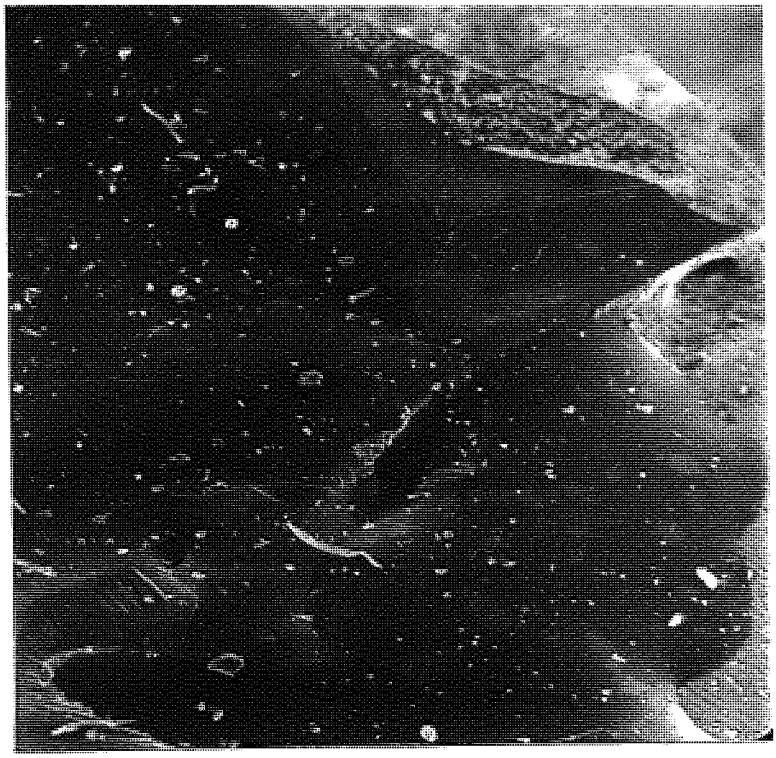
This material was precipitated from the acrylic acid copolymer solution with methanolic strontium hydroxide solution. The precipitate was filtered off dried and ground as before.

The dough moulding behaved similarly to the C90 material and showed the attendant poor physical properties.

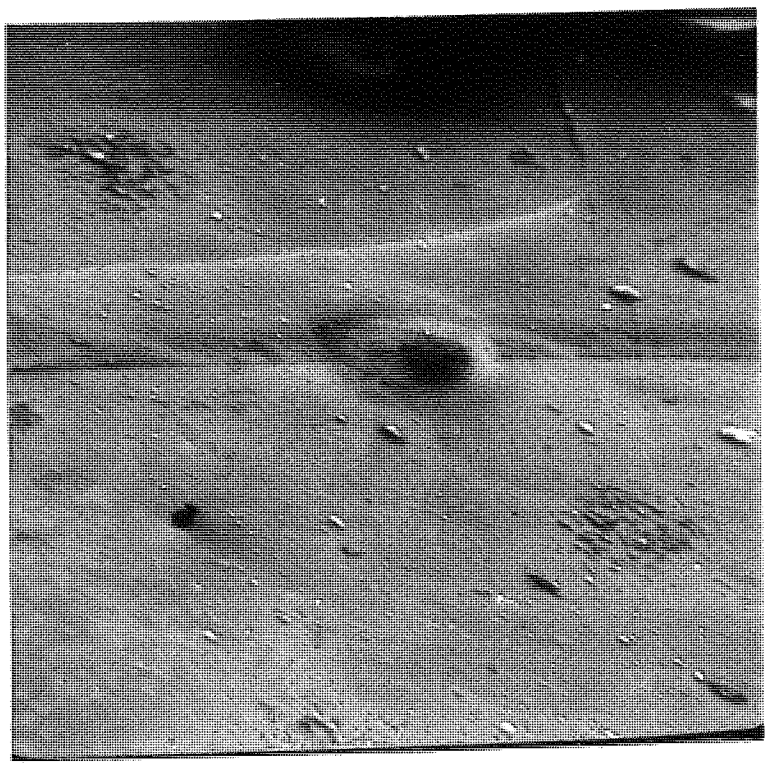
	Ultimate Flex Strength (Nmm^{-2})	Modulus (Nmm^{-3})	Deflection at Break (mm)
Dry	39.8	0.845	1.55
Wet	41.1	0.791	1.8

5.10.1.2 In the field of polymer composites in general much use is made of coupling agents to promote filler-polymer bonding. It was hoped that an extension of such a system could be used in the present case by including a polymerisable solvent for C9 copolymer into the dough moulding monomer. From previous studies (Chapter 4) it seemed that only very polar monomers could be expected to serve in this capacity, and the materials selected for study were acrylic acid and 2-hydroxy propyl acrylate (HPA). Qualitatively it had already been found possible to dough mould C9 quite successfully with

PLATES 5.14, 5.15 FEATURELESS FRACTURE SURFACES OF 'C9' MOULDINGS DOUGHED WITH ACRYLIC ACID



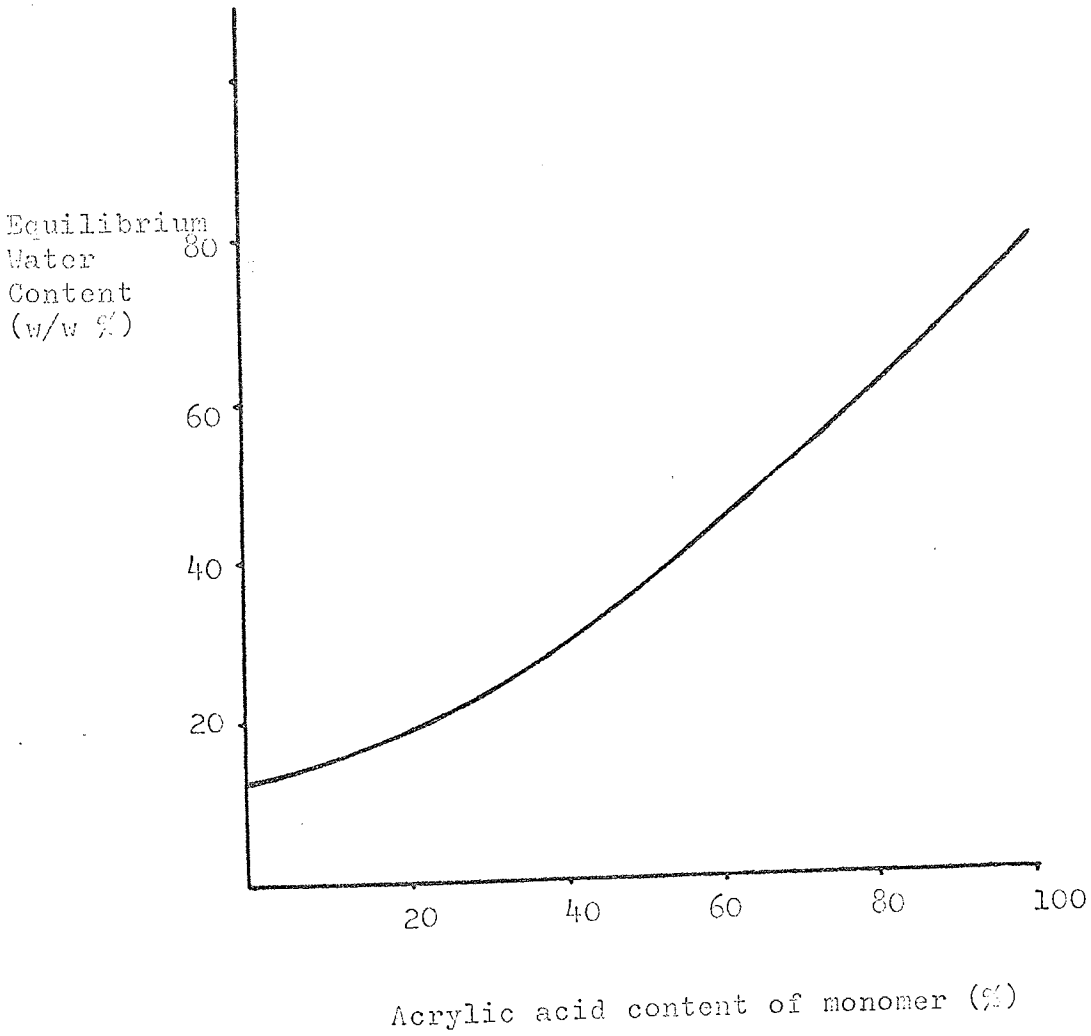
5.14 SEM X 60



5.15 SEM X 2,000

GRAPH 5.23

The water uptake of C9 dough moulded with monomer containing acrylic acid

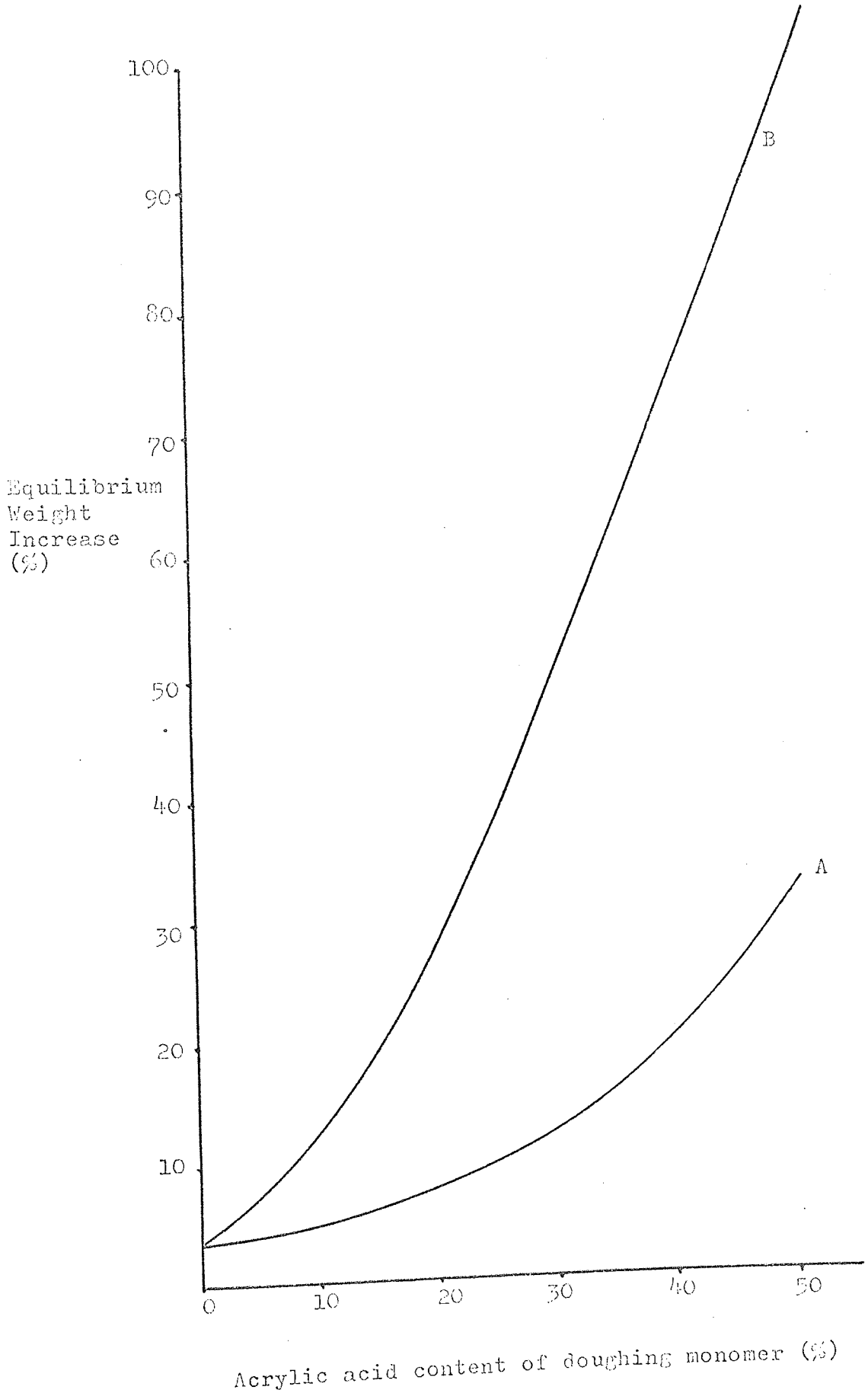


determination of equilibrium water absorption - Graph 5.24. It is seen that no great increase in water sorption resulted when less than 20% of acrylic acid was used, but above this level an increasingly marked effect was noted. Unfortunately, however small the increase in water sorption, there exists a reluctance to use in the mouth any materials containing free acrylic acid due to an adverse tissue response. In addition acrylic acid is said to cause 'blanching' in the dough moulding of dentures (a whitening in the thinner areas of the moulding). From the clinical point of view it would appear necessary to neutralise any residual polyacrylic acid in the moulding, though the blanching problem is not considered to be excessive at low concentrations of acrylic acid. It has been found previously that it is not possible to completely neutralise the acid groups in a polymer by ion exchange with a zinc salt. It was therefore decided to carry out the neutralisation with saturated calcium hydroxide solution. The equilibrium weight increase of samples in this solution are shown as the upper curve on Graph 5.24. In this case the more important parameter would appear to be the weight increase after redrying - a measure of the calcium uptake. The theoretical and observed values are compared in Graph 5.25, the theoretical value was superimposed on the observed 2.8% weight loss of the acrylic acid-free sample (B5). Comparison of these curves once more reveals that low levels of acrylic acid have little effect on the polymer properties. This is presumably due to the fundamentally hydrophobic nature of the polymer and the consequent difficulty of penetration by ionic species. The theoretical weight increase due to uptake of calcium ions was approached only at high acrylic acid contents.

In a further series of mouldings C9 copolymer was dough moulded

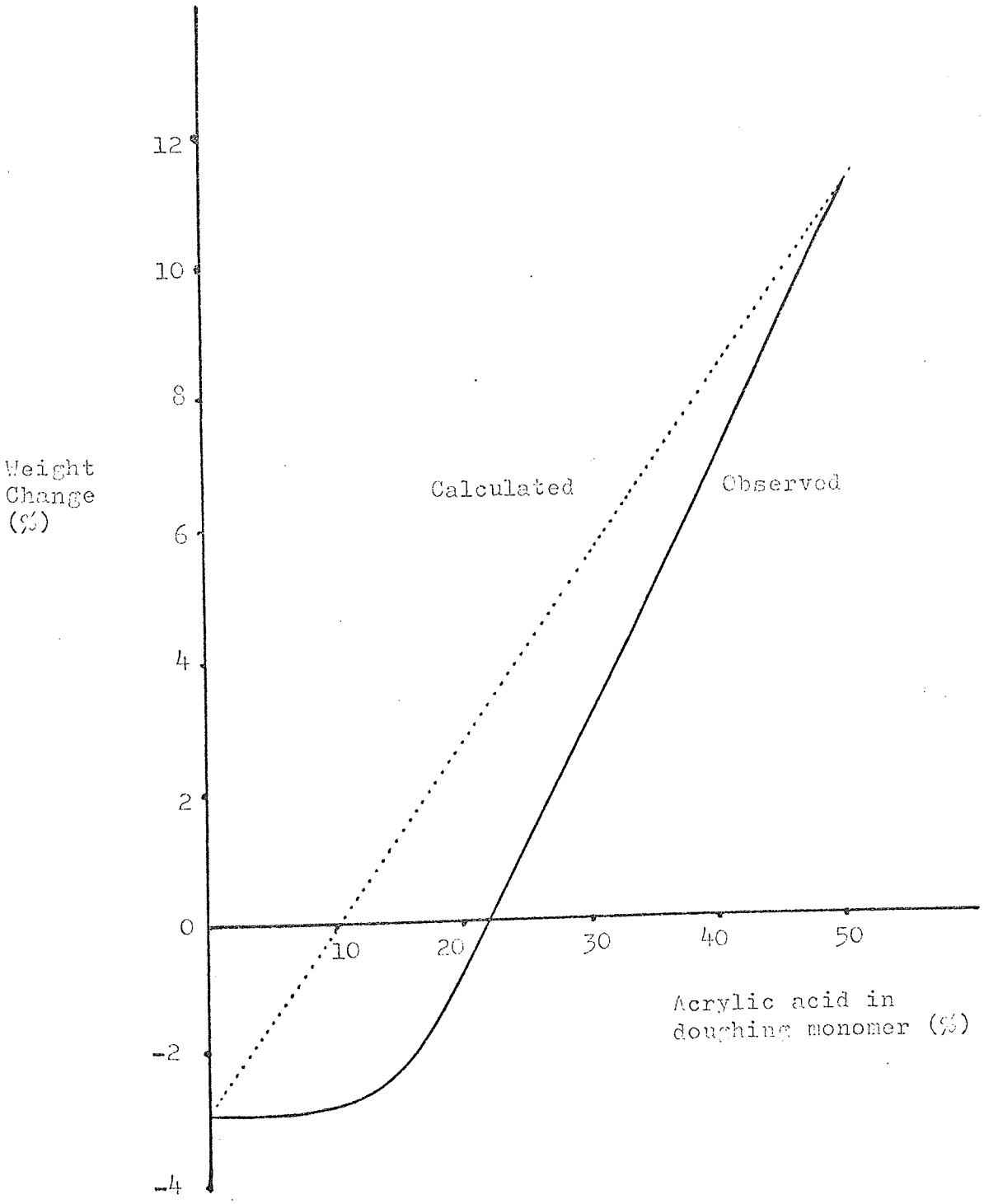
GRAPH 5.24

Weight increase of B5 mouldings containing acrylic acid in A) water, and B) calcium hydroxide solution



GRAPH 5.25

Weight increase of B5 + acrylic acid dough mouldings after calcium hydroxide solution soak and redry (ie calcium ions absorbed through ion exchange).



without Stellon polymer, using 100% acrylic acid, 50 : 50 and 75 : 25 with methyl methacrylate monomer. All of these systems produced good, though rubbery, doughs and yielded virtually transparent mouldings. Again the water sorption and calcium hydroxide solution soak were performed and the results are presented as Graph 5.23. Soaking in calcium hydroxide solution yielded rubbery soft materials, but on redrying these disintegrated to coarse powders. The water sorption curve presents nothing surprising as a very high level was expected for materials so rich in acrylic acid. However the weight increase in lime water appears to be reversed, high acrylic acid content yielded lower extents of swelling. Explanation of this behaviour is felt to be outside the scope of this investigation but it seems likely that in a formulation with a high acrylic acid content, rapid neutralisation and subsequent cross-linking could occur in a surface layer. The character of the surface may then be sufficiently changed to inhibit further absorption.

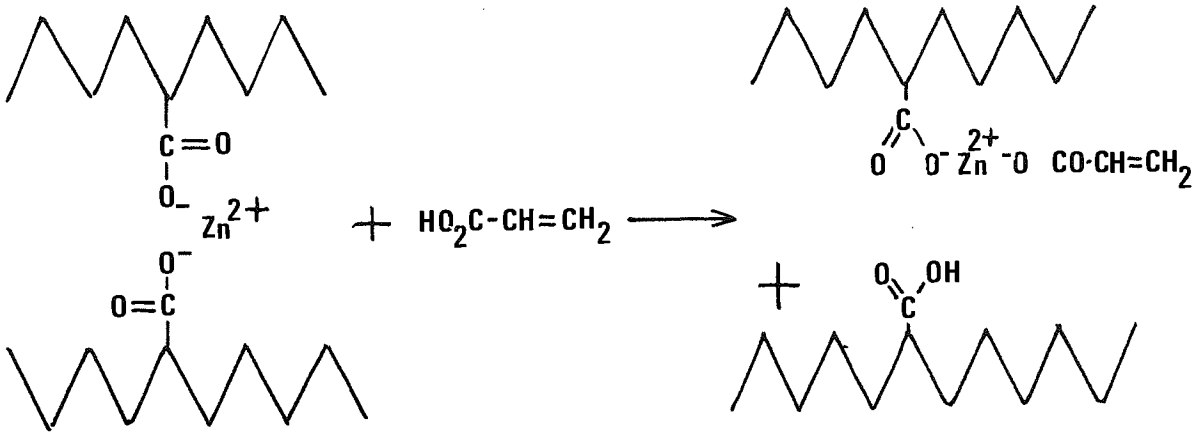
Flexural strength assessment of the B5/acrylic acid series yielded the following results:

TABLE 5.11

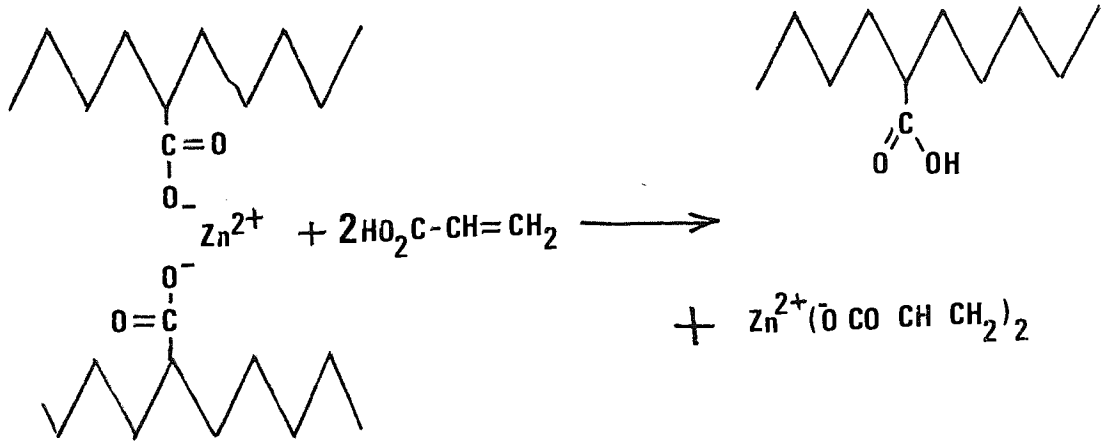
FLEXURAL STRENGTH PROPERTIES OF B5 MOULDINGS CONTAINING ACRYLIC ACID

Acrylic Acid Content of Monomers (%)	Flexural Strength Nmm^{-2}		Initial Modulus Nmm^{-3}		Deflection mm	
	Dry	Wet	Dry	Wet	Dry	Wet
0(B5)	50	61	0.72	0.68	2.2	2.3
8	51.23	80	0.677	0.653	2.6	5.2
16	31.85	70.2	0.742	0.603	1.5	4.5
25	50.1	41.9	0.750	0.349	2.2	8.3
33	46.85	31.4	0.814	0.56	2.05	2.2
50	44	6.1	0.801	0.04	1.9	No Break

The ultimate strength, and modulus figures are also presented graphically (Graphs 5.26, 5.27). The major points of note in these parameters is the relatively little effect that acrylic acid had on a dry specimen, and, in low concentrations, on the wet samples. However, at 50% the effect was catastrophic, both quantities fell virtually to zero. This behaviour may be explained if one considers the molar ratios involved in the various moulding systems.
10% AA ≡ 1 mole per mole of zinc polyacrylate. Sufficient acrylic acid is present to break the cross links and yield linear polymer in the dough.



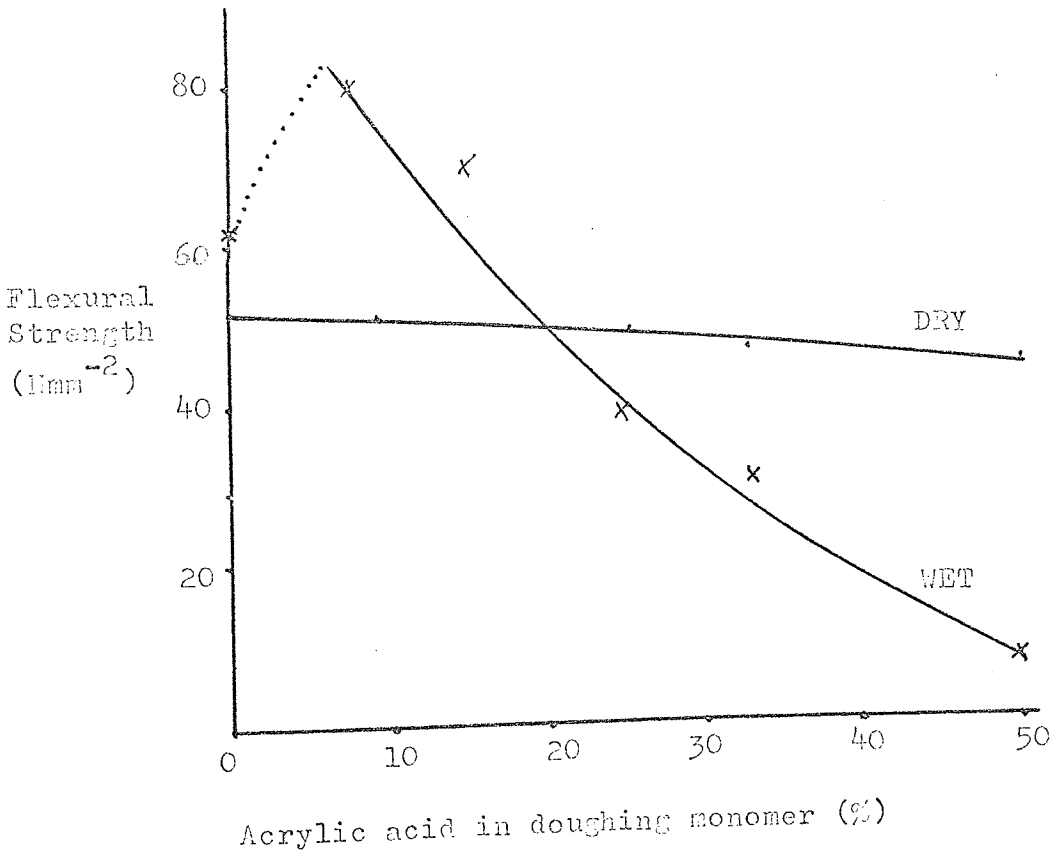
At 20% acrylic acid ≡ 2 moles per mole zinc polyacrylate, there is sufficient acrylic acid present to remove all the zinc from the copolymer.



These reactions are favoured by the lower pK values of the monomeric acid than in the copolymer. Thus, after doughing with > 20% acrylic

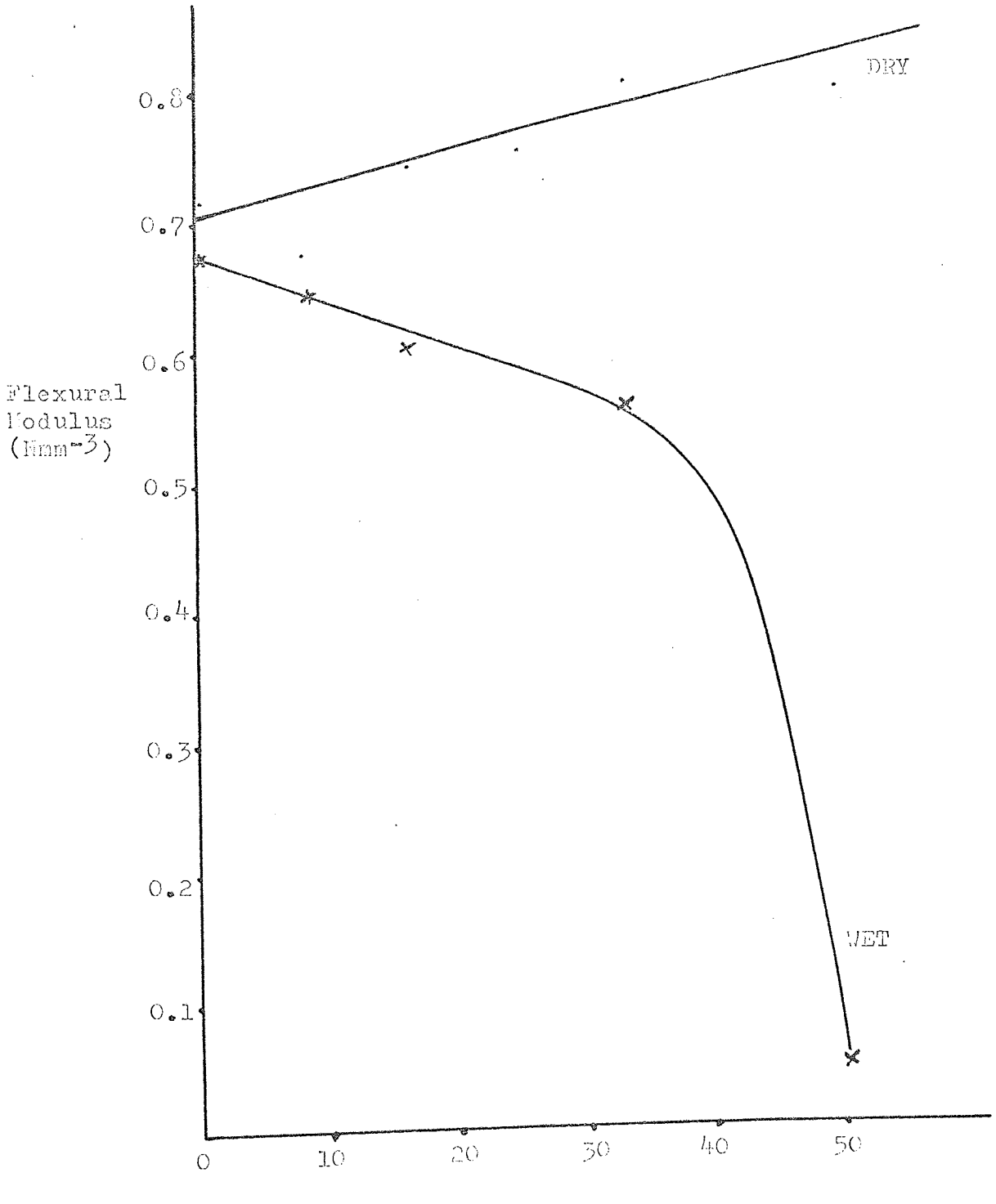
GRAPH 5.26

Ultimate flexural strength of B5 mouldings containing acrylic acid



GRAPH 5.27

Initial flexural modulus of B5 mouldings containing acrylic acid



acid and subsequently polymerising the product is expected to consist of linear methyl methacrylate/acrylic acid copolymer, plus a terpolymer of zinc acrylate, methyl methacrylate and acrylic acid. As the acrylic acid content of this terpolymer is increased it is to be expected that the water sensitivity should increase rapidly (as shown by the early study on terpolymers in Chapter 4). It is interesting to note that the breaking load of the wet samples is higher than the dry material at 21% acrylic acid, and drops away rapidly above this level. It would appear then that the low acrylic acid content samples would be almost satisfactory from a physical strength viewpoint, though the dry strength is not improved, and presumably the clinical objections still stand. It should be noted that a poly acrylic acid solution neutralised in the mouth with zinc oxide forms the basis of many new restorative (filling) materials (117-124) and is quite acceptable toxicologically (and incidentally in physical strength).

However, despite the improvements made in other respects the deflection at break of all but the high acid content samples was still low even when wet, and all of the samples broke at less than 2.6 mm deflection dry.

The sample moulded with 50% HPA in the monomer showed similar results.

Dry		Wet
38.4 Nmm^{-2}	Ultimate Strength	26.8 Nmm^{-2}
0.72 Nmm^{-3}	Initial modulus	0.396 Nmm^{-3}
1.6 mm	Deflection	Unbroken

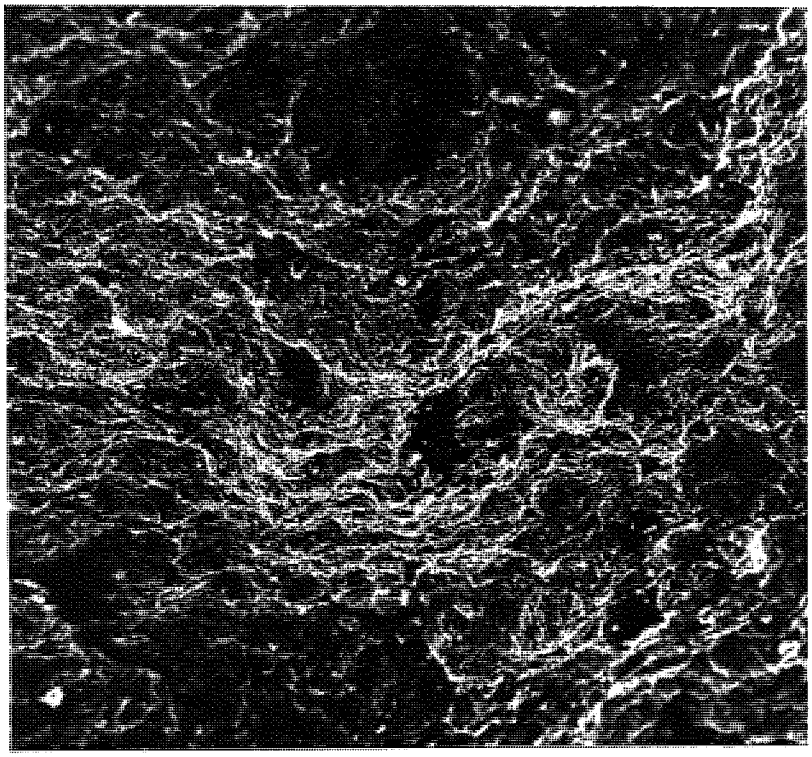
This approach seems to be a qualified success though due to clinical reluctance to use materials containing acrylic acid further clarification of the role of C9 in the dough moulding is needed.

5.11 ASSESSMENT OF THE EXTENT OF INTERACTION BETWEEN ZINC-RICH COPOLYMERS AND THE METHYL METHACRYLATE MATRIX

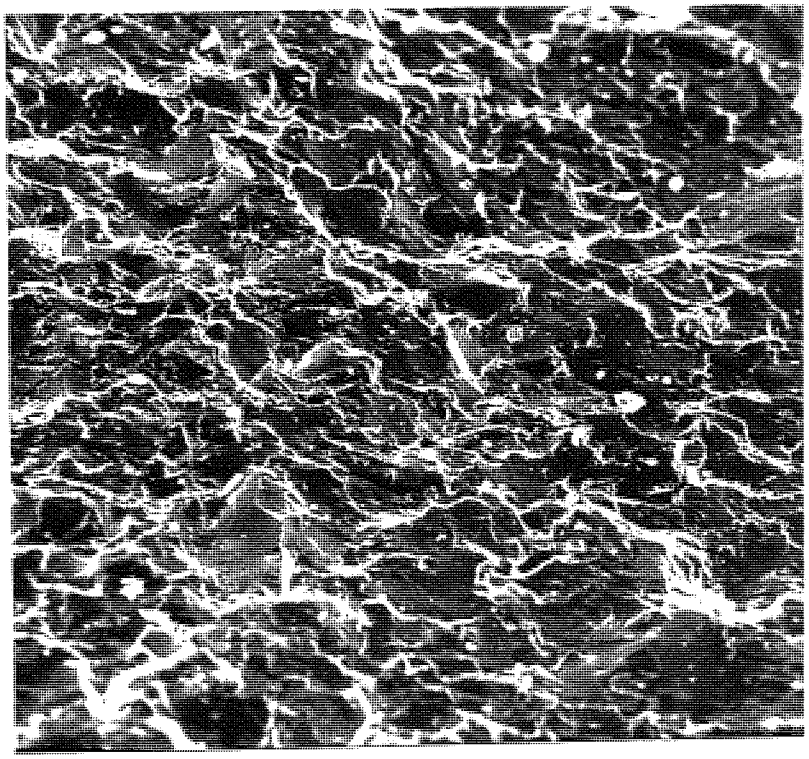
Zinc acrylate/methyl methacrylate copolymers are expected to behave as interacting fillers in a polymethyl methacrylate matrix, barium sulphate is known to behave as an inert filler. A series of mouldings were therefore prepared containing similar quantities of each filler judged on a % by volume basis. (The effect of the high density of barium sulphate is shown by the conversion curve weight % to volume % in Graph 5.32.) A comparison of the properties of these samples was then used as an indication of the degree of interaction. In order to extend the range of this test beyond that attainable by dough moulding, a pressing process was adopted. The mould used was simply a pair of polished steel plates with a 3 mm thick separating sheet of brass, from which was cut an aperture 35 mm x 75 mm. 'Melinex' (polyethylene terephthallate) separating sheets were used (supplied by Bexford Limited) and the moulding was carried out at 180°C. A 2 minute preheat was used, followed by 6 minutes at 28 tons (overall) pressure. Using this process mouldings could be prepared of up to 65% v/v filler. In this way it was also possible to assess the difference (if any) in structure, resulting from the presence of monomer in the dough moulding process with the resulting possibility of grafting onto the filler.

The results of fracture surface photography on samples containing 37% v/v filler were very significant. It was not possible to achieve a dough moulding of barium sulphate-filled material at this loading, as it corresponds to 70% w/w. The results for C9-containing dough moulding, C9-containing pressing and the barium sulphate loaded pressing are shown in Plates 5.7, 5.16 and 5.17 respectively. The following observations are immediately obvious:

PLATES 5.16, 5.17 FRACTURE SURFACES OF HOT PRESSINGS OF POLYMETHYLMETHACRYLATE FILLED TO 35% v/v WITH



5.16 BARIUM SULPHATE
X 250



5.17 'C9' COPOLYMER
X 250

a) At this level, barium sulphate had a disastrous effect upon the structure of the polymer. The fracture surface bore no resemblance to that of 'Stellon' and the surface appears to be covered with filler particles.

b) Though severe, the effect of C9 in a hot pressed sample was much less than that of barium sulphate. Though a great deal of 'filler' is visible it is possible to see some of the conchoidal fracture typical of the virgin polymer.

c) The dough moulded C9 composite (B5) exhibits a fracture almost identical to the control. No filler is visible.

It seems then that C9 behaves, as hoped, as an interacting filler in a dough moulding, and that the filler is truly bound into the matrix. This cannot really be said of the same material in a hot pressing, when no monomer is present to 'tie in' the filler. A further testimony to this interaction was provided by the near transparency of the C9 series (Plate 5.18) compared with the opacifying effect of barium sulphate (Plate 5.19). The results of the flexural strength testing of these series of composites are summarised in Graphs 5.28 - 5.31.

The fundamental properties of composite materials are common to all of these systems, viz:

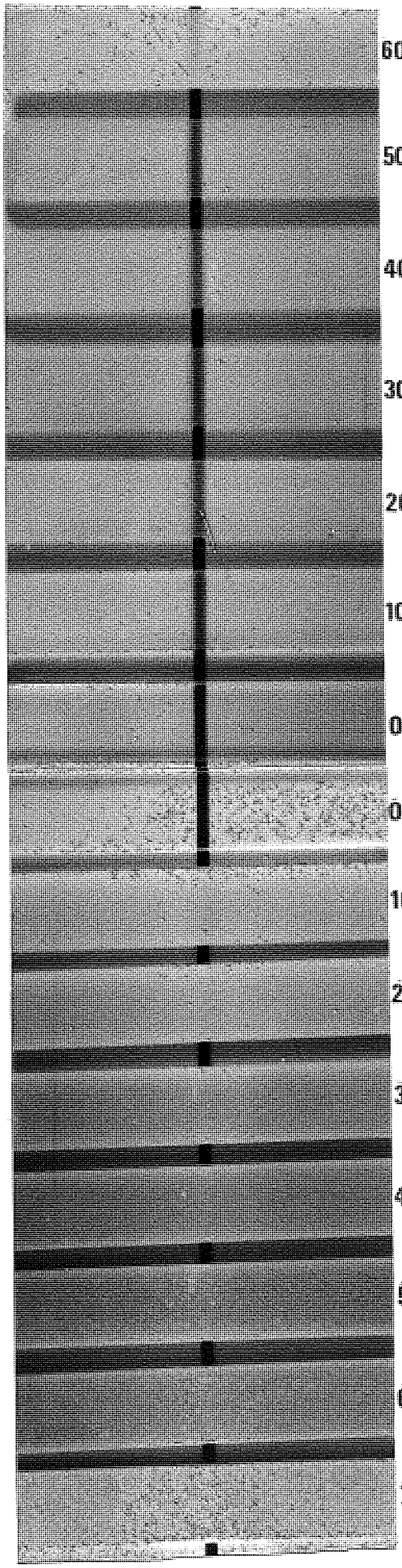
An increase in the filler content causes:-

1) An increase in modulus and

2) A decrease in the deflection at break.

In addition a progressive reduction in the ultimate breaking strength was observed throughout. The high barium sulphate composites failed in a friable mode whereas the materials rich in C9 exhibited brittle

PLATES 5.18, 5.19 VISUAL TRANSPARENCY/OPACITY IN HOT PRESSED FILLED ACRYLICS



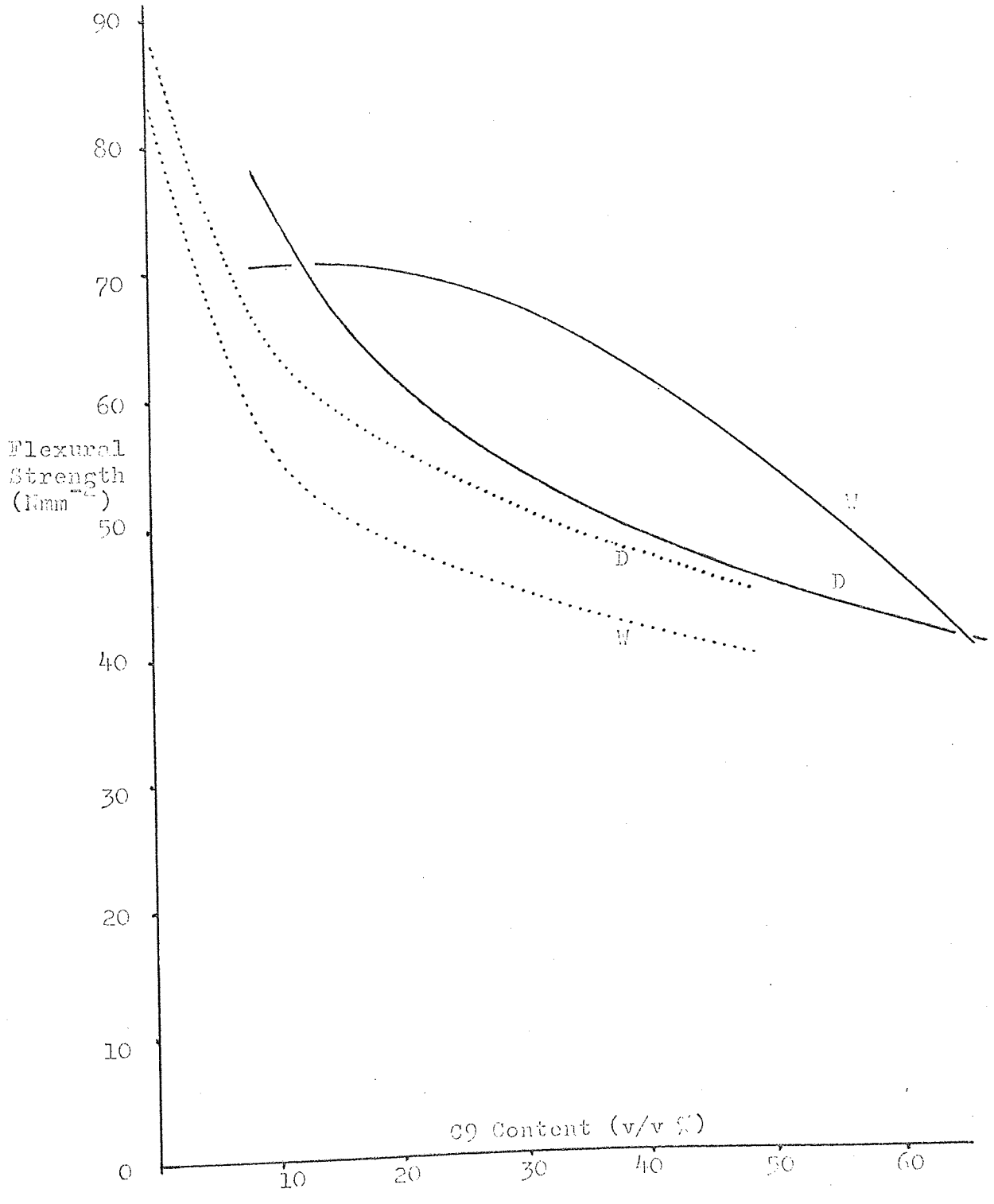
5.18 'C9' FILLED (% w/w)

5.19 $BaSO_4$ FILLED (% w/w)

GRAPH 5.28

Ultimate flexural strength of composites containing C9 copolymer

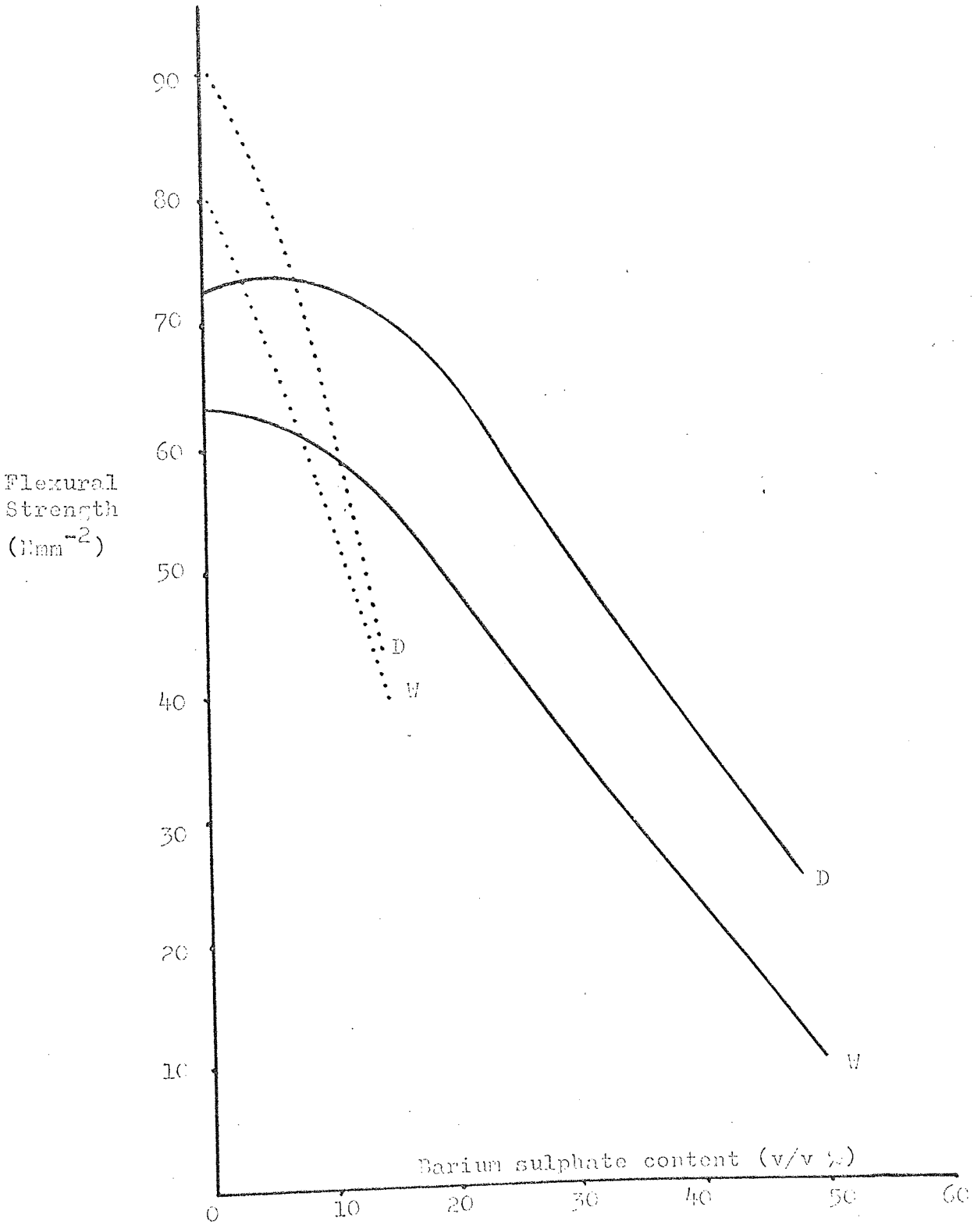
solid line = hot pressing
dotted = dough moulding
D = tested dry
W = soaked 7 days 37°C



GRAPH 5.29

Ultimate flexural strength of composites containing barium sulphate filler

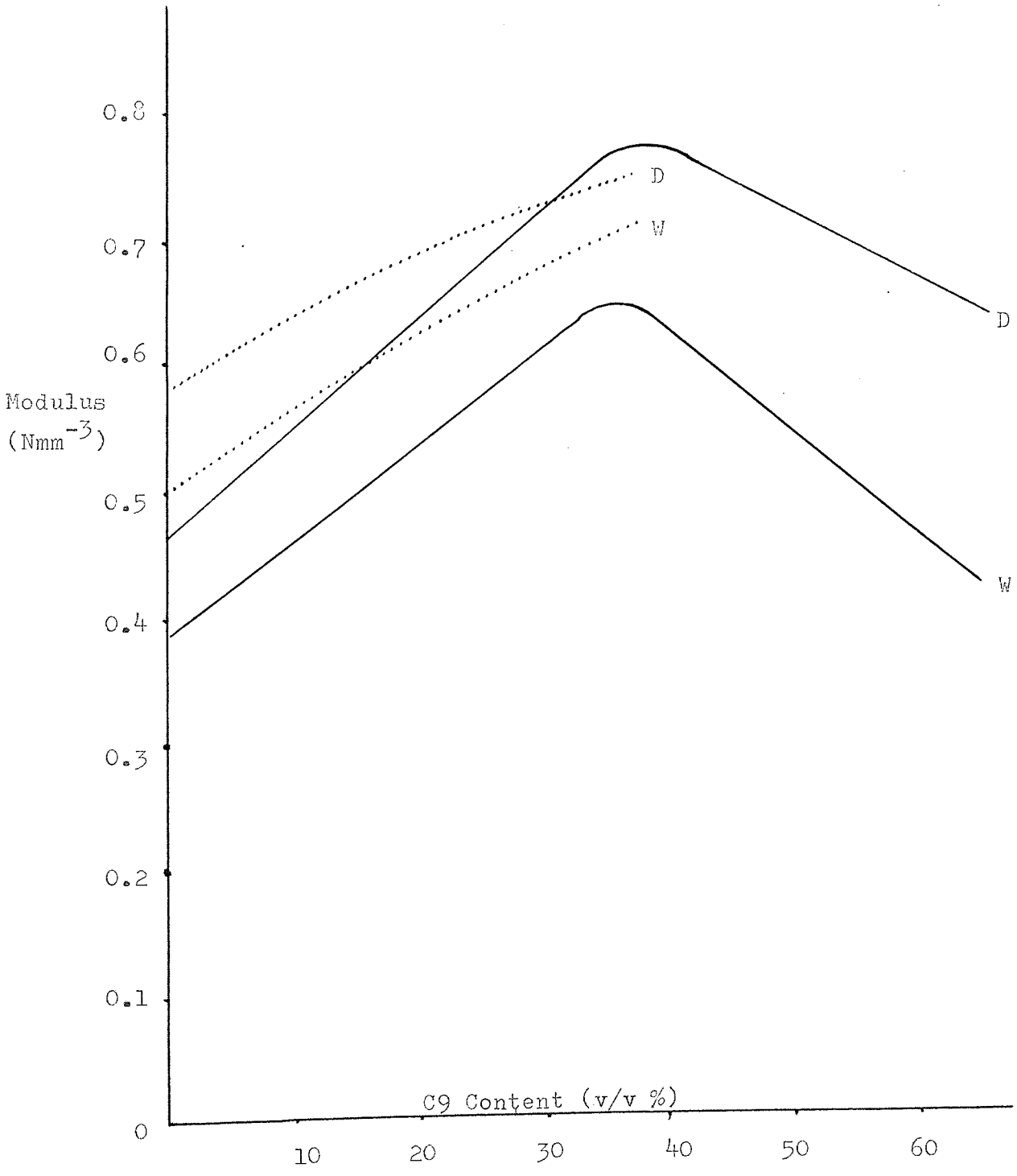
solid line = hot pressing
dotted = dough moulding
D = tested dry
W = soaked 1 week 37°C



GRAPH 5.30

Initial flexural modulus of composites containing C9 copolymer

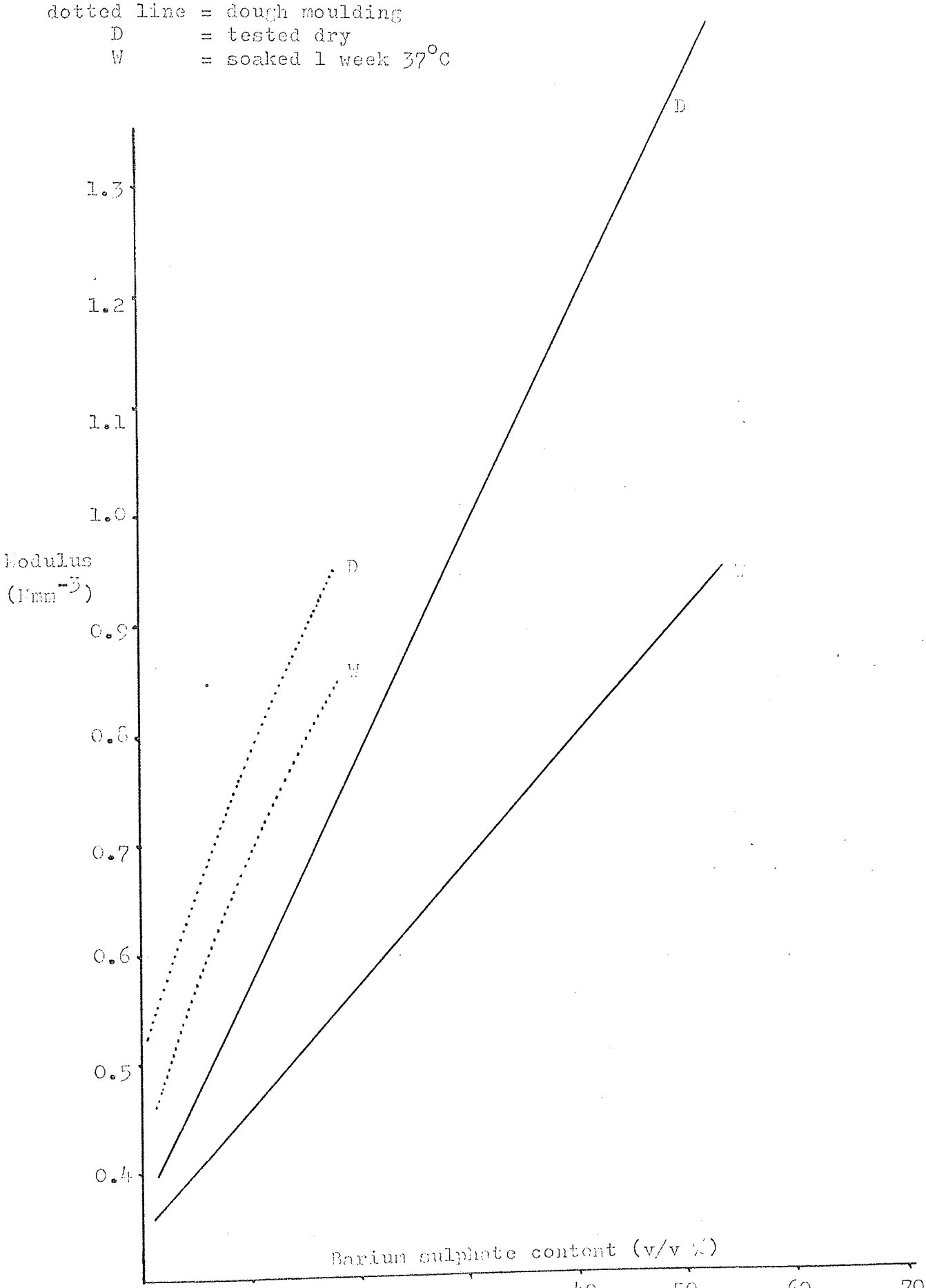
solid line = hot pressing
dotted line = dough moulding
D = tested dry
W = soaked 1 week 37°C



GRAPH 5.31

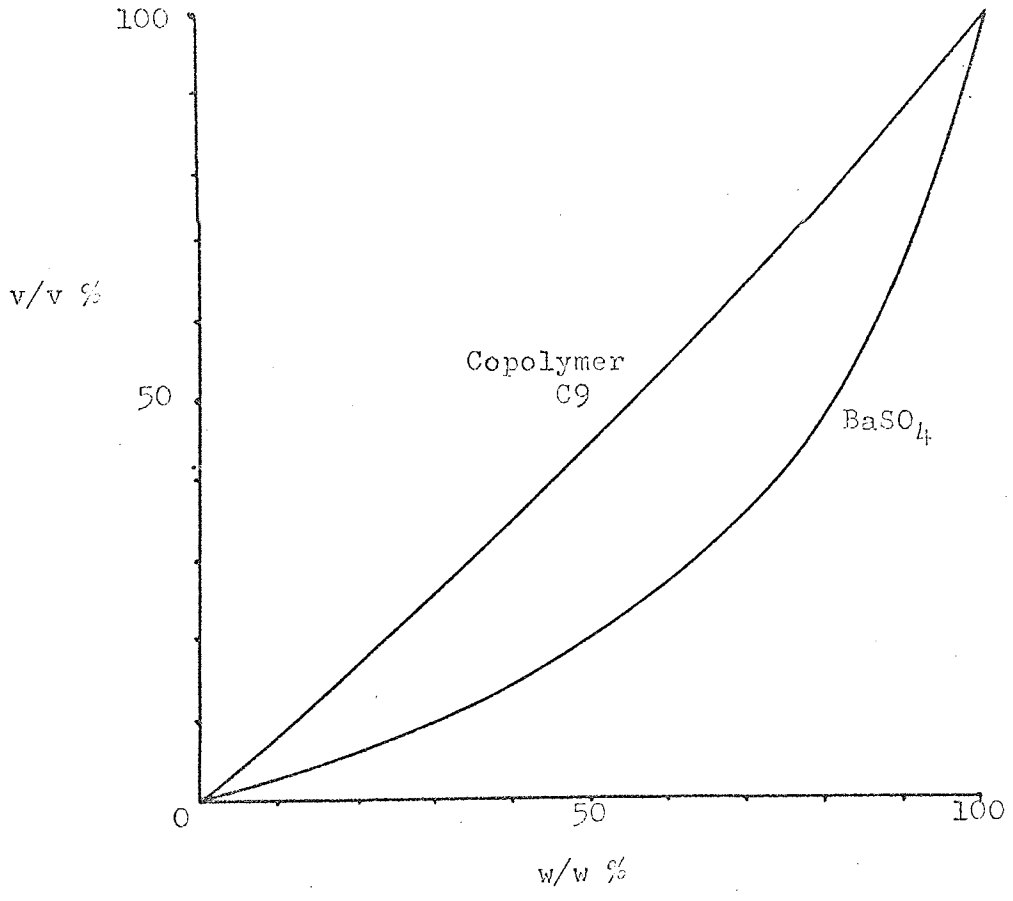
Initial flexural modulus of composites containing barium sulphate filler

solid line = hot pressing
dotted line = dough moulding
D = tested dry
W = soaked 1 week 37°C



GRAPH 5.32

A Calibration Curve for the Conversion of Weight Percentage of Filler to Volume Percentage



failure and the attendant conchoidal fracture surface. This observation was equally valid for dough mouldings and for hot pressings.

The major difference observed between the two series in the flexural properties was almost solely one of degree. In all respects the formulations containing C9 were less severely affected than the corresponding barium sulphate-loaded composites. This difference was not sufficient to lead to the conclusion that C9 behaves other than as an inert filler though this is suggested.

The occurrence of a maximum in the graphs of modulus vs composition for the C9 series (Graph 5.30) cannot be explained, but is considered to be a valid observation as it was not contradicted by any samples. These samples were taken from eight completely independent mouldings and so the consistency could not be explained by random factors operating in a particular moulding.

On consideration of all the data, it is strongly suggested that C9 has some interaction with methyl methacrylate monomer in a dough moulding, but less so in the hot pressing process. The similarity in physical properties of samples prepared by the two techniques was therefore unexpected, and disappointing.

5.12 TOXICOLOGY

Specimens of B5 dough moulding were implanted in rabbits at Birmingham Dental Hospital, and were confirmed to be satisfactory in terms of tissue response over a period of one year.

5.13 SUMMARY

5.13.1 Composites containing C9 were found to be satisfactory in all respects except for physical strength (though reservations are

held concerning their moulding properties). The lack of physical strength is thought to be due to the internal structure of the copolymer powder, though experiments to prove this have been inconclusive.

5.13.2 Incorporation of small quantities of acrylic acid in the doughing monomer improved the moulding properties considerably, and also the wet flexural properties, though the dry polymer was relatively unaffected.

5.13.3 Modification of the copolymer with flexibilising comonomers yielded low modulus materials though the strain tolerance was unimproved.

5.13.4 Moulding with a flexibilising monomer at the doughing stage had a similar effect.

5.13.5 Moulding with a hydrophilic (and potential chelating) comonomer at the doughing stage produced a very water sensitive composite, though of unimproved properties in the dry state.

CHAPTER 6

FURTHER OBSERVATIONS

6.1 HOT PRESSED MATERIALS

It has already been stated that zinc polycinnamate is reportedly fusible and by implication mouldable by conventional thermoforming techniques. Polymerisation of this material was briefly attempted, but owing to the late discovery of the reference it was not pursued. However, if the cinnamate is thermally fusible then so should the acrylate be, for the cinnamate is the B-phenyl acrylate. Of course in the early stages of their preparation each copolymer was tested for fusibility, but this was confined to the observation of any melt state on heating a sample on a spatula. In the light of the new information a systematic attempt was made to press the various copolymers into plaques.

From TGA curves it was apparent that the thermal depolymerisation of polymethylmethacrylate is rapid at temperatures over 250°C and even at 200°C is significant. A ceiling temperature for the pressing operation was thus indicated.

The copolymers containing low concentrations of zinc acrylate were quite readily pressed at 190°C at approximately 7 tons per square inch pressure, using a 2 min preheat followed by 6 min at pressure, and then cooling to 60°C under pressure before opening the mould. Prior to moulding the 'plaque' copolymers were ground to 80 mesh in a hammer mill. At higher zinc acrylate contents than C9 (54% w/w) it was found impossible to press plaques even at 250°C, though thin films could be achieved. The major difficulty with these materials was one of shrinkage, causing shattering of the

moulding on cooling. In addition, fusion of the moulding was not complete and though a central area of tranaparent material was usually present, high zinc contents invariably led to increasing areas of opaque compressed powder.

Even at temperatures in excess of 350°C pure zinc polyacrylate was not found to be mouldable. Small transparent, fused areas were observed in the compressed powder, but could not be removed from the plate. At this temperature degradation of the metal acrylate was beginning and discolouration was observed. The fused areas were found to be very hard, and resistant to chipping from the plate.

The moulding properties are summarised in Table 6.1. Pressings at temperatures $< 200^{\circ}C$ utilised 'Melinex' separating sheets, above this temperature, commercial mould release agent was employed.

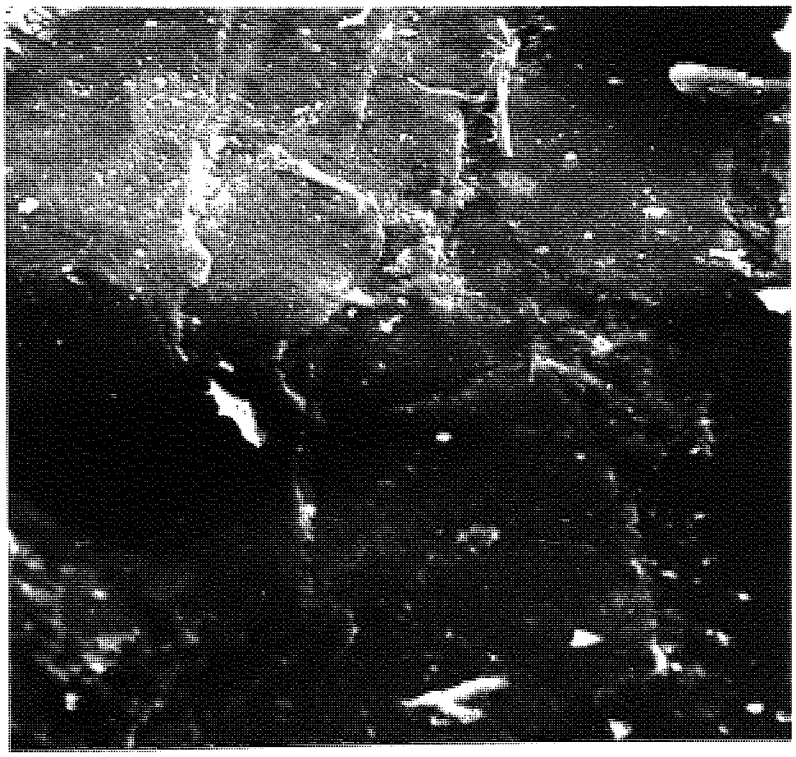
The universally observed brittleness of the zinc acrylate copolymers was disappointing and difficult to explain in the light of previous reports (74). Even the plaque copolymer C5 which was tough and transparent in its original form became translucent brittle and weak when the ground powder was hot pressed. Incomplete fusion of the polymer particles appeared to be the cause of this behaviour and to eliminate this effect a further pressing was made directly from the solid plaque. This sample was equally translucent and weak, though fracture in this sample was clearly seen to be due to delamination. The anisotropic nature of C5 has already been indicated in scanning electron micrographs, but the properties of the hot pressing confirm this observation. From these observations it appears that the zinc ion cross links were not thermally labile at the pressing temperature and the structure of the gel was therefore destroyed in the pressing process. This behaviour would not be

TABLE 6.1

THE MOULDABILITY OF ZINC ACRYLATE COPOLYMERS UNDER CONDITIONS OF HIGH TEMPERATURE AND A PRESSURE OF 7 TONS/IN^2

Polymer	Zinc Acrylate Content	Observations
Stellon	0	Readily moulded at 180°C to give a transparent plaque, or, without the spacer, a film.
C1	36	Moulded easily to a film, at 185°C but the product was translucent and brittle
C2	165	As for C1 but the film was more nearly transparent
C5 C6	16) 26)	As for C1 - a degree of spontaneous cracking was apparent on opening the mould.
C9	52	Moulding was satisfactorily achieved to both film and plaque at 195°C, but the products tended to shatter on cooling. The material was virtually transparent, though brittle and weak. Fracture surfaces were characterised by a granular appearance, suggesting poor particle fusion (plate 6.1)
C10	59	A temperature of 200°C was required in moulding a film, but the product was white opaque and brittle.
C11	72	At temperatures below 220°C no fusion was achieved, but at this temperature areas of almost transparent yellowish film were visible within the powder.
C12	75	Similar to C11 but temperatures in excess of 250°C were needed.
Zinc Polyacrylate	100	Even at a temperature of 320°C only tiny areas of fusion were seen and at this temperature degradation was significant (the pressing showed a yellowing at the surface.

PLATE 6.1 TYPICAL GRANULAR FRACTURE SURFACE OF A 'C9' HOT PRESSED COPOLYMER PLAQUE (54% w/w ZINC ACRYLATE)



contradictory to previous work in which the zinc ions were only introduced in the hot pressing process, though by inference such mouldings would subsequently be unreformable.

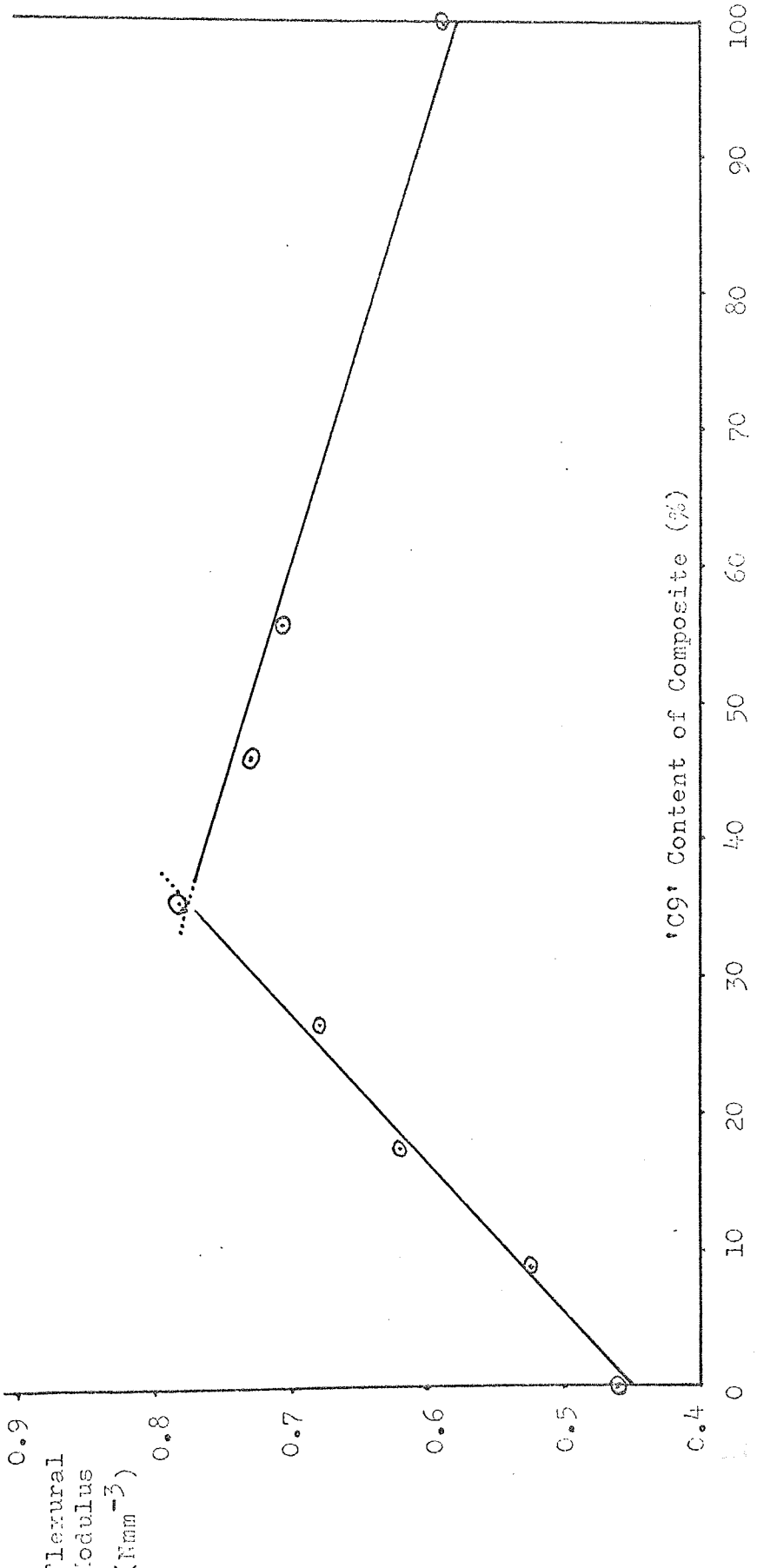
By very careful handling a flexural test sample was cut from the C9 pressed plaque (though extensive fracturing precluded the cutting of more than one speciman). On testing (dry), this sample exhibited the predicted minimal deflection at break (1.1 mm) with the accompanying low ultimate breaking load (27.6 Nmm^{-2}). The initial modulus fitted in well with the projected value from Graph 5.30 confirming the existence of a maximum in the graph of modulus vs C9 content of a composite - Graph 6.1.

The water sorption behaviour of C9 was determined on a hot pressed plaque, and is shown in Graph 6.2. The high equilibrium water content (16.9%) is expected though is somewhat higher than predicted from the results for B5 mouldings (40% w/w C9). On redrying at 60°C under vacuum a net weight loss of 3.9% was observed which could have been due to dissolution of soluble material, or excessive final drying.

As a further attempt to maximise the interaction between C9 and methyl methacrylate in a B5 dough moulding (40% w/w of C9), a moulding was subjected to compaction under the previously described conditions of hot pressing at 180°C. Under these conditions it was hoped that a more homogeneous material would result through elimination of any microscopic porosity and complete polymerisation of traces of monomers. The resultant plaque was indistinguishable from its parent dough moulding, even the surface whitening (derived from the alginate moulding system) remained, though considerable flow had taken place as evidenced by a quantity of 'flash'. (This confirms the diagnosis that the whitening is a hydrolysis product,

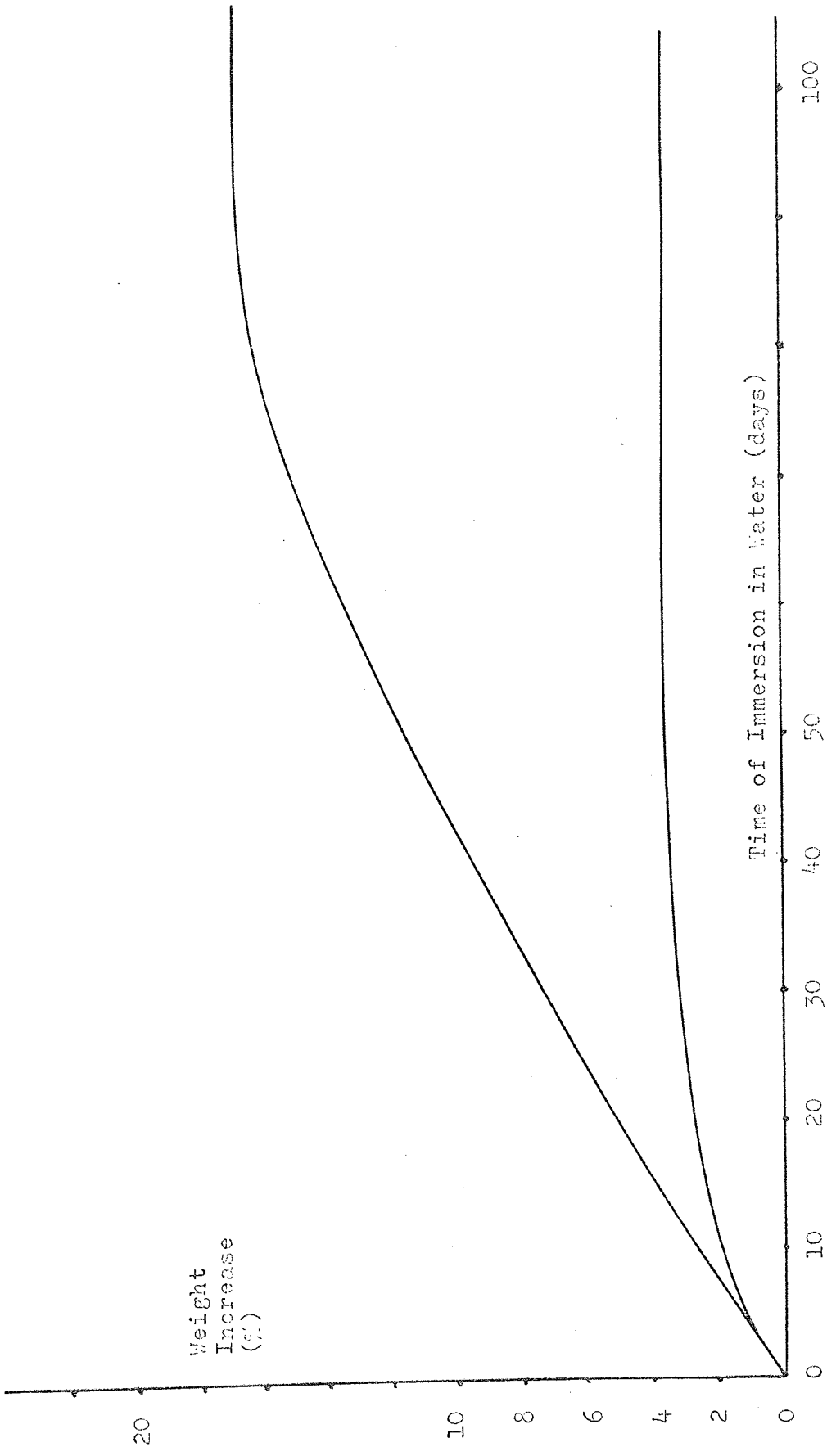
GRAPH 6.1

An Extension of 5.30 - The Modulus of High 'C9' Content Hot Pressed Composites as a Function of Composition



GRAPH 6.2

Water Sorption of Hot Pressed 'C9' Copolymer



as the alternative of porosity would have been rectified by the thermo-forming process.) Flexural properties were totally unaltered by this process and the similarity to the parent dough moulding was exact in all respects. Consideration of this information and that presented earlier (§ 5.11) leads to the conclusion that for this two component composite the interphase bonding cannot be improved by physical means and a more fundamental modification is indicated.

6.2 NOVEL MONOMER SYSTEMS

6.2.1 Copolymers were prepared, in a manner identical to that used for C9, of zinc acrylate/styrene and zinc acrylate/2-hydroxypropyl-acrylate (HPA). Both of these systems polymerised readily, though the ZA/HPA system was very reactive and within 1 hour had polymerised to 100% conversion giving a copolymer of 25% w/w zinc acrylate. The styrene copolymer was more similar to C9, and had a zinc acrylate content of 51% w/w. Both of these copolymers were precipitated as fine white powders. Their dough moulding properties were not improved over C9, and the styrene copolymer could not be hot pressed into a coherent film even at 250°C. The HPA analogue was readily pressed into a thin sheet at 200°C (as might be expected from its lowered zinc content). This material was almost transparent, but differed from previous copolymers in that it was quite flexible and tough. However, on immersion in water rapid swelling took place and ultimately the sheet broke up to yield a highly swollen gelatinous mass. This behaviour was surprising considering the extent of cross linking arising from the divalent zinc. By contrast HPA polymers containing only 1 - 5% of covalent cross linking agents (eg ethylene glycol dimethacrylate) swell in water to give a high water content coherent gel and do not break up (125). It may be

that in the hydrated state the ionic bonds become more labile resulting in an effective reduction in the cross link density. Intensive study of this effect was not considered to be justified.

It should be mentioned here that these two novel copolymers were not considered primarily for potential dental applications, but simply as extensions to the chemical study. At the same time it was hoped that copolymers of their type may find applications where radiopaque polymers are desirable (eg in interior trim for cars), though the observed properties do not seem encouraging.

6.2.2 Replacements for zinc acrylate

6.2.2.1 Caesium acrylate

It has already been shown that potassium acrylate can be readily copolymerised with methyl methacrylate and that the copolymer may be dough moulded without difficulty (§ 5.10). Replacement of potassium (Z = 19) by caesium (Z = 55) would be predicted to confer the desired radiopacity on this formulation. Caesium acrylate was found to polymerise more readily than potassium acrylate and thus required more careful control of the temperature used for drying the monomer ($< 50^{\circ}C$ under vacuum). Copolymerisation with methyl methacrylate in the C9-type system proceeded rapidly to give a viscous solution which was precipitated into water filtered off and dried at $110^{\circ}C$ under vacuum. As expected the resulting polymer behaved similarly to the potassium analogue and no qualitative effect was noted which would render it unsuitable for dental use. Unfortunately the price of caesium acrylate meant that continued investigation was pointless. Caesium hydroxide is sold at £1.10 per gm, while the carbonate retails at £1.10 per 10 gm. Consideration of the cost of the acrylic acid used and the process

costs leads to a predicted price for caesium acrylate of £100 per pound as a minimum, and twice this figure would appear more likely. This contrasts with the£7.30 per pound charged for a small scale custom synthesis of zinc acrylate.

From the cost point of view it appears that zinc is the only potentially successful element which can be hoped to comply with the requirements (hopefully £1 per pound). It is thus logical to consider the possibility of incorporation of the zinc by systems other than the acrylate copolymers of the C9 type.

6.2.2.2 Zinc cinnamate

This material has been mentioned briefly before both in this chapter, and the previous one. Preparation of the monomer was by the method of Freedman and Elliot (116) viz digestion of a suspension of zinc oxide in a refluxing solution of cinnamic acid (BDH laboratory reagent) in toluene for 6 hours. The product was then filtered off and purified by recrystallisation from dimethyl formamide. The above reference details the polymerisation and copolymerisation with cinnamic acid and vinyl carbazole in the melt state at 210°C. The products were hard glassy polymers, readily fusable. Zinc cinnamate is also reported to be readily thermally polymerised in solution in dimethyl formamide even in the absence of initiators. To maintain consistency with previous studies this was the system investigated.

A copolymerisation of the style of the C9 type (25% zinc cinnamate : 75% methylmethacrylate) was performed under nitrogen in refluxing dimethyl formamide solution (0.1% benzoyl perioxide initiator was used). After three hours an increase in viscosity was noted, and the reaction stopped. The solution was cooled and

the polymer precipitated in ether. After drying thermogravimetric analysis yielded a figure for zinc content equivalent to 65% w/w zinc cinnamate.

This product was not dough mouldable with methyl methacrylate, nor was it readily processable by the hot pressing technique. Further study of this system was not possible owing to its late discovery (in an engineering journal).

6.2.2.3 Ethylene sulphonic acid derivatives

Ion exchange resins (for cations) usually contain sulphonic acid or acrylic acid functional groups. In this study interest has been centred on the acrylates. At this stage a brief investigation of the suitability of the sulphonates for dental applications is considered appropriate.

Ethylene sulphonic acid (127) and sodium ethylene sulphonate (126) are reportedly readily polymerisable by redox initiator systems. The polymers are glassy solids, though soluble in water.

Sodium ethylene sulphonate was obtained from Polysciences Ltd as a 40% aqueous solution. This was rotary evaporated to dryness under vacuum at 60°C and the solid recrystallised twice from methanol to yield a white crystalline product. The free acid could not be obtained and though it may be prepared from the sodium salt by reaction with hydrogen chloride gas in concentrated aqueous solution (from which sodium chloride precipitates) this was not considered worthwhile.

Instead it was hoped to precipitate the zinc polyethylene-sulphonate from a solution of the sodium polymer. Thus an aqueous solution of sodium ethylene sulphonate (20% w/v) was polymerised at room temperature using a potassium persulphate/sodium bisulphite

initiator system. The viscosity rose considerably over 24 hours and the presence of polymer was proven by the presence of a precipitate when a sample of the solution was dropped into methanol. However, when dropped into an aqueous solution of zinc acetate or zinc chloride no precipitate was formed. This was felt to be a significant observation as it indicates that, were it prepared, the zinc polyethylenesulphonate, or its copolymers, would be excessively water sensitive, if not soluble. The reason for this behaviour is not known, but may be predicted as being due to a higher degree of ionisation in the zinc-sulphonate system than in the zinc-carboxylate system. Obviously further investigation of this topic is desirable, but it cannot be justified in this study.

CHAPTER 7

DISCUSSION

The essentially objective nature of this work, together with the need for interpretation of many of the experimental results, has led to the inclusion of much of what would normally be deemed 'discussion' in the appropriate experimental chapters. This has resulted in a study in which each step is very dependent on the previous one, and in its turn indicates the requirements of the next phase.

The purpose of this chapter is therefore not to repeat the interpretation and implications of these experimental results, but to consider in more detail some of the results and observations less directly relevant to the ultimate objective.

7.1 THE DOUGH MOULDING PROCESS

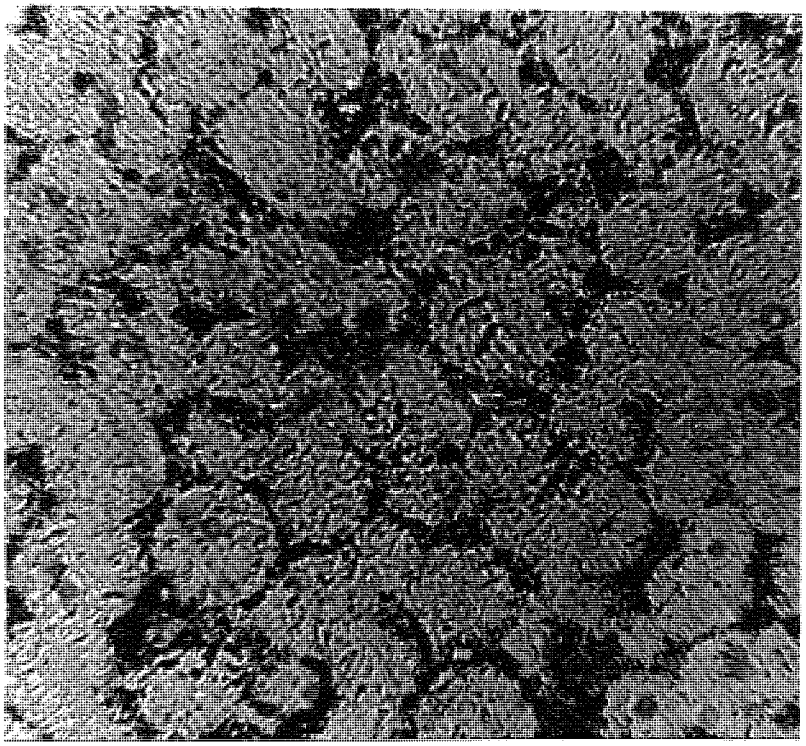
In a system of uncrosslinked polymethylmethacrylate microspheres, and monomer solvent, 'doughing' was expected to be the visible indication of the dissolution of the polymer. The resultant dough is, apart from air bubbles, visibly homogeneous and almost transparent and flows like a very viscous fluid.

It was thus a surprise to find that the polymer spheres were still distinguishable, undistorted and with no detectable change in size, in the cured moulding (plate 5.4 - thin section optical micrograph). This effect had previously been observed in all highly filled materials so examined (63). However, some dissolution of polymer must have taken place for the doughing process to proceed.

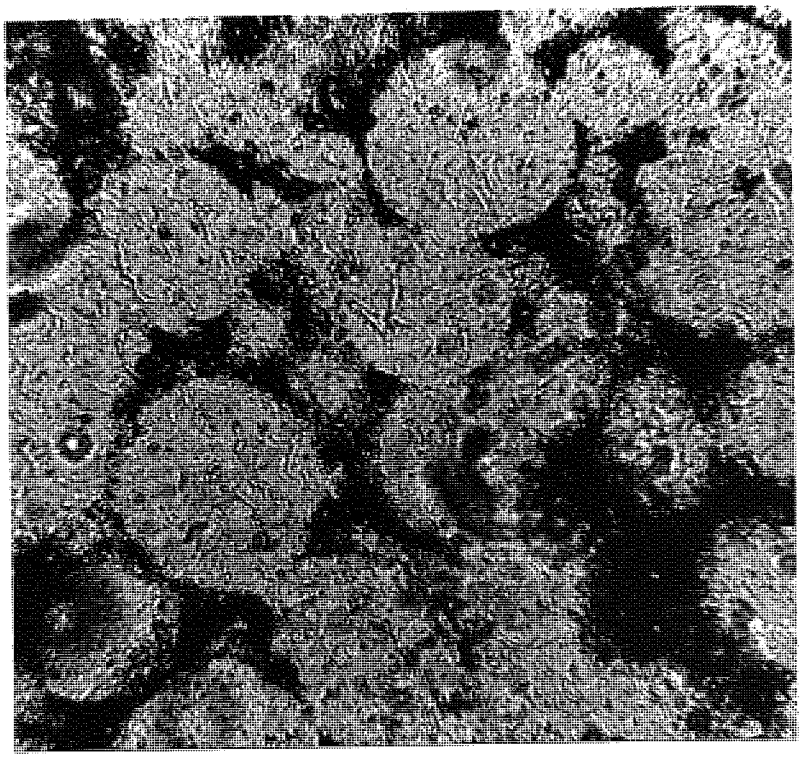
Comparison of plate 5.4 with that of dry 'Stellon' powder (plate 5.3) indicates that the finest particles may have been preferentially dissolved. It is to be expected that these particles of high specific surface area should be most rapidly dissolved, though it is equally possible that their absence from plate 5.4 is due to lower resolution caused by the sample preparation technique. As a test of this hypothesis dough mouldings were prepared from polymers of different particle size. A sample of 'Stellon' polymer was sieved to obtain one fraction of particles $> 120\,\mu$ diameter and another $< 75\,\mu$. Dough mouldings were then prepared containing 20% w/w barium sulphate filler (for at this stage the dispersion of filler particles was being investigated). As predicted the smaller polymer particles caused an acceleration in the doughing process and the large particles a retardation. The resolution of the polymer spheres in optical thin section micrography was excellent in both cases. (The appearance of spheres of apparently small size in the large particle sample may be due to the sectioning not being across their greatest diameter. Sections were cut 5-15 μ thick and the sphere diameters $> 120\,\mu$.) (Plates 7.1, 7.2)

Despite the visible boundary between the polymer spheres and the matrix there does not appear to be any weakening at the inter face. Almost without exception stereoscan micrographs of the fracture surface of composites shows a total absence of part-spherical depressions or projections. This indicates the predominance of fracture <u>through</u> the spheres rather than a breakdown of the interphase bonding. Hence despite the <u>apparent</u> lack of interaction there does seem to be effective penetration of the sphere surface by monomer and subsequently, on curing a strong bond is formed. The only exception to this observation was the fracture

PLATES 7.1, 7.2 THIN SECTION OPTICAL MICROGRAPHS OF DOUGH MOULDINGS FILLED TO 20% w/w BARIUM SULPHATE



7.1 STELLON POLYMER PARTICLES
< 75 μ X 250



7.2 STELLON POLYMER PARTICLES
> 120 μ X 250

surface of the material prepared from small polymer spheres described above. This is shown in plate 7.3 and the surface is typified by undulations and the presence over all of the visible area of filler particles. By contrast, plate 7.4 shows the fracture surface of the composite made from large polymer spheres. Little filler is visible and the area is flat and basically similar to unfilled material. Both of these composites were filled to the extent of 17.5% v/v of the intersphere phase, their dissimilar fracture behaviour can therefore only be due to the different distributions of that filler.

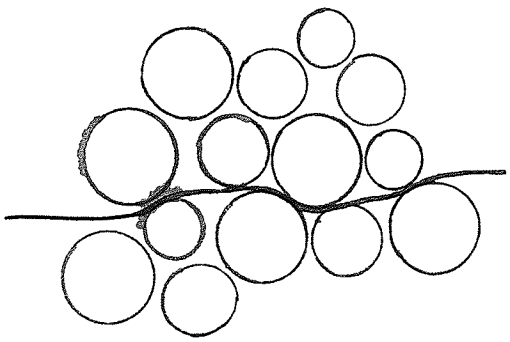


Fig 7.1

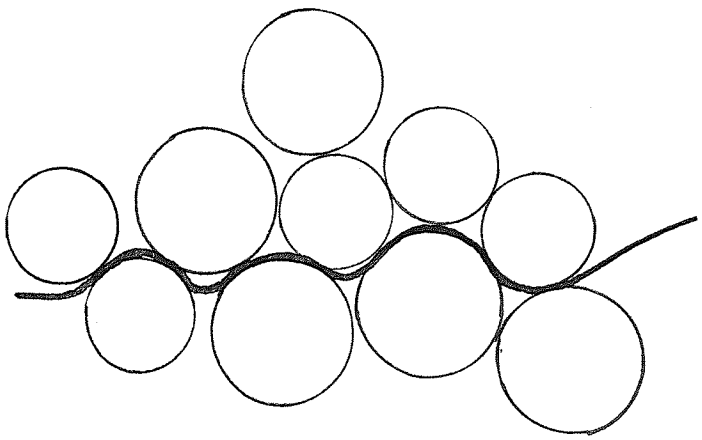
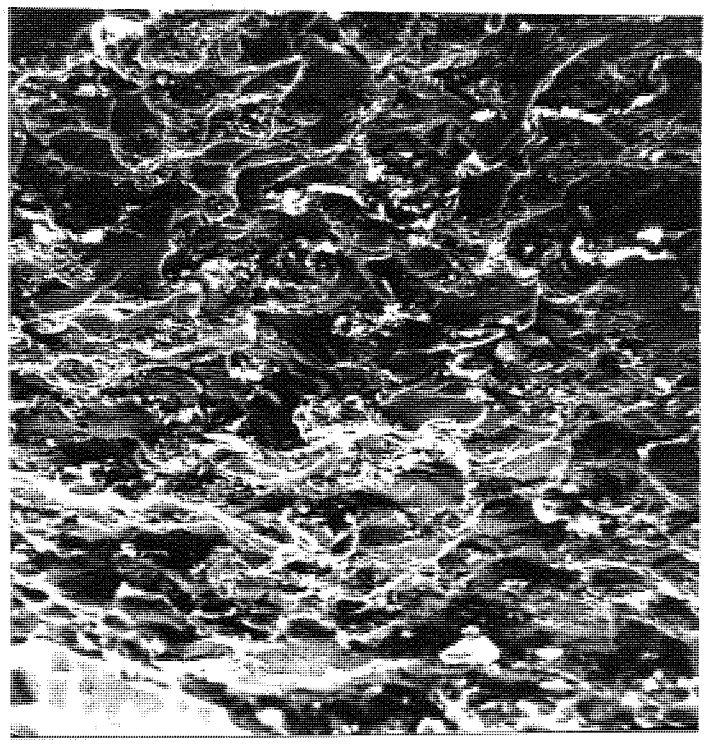


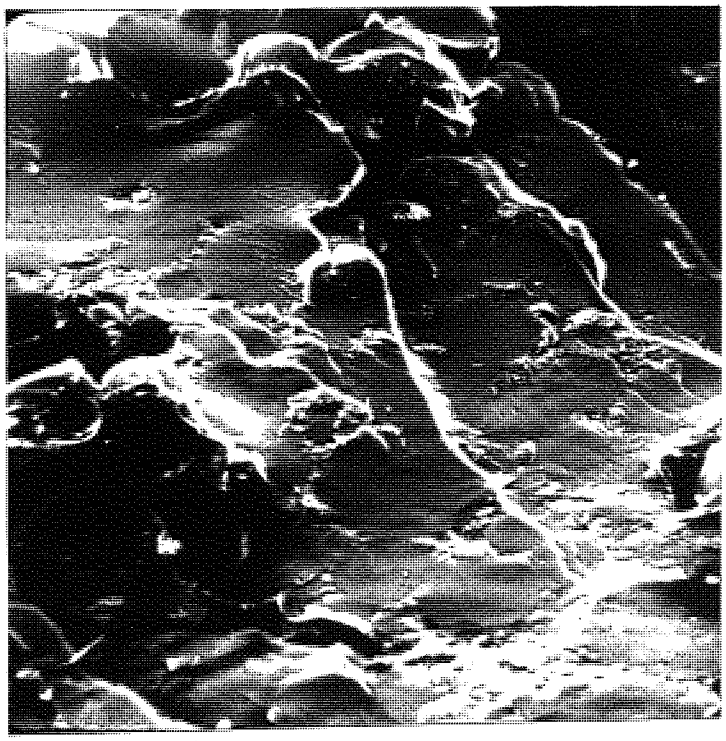
Fig 7.2

It is proposed that this difference is due to the differing crack lengths required to fracture in the filled phase. In the small sphere composite (Fig 7.1) it is seen that a crack may propagate almost linearly without leaving the filled phase. On the other hand the deviation from linearity in the large sphere material is considerable (Fig 7.2). The difference in energy associated with the increased crack length makes it more favourable for a shorter crack to propagate through the stronger unfilled phase. The

PLATES 7.3, 7.4 FRACTURE SURFACES OF BARIUM SULPHATE FILLED DOUGH MOULDINGS



7.3 STELLON POLYMER PARTICLES
< 75 μ
SEM X 250



7.4 STELLON POLYMER PARTICLES
> 120 μ
SEM X 250

fracture surface thus shows filler only in narrow interspherular bands.

This difference in behaviour according to polymer particle size does not imply an improvement or otherwise in physical properties. The flexural strength is unaffected, though the fracture energy is dissipated in the one case by large area, low energy cracks and low area high energy in the other.

This study was also approached from the opposite direction, as it were, using normal 'Stellon' polymer powder and varying the particle size of the filler. Thus 'B5' type mouldings (containing 40% w/w 'C9') were prepared using fractionated C9 powder

1) < 200 mesh (75 μ)

2) 100-200 mesh (75-150 μ)

3) > 80 mesh (150-200 μ)

The sample < 75 μ contained a large proportion of particles of 1-10 μ.

These materials showed no differences in appearence, strength or radiopacity, or in the quality of the fracture surfaces. The absence of visible filler particles in the surface implies that fracture occurs through the particles rather than around them. This is especially so in the sample containing the large filler particles as these were larger than the polymer spheres and would have been readily resolvable.

The following conclusions were drawn:-

The processes involved in dough moulding are effective in producing a material of nearly complete homogeneity.

The incorporation of filler particles into a dough-moulding causes a weakening of the composite.

Filled composites fractured almost exclusively along the shortest possible crack, though this meant that fracture proceeded through the

prepolymer spheres rather than the highly filled phase.

This fracture route was maintained when large particles of polymeric filler ('C9') were incorporated in the matrix. It would therefore seem that the particles are bound into the composite and crack propagation proceeds through, rather than around them.

7.2 RADIOGRAPHY

In comparisons of calculated and observed mass attenuation coefficients, both for barium sulphate and 'C9' composites, an increasing divergence was noted at high levels of radiopacifier.

In the case of the barium sulphate filled material this deviation is above the theoretical value by up to 50% at 40% w/w filler. The zinc acrylate copolymer composite agreed with the calculation more closely, but was 8% below theoretical in the Pure copolymer (54% zinc acrylate). These observations cannot be explained by experimental error as in both cases the unfilled material gave the predicted value, and all members of the series gave points on the appropriate curves with almost no scatter.

It was thus concluded that the deviation was a result of inhomogeneity in the x-ray beam. It has already been stated that filtration can only yield an effectively homogeneous beam in the material of the filter, which in other absorbers may behave differently. This was felt to be the cause of the deviation for the zinc compound, and the error is not large enough for confidence in the test to be lost. However the large deviation for the barium sulphate composites would appear to be too severe for this explanation.

A tentative scheme for over-absorption by high loadings of radiopacifier was put forward in chapter 2. Here it was suggested that at anything above a minimal loading of heavy atom the effective

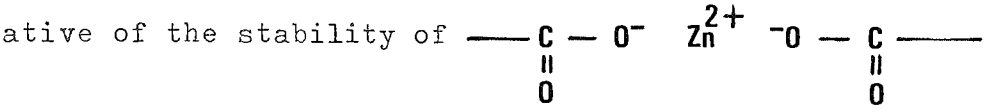
wavelength of the x-ray beam became lengthened by the presence of low energy scattered radiation. This system cannot be subjected to any such simple analysis owing to the presence of the barium K absorption edge at 0.32 Å. At this point the mass attenuation coefficient of barium rises from 5 to 30. The experimental test wavelength was 0.329 Å (effective) and it is probable that some shorter wavelength component was present.

Calculating back from the observed values gives an attenuation coefficient for barium of 8.5 - 9.5 for all points on the curve. This would mean that approx 16% of the x-radiation was of a wavelength below the absorption edge. Such a figure would not be unreasonable for a filtered beam as filtration preferentially absorbs long wavelengths and the resultant beam may still contain a restricted spectrum of short wavelengths. This would also have the effect of marginally reducing the observed attenuation by zinc atoms, though the overall effect over the spectral average wavelengths could not be predicted with accuracy.

The ultimate conclusion must be that without extensive study of the examining beam spectrum and the absorption behaviour of the atom under different beam wavelengths, exact calculations of the absorption behaviour in the region of an absorption edge cannot be made. Conclusions are therefore not drawn from the data obtained on composites containing barium sulphate. Experimental results determined for materials in which zinc, bromine and caesium were the radiopacifying element are still held to be valid and reliable for the particular conditions of examination.

7.3 CROSS-LINKING EFFECTS OF ZINC ACRYLATE

When this investigation was begun it was expected that copolymers

containing zinc acrylate should be cross linked through the zinc atom. At this time the 'unknown quantity', was the extent of ionisation of the salt in the various environments, and hence the lability of the cross links. It is known that formulations containing low proportions of copolymerised zinc acrylate with elastomeric comonomer systems are being investigated in the field of thermoplastic elastomers. If a satisfactory product is prepared by this route it is indicative of the stability of  cross links at normal temperatures and their lability at moulding temperatures (not expected to exceed 250°C in consideration of the stability of the comonomer units). Such a product is marketed by Dupont as 'Surlyn A' (containing approx 5% acrylic acid copolymerised with ethylene) which is intended for metallation in compounding. The extent of the subsequent thermoplastic flow is not known, but is thought to be a source of difficulty as compression moulding is the only recommended processing technique. Current thought on the structure of these materials is that the ionic regions form micelles within a covalent matrix and are equally effective in the 'cross linking' effect whether monovalent or divalent metal atoms are employed. This leads one to suppose that the bonding is almost wholly ionic and potentially labile.

However these systems are of very low zinc content and whether the conclusions have any validity in the zinc-rich systems of this study is questionable.

Of the zinc acrylate copolymers of this study the lowest zinc content was C5 (16% zinc acrylate). This material was obtained in a plaque form, visibly identical to pure polymethylmethacrylate. The flexural strength was considerably reduced, though the material

was tough and flexible, so that no break occurred in the test.

Sample	Flexural Strength (Nmm^{-2})		Modulus (Nmm^{-3})		Deflection (mm)	
	Dry	Wet	Dry	Wet	Dry	Wet
C5	49.5	44.1	0.41	0.37		
Stellon	80	83	0.58	0.506	6.5	7.5

A true copolymer structure was confirmed by the inextractibility of either the zinc acrylate (by water) or polymethyl methacrylate (by toluene). The earlier stereoscan photographs of C5 fracture surfaces (plates 5.9 - 5.11) illustrated the fundamental similarity to the zinc-free polymer, but also the existence of some anisotropy. No phase boundaries such as would be expected from micellar aggregates were visible (though the resolution may not have been adequate).

In hot pressing C5 exhibited good flow, both when pressed from the plaque, and from a powder ground from the plaque. The resultant film was not transparent but still had the appearance of a compressed powder, even when pressed from the plaque. This material was too brittle and weak for any test pieces to be cut. Such a drastic change in properties seems to indicate a breakdown in the internal structure of the polymer. Flow of the extent observed in a cross linked polymer can only be achieved by the breaking of some bonds. It is not known whether those broken were the -Zn- ionic cross links or main chain covalent bonds. The reported work on thermoplastic elastomers leads one to predict the preferential failure of the ionic bonds. In retrospect 'before and after' chain molecular weight determinations could have been used to distinguish between the two systems. In the formic acid treatment all the zinc ion cross links

are broken and thermal cleavage of these bonds would not affect the determined molecular weight. On the other hand main chain cleavage would.

Whichever system operates at the high pressing temperatures it is apparent that the process is irreversible. No homogeneous material was produced by the hot pressing process, of any zinc acrylate copolymers. A typical fracture surface was shown in plate 6.1 (hot pressed 'C9') and is typified by the rather dull and granular appearance. No evidence is visible of any conchoidal fracture, such as was seen in dough mouldings.

The effects of zinc acrylate powder copolymers on dough mouldings was not as expected of a non interacting filler. Barium sulphate filled composites showed the expected reduced breaking load and deflection at break and increased modulus. Failure in highly filled materials was always by a 'progressive' and 'friable' mode (the stress/strain curves had rounded peaks). Thin sections of these materials could be cut on a microtome with no more difficulty than pure 'Stellon'. This was not so with materials containing 'C9'. The breaking load and deflection at break were less affected, the modulus showed a maximum at 35% v/v C9, and the stress/strain curves invariably typified brittle failure (sharply pointed peaks). This resulted in fragmentation of the sample when microtoming was attempted and no thin sections could be prepared. It has already been pointed out that this fracture proceeded through, rather than around, filler and prepolymer particles.

The only system discovered which destabilised the cross links so as to give improved doughing and moulding properties utilised acrylic acid in the doughing monomer. The use of 8% w/w acrylic acid in the monomer (3% overall on the moulding) produced a

moulding which satisfied the flexural strength requirements of the British Standard though exhibited a lower deflection at break than did 'Stellon'. If tested dry however there was virtually no improvement over the acrylic acid-free moulding. There exists considerable relectance in the dental field to employ acrylic acid in this function due to reported 'blanching' and adverse effects on the pigments used. The problem of tissue reaction in the mouth would not be expected to give serious problems. At such a low loading, and expecting a high conversion in polymerisation (a reasonable assumption based on monomer reactivity) there is not likely to be any appreciable toxicity. In view of the aqueous solubility of acrylic acid any residual monomer would be readily removed on soaking in water. An acrylic acid content of 3% overall produced a moulding having an equilibrium water content of 4.5% w/w compared with 3.3% for the acrylic acid-free B5 moulding, 1.8% for pure 'Stellon' and 2.2% for 'Radiopaque Stellon'. Though comparison cannot be made with the British Standard due to different sample configurations and drying conditions it seems that the acrylic acid moulding may not seriously exceed these requirements.

Toxicologically this moulding could not be faulted as the zinc oxide/polyacrylic acid system has been extensively studied and concluded to be acceptable (117-124). Thus apart from the moulding problems associated with acrylic acid systems the only obvious faults with such a moulding are not serious:-

The material is brittle when dry, but would never be expected to endure stress in this state.

The relatively high equilibrium water content may give rise to absorption of bacteria and 'fouling' but recommended denture cleaners contain sterilants.

Obviously it would be premature to claim success for this material. Having reached this stage it becomes necessary to re-assess the long-term aqueous zinc extraction from the more hydrophilic matrix. Such aspects as dimensional stability both in moulding and in use must also be evaluated.

Though a promising system, even if its properties were wholly acceptable the radiopacity is not adequate. 'C9' copolymer and the allied 'B5' dough moulding were both selected as compromise formulations having minimal zinc contents. It would now seem worthwhile to prepare a range of mouldings from high-zinc acrylate-content copolymers using acrylic acid in the doughing monomer.

It is felt, then, that the ultimate suitability of a zinc acrylate/methyl methacrylate copolymer is indicated.

This study has served to identify the many problems associated with the production of a radiopaque denture base, quantify them where possible and indicate possible solutions. The particular system studied in most detail was never envisaged as a commercial product but as a model compound for directing the further evolution of zinc-containing copolymers towards this goal. In this respect it is considered to be a success and worthy of continued study.

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