

Durham E-Theses

Studies of surface modification of polymers via photo-initiated grafting

Linda Margaret Preston

How to cite:

Preston, Linda Margaret (1990) Studies of surface modification of polymers via photo-initiated grafting. Masters thesis, Durham University.

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a <https://etheses.durham.ac.uk/id/eprint/6234/> is made to the metadata record in Durham E-Theses
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the [full Durham E-Theses policy](#) for further details.

The copyright of this thesis rests with the author.
No quotation from it should be published without
his prior written consent and information derived
from it should be acknowledged.

Studies of Surface Modification of Polymers via Photo-initiated Grafting

A thesis submitted for the degree of Master of Science

by

Linda Margaret Preston, B.Sc. (Dunelm)

UNIVERSITY OF DURHAM

1990



25 JUN 1991

This thesis is dedicated to Paul,

and to my Parents

Abstract

Industrial biosynthesis of proteins used in medical therapy involves filtration through polymeric membranes in order to separate them from fermentation mixtures.

At present, the overall yields of such processes are low and consequently the products are very expensive. This is chiefly because the membranes foul by settlement of proteins on them which eventually bind and plug the pores.

The membranes in question are at present made from materials which have hydrophobic surfaces. It was believed that a neutral, water-binding surface would reduce or eliminate fouling.

In order to create such a surface, a vapour-phase, photoinitiated grafting process, developed by Rånby²⁸, was used to graft poly(HEMA) onto the surface of Ultem films and membranes.

The grafted surfaces were characterised by contact angle measurements with water and ESCA, and tested for fouling propensity. It was shown that this technique is suitable for grafting poly(HEMA) onto Ultem films and membranes, and that the graft results in a significant reduction in the protein fouling propensity.

Acknowledgments

Firstly, I would like to thank Prof. Jim Feast for his help and supervision during this project. Thanks are due also to Dr. W.F. Pacynko for his industrial supervision, and to British Petroleum for providing the funding for this work.

Lastly, I would like to thank members of the polymer group whom I have worked with during the past year for their friendship, advice and encouragement.

Memorandum

The work of this thesis was carried out in the Chemistry Laboratories of the University of Durham between July 1989 and June 1990. This work has not been submitted for any other degree and is the original work of the author, except where acknowledged by reference.

CONTENTS

	Pg
Abstract	
Acknowledgements	
Memorandum	
<u>CHAPTER 1</u>	<u>INTRODUCTION</u>
1.1	Protein Structure and Adsorption onto Surfaces 1
1.2	Ultrafiltration and Microfiltration 7
<u>CHAPTER 2</u>	<u>POLYMER SURFACE MODIFICATION</u>
2.1	Non-covalent Coatings on the Original Surface 10
2.2	Covalently-attached Coatings 14
2.3	Modification of the Original Surface 15
2.4	Plasma Techniques 17
<u>CHAPTER 3</u>	<u>PHOTOGRAFTING</u>
	Basic Photochemistry and Background 19
	Photografting Techniques 25
<u>CHAPTER 4</u>	<u>CHARACTERISATION OF TREATED FILMS</u>
(a)	Contact Angles 26
(b)	ESCA 32
(c)	Tests for Fouling Propensity 35
(d)	Differential Scanning Calorimetry (DSC) 35

CHAPTER 5 EXPERIMENTAL WORK

5.1	The Grafting Procedure and Experimental Set-up	39
5.2	UV-irradiation of Polyethylene Films	42
5.3	Grafting of Poly(acrylic Acid) onto Polyethylene	45
5.4	Grafting of Poly(HEMA) onto Polyethylene	48
5.5	Grafting of Poly(HEMA) onto Ultem Film	49
5.6	Grafting of Poly(HEMA) onto Ultem Membrane	54
5.7	Overall Conclusions	55

CHAPTER 6 SUGGESTIONS FOR FURTHER WORK

	Suggested Modifications to Grafting Set-up	56
	Suggested Further Experiments	58

<u>APPENDIX 1</u>	60
--------------------------	----

<u>APPENDIX 2</u>	61
--------------------------	----

<u>APPENDIX 3</u>	62
--------------------------	----

<u>APPENDIX 4</u>	64
--------------------------	----

<u>APPENDIX 5</u>	65
--------------------------	----

<u>APPENDIX 6</u>	66
--------------------------	----

<u>APPENDIX 7</u>	67
--------------------------	----

<u>APPENDIX 8</u>	69
--------------------------	----

Chapter 1

Introduction

Industrial biosynthesis of proteins used in medical therapy involves filtration through polymeric membranes in order to separate them from fermentation mixtures. The techniques generally used are ultrafiltration and microfiltration. These will be described in more detail in section 1.2. Overall yields of such processes are at present very low and consequently the products are very expensive. This is chiefly because the membranes foul by settlement of proteins on them which eventually bind and plug the pores.

The membranes in question are at present made from materials which have hydrophobic surfaces. It is thought that a neutral, water-binding surface would reduce or eliminate fouling. The aim of this research is to create such surfaces on the membranes by grafting, and to test their effectiveness.

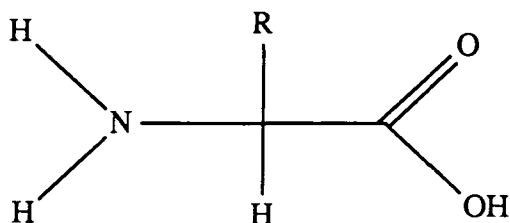
This chapter is divided into two sections. Section 1.1 describes protein structure, how proteins adsorb onto various types of surface, and explains why we have aimed to create a surface with the properties outlined above. Section 1.2 gives a brief account of ultrafiltration and microfiltration techniques and the problems encountered, which this work attempts to overcome.

Section 1.1

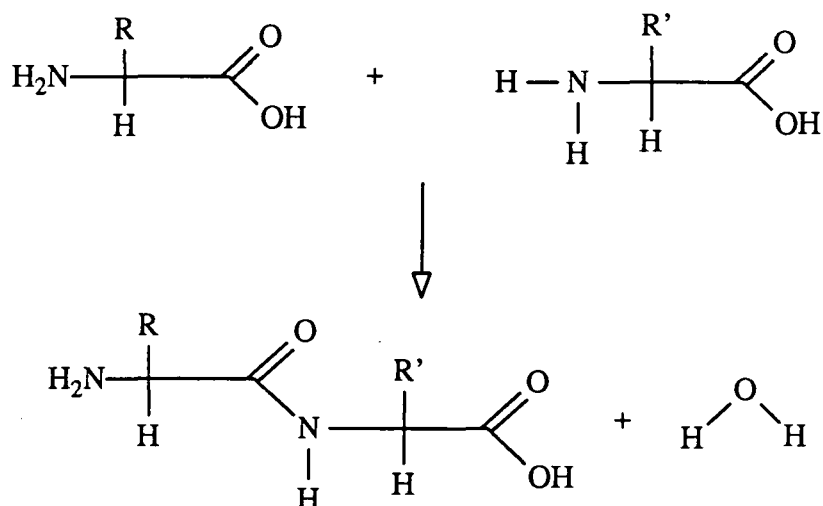
Protein Structure and Adsorption onto Surfaces

Protein Structure

Simple proteins consist only of amino-acid residues linked in a sequence which is specific for each particular protein. Amino-acids have the general formula shown in Fig 1.1.1.

Fig 1.1.1

α -Amino-acids react to form peptides by linking of the amino group of one acid to the carboxylic group of another via an amide bond, with elimination of water. Fig 1.1.2 shows condensation of two aminoacids to form a dipeptide.

Fig 1.1.2

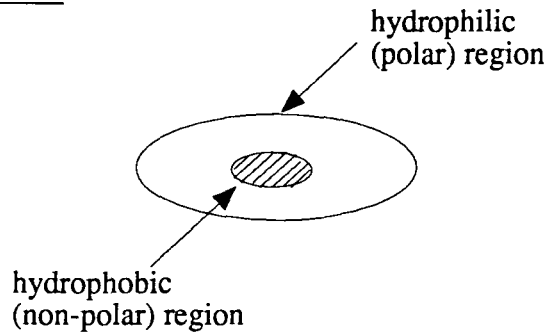
A large number of amino-acid residues linked together in this way is called a polypeptide. There is no rigid distinction between a simple protein and a polypeptide but generally, a peptide chain containing more than one hundred amino-acid residues is referred to as a protein¹.

Free aminoacids are amphoteric in aqueous solution, ie. they can behave as acids and bases. This results from their ability to exist as a zwitterion, since all aminoacids contain at least one amino and one carboxyl group, ie.

(Fig 1.1.5). This conformation is stabilised by:

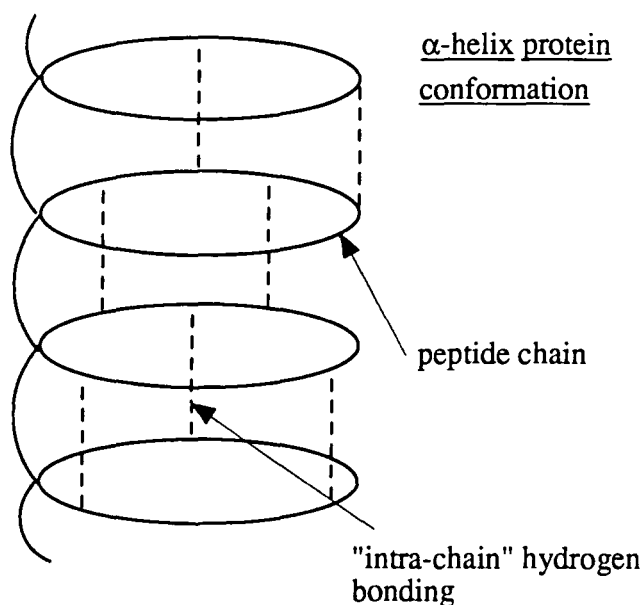
- (i) hydrogen-bonding between the carbonyl oxygen of an amino-acid residue and the N-H hydrogen of the fourth residue down the chain and
- (ii) by hydrophobic interactions between the non polar side chains of amino-acid residues from different parts of the polypeptide chain (Fig. 1.1.4).

Fig 1.1.4

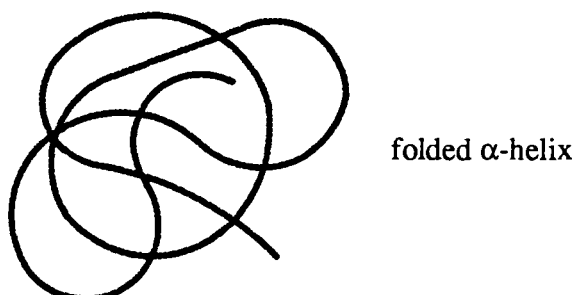


The driving force for these interactions is a positive entropy change resulting from the effective exclusion of water molecules from the vicinity of the hydrophobic groups. The introduction of a hydrophobic group into an aqueous environment is accompanied by a decrease in entropy due to an increase in order of the water molecules around the hydrophobic group; hence isolation of the hydrophobic groups will be accompanied by an increase in entropy.

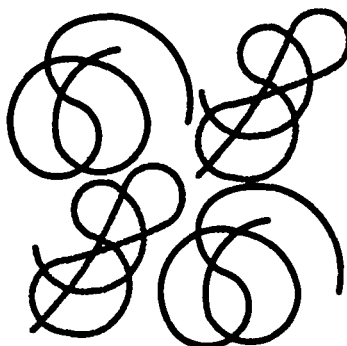
Van der Waals forces will also stabilise this conformation to a certain extent.

Fig 1.1.5

Most proteins do not exist wholly in a particular conformation, for example they may exist partially in an α -helix conformation, and partially in another. The overall folding of the structure is termed the tertiary structure. For example, if a hypothetical protein can be imagined to exist mainly in a α -helical conformation, its tertiary structure is the way in which the α -helix is folded, see Fig 1.1.6, in which the solid line represents an α -helix and its deviations from linearity are caused by structural features such as proline residues, and steric and polar interactions between side chain residues.

Fig 1.1.6Tertiary Protein Structure

Still more complex proteins have a quaternary structure. This occurs when a protein molecule is made up of a number of non-covalently bonded polypeptide chains or "subunits". The quaternary structure is the arrangement in space of the "subunits" relative to one another, and any prosthetic groups (Fig. 1.1.7).

Fig 1.1.7Quaternary
Protein
Structure

Hypothetical arrangement of folded
polypeptide chains

Protein Adsorption onto Surfaces

This section sets out to discuss why the membranes used in protein separation foul, and to explain why we have attempted to create a neutral, hydrophilic surface in order to reduce fouling.

Protein adsorption from aqueous solution onto hydrophilic and hydrophobic silicon surfaces has been studied by ellipsometry.³ It was found that adsorption onto the hydrophobic surface was almost totally irreversible, whereas adsorption onto a hydrophilic surface was reversible to a small extent.

This irreversibility of adsorption is believed to be a result of conformational changes in the protein, brought about by breaking of intramolecular bonds. The driving force for such a loss of secondary structure is an increase in entropy. This can be illustrated by considering a simple α -helix. The secondary structure, formed as a result of intra- molecular hydrogen-bonding, impedes rotation about the bonds between the amide links and the sp^3 carbons in the polypeptide chain. Hence reduction in α -helical content will result in increased bond rotation and an increase in the entropy of such a system.

Proteins desorbed from surfaces have been studied by circular dichroism⁴ and found to contain a decreased α -helical content as compared with the native molecule.

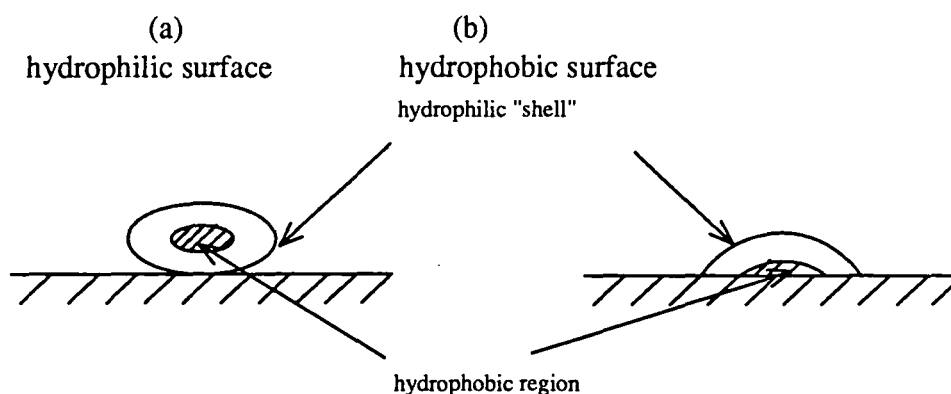
In the adsorbed state, hydrophobic side chains may be accommodated at a non-polar surface to prevent contact with water, hence intramolecular hydrogen-

bonding in an adsorbed protein is less important in stabilising the structure (Fig 1.1.8a).

Proteins may adsorb at a charged surface via strong electrostatic interactions, which are difficult to break, hence we have attempted to create a neutral surface on the membrane.

In particular, the introduction onto a surface of hydrophilic comonomers which are capable of hydrogen-bonding to proteins have been found to decrease the extent of conformational change experienced by the protein.⁵ Presumably this is because extensive interactions with the surface can take place via the protein's hydration shell, without necessitating any conformational rearrangement (Fig 1.1.8b).

Fig 1.1.8



Hence hydrophilic, hydrogen-bonding monomers such as 2-hydroxyethyl methacrylate (HEMA) have been chosen to graft onto the membranes to produce a surface to which proteins will adsorb reversibly and from which they can be readily eluted.

Section 1.2

Ultrafiltration and Microfiltration

Ultrafiltration and microfiltration both operate under the same working principle. Protein solution (or fermentation mixture) is filtered through a semi-permeable membrane. A higher pressure is applied to the side of the

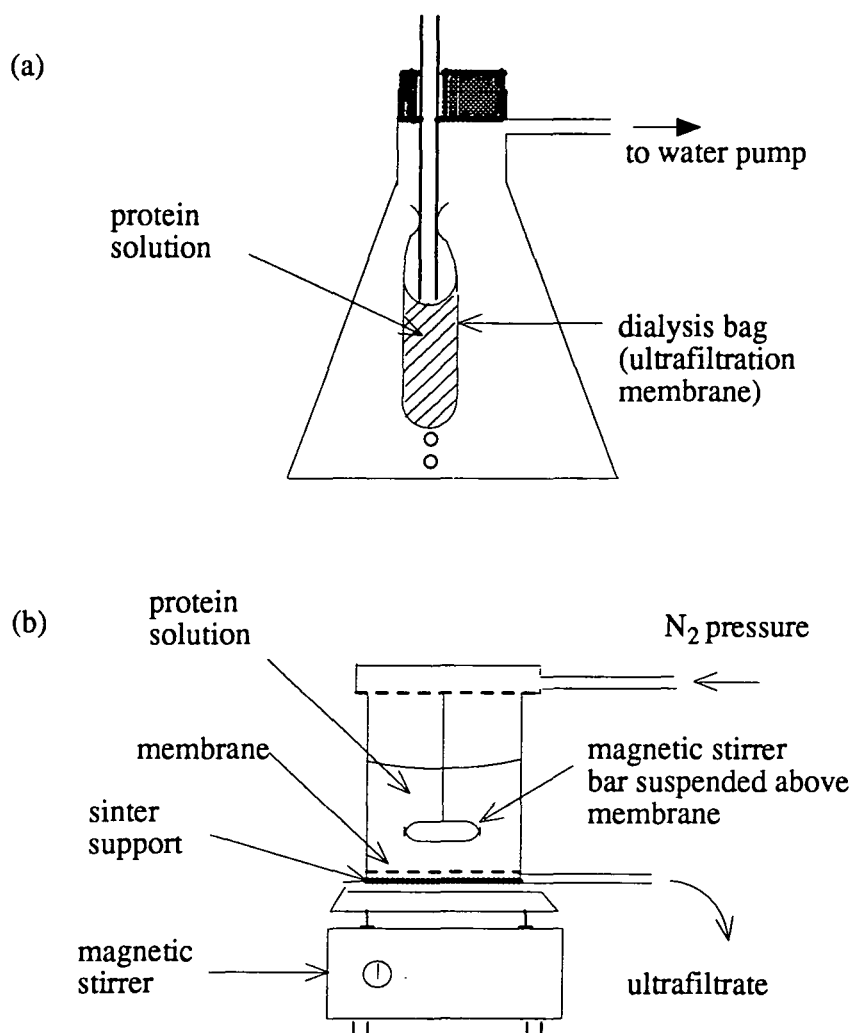
membrane containing the macromolecules, forcing smaller molecules through the membrane pores.¹ The smaller molecules are continuously removed as they filter through the membrane.

Microfiltration differs from ultrafiltration only in that the average pore size of the membranes is larger in microfiltration. Microfiltration membranes have an average pore size of $0.05\mu\text{m}$ or larger, whereas ultrafiltration involves use of membranes with an average pore size smaller than $0.05\mu\text{m}$. The membranes contain a range of pore sizes, so there is no absolute cut-off point with respect to molecular size, hence a proportion of molecules with sizes close to the stated cut-off size will pass through.⁶ The membrane should be chosen such that the protein of interest has a size 30% to 50% larger than the quoted cut-off size, so that nearly all of it will be retained.

Ultrafiltration (and microfiltration) are limited in that proteins are separated into only two fractions; "larger" and "smaller" molecules with respect to the cut-off size of the membrane in question. Hence they are used as methods of concentrating protein solutions, complemented by more discriminating protein purification techniques such as gel filtration.⁶

In the laboratory, ultrafiltration can be performed using membranes in several configurations which include hollow fibres and stirred cells (Fig 1.2.1b). In addition to performing protein concentrations, ultrafiltration membranes may also be used for dialysis applications as shown in figure 1.2.1a.

Fig 1.2.1



The main problem encountered in ultrafiltration and microfiltration is irreversible adsorption of proteins on the membranes, which shortens the life of the membrane as well as decreasing the final yield of protein and which this work attempts to reverse.

Chapter 2

POLYMER SURFACE MODIFICATION

Modification of polymer surfaces allows the surface composition and properties of a polymer to be altered without altering bulk properties such as mechanical strength.

This chapter sets out to give a brief overview of some of the techniques used in polymer surface modification and their applications.

Surface modification techniques can be classified under three main categories⁷, which are covered in sections 1,2 and 3 of this chapter. Section 2.1 describes formation of coatings which are not covalently bonded to the original polymer surface; section 2.2 describes formation of coatings which are covalently bonded to the original surface, and section 2.3 describes methods of modifying the original surface. Modification of polymer surfaces by plasma techniques is described separately in section 2.4, since this type of surface treatment can be classified as formation of covalently-bonded coatings or modification of the original surface depending on the nature of the gases used in the plasma. The techniques which will be mentioned in this chapter are summarised here in a flow chart (Fig 2.0.1).

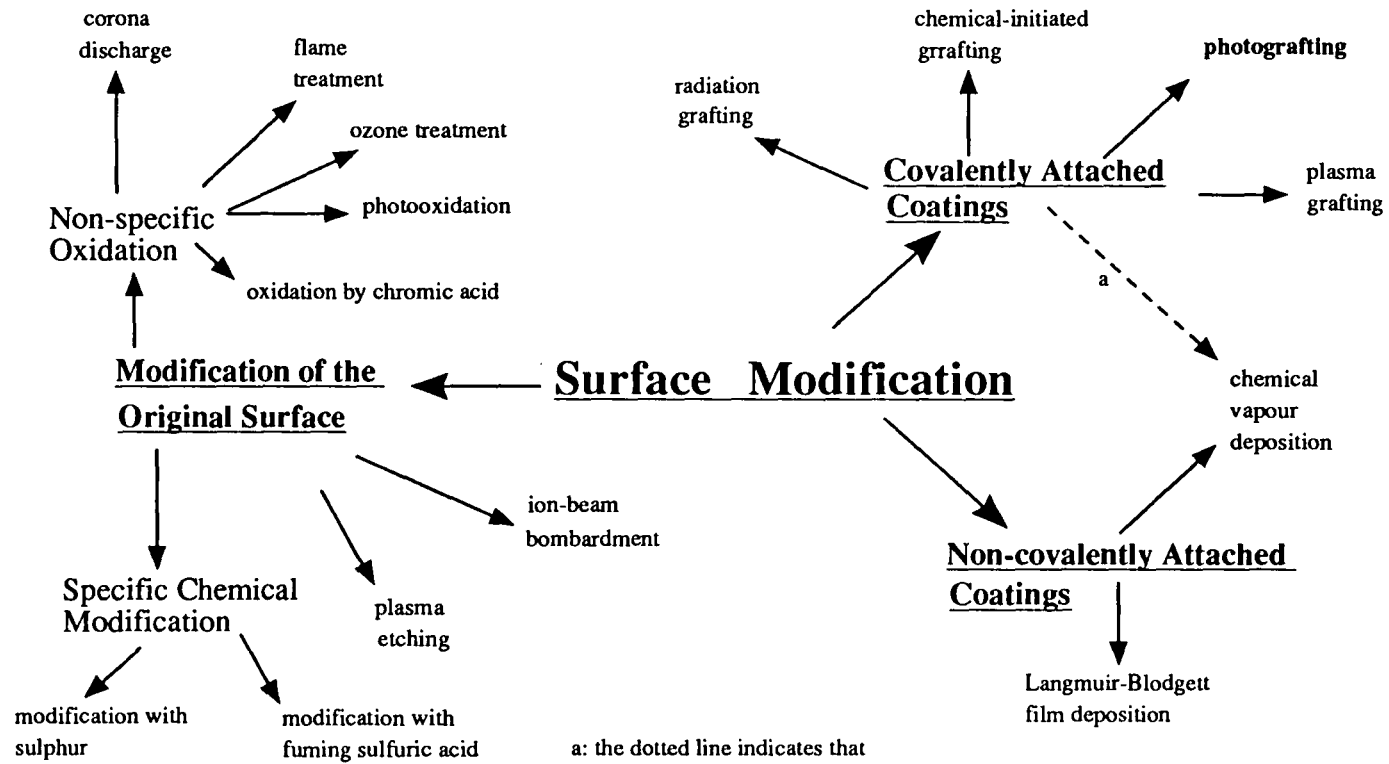
Section 2.1

Non-Covalent Coatings on the Original Surface

This section describes deposition of films on polymer surfaces by the Langmuir-Blodgett technique and by Chemical Vapour Deposition (CVD).

(a) Langmuir-Blodgett Film Deposition

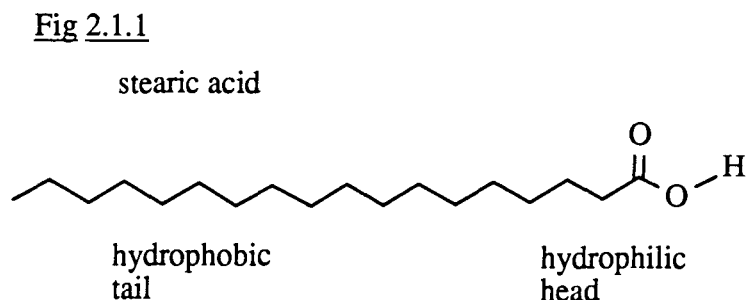
Amphiphilic molecules (those which have a hydrophilic head group and a hydrophobic tail group) can be assembled at an air-water interface to form a monolayer (a Langmuir film). An example of such a molecule is stearic acid,



a: the dotted line indicates that there may also be some covalent bonding in CVD

Fig 2.0.1

which has the chemical formula $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ (Fig 2.1.1).

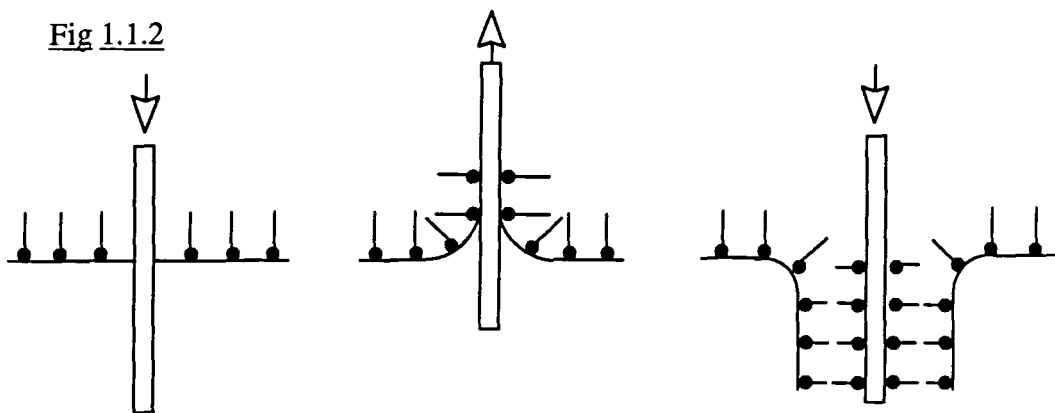


This phenomenon forms the basis for the Langmuir-Blodgett technique. The amphiphile (or surfactant) is first dissolved in a suitable solvent, which must have the following properties: it must be able to dissolve the surfactant to a concentration of 0.1 - 1.0mg/ml; it must not be miscible with water; it must not react chemically with the surfactant, and it must be sufficiently volatile to evaporate reasonably quickly, leaving no traces in the condensed monolayer.⁸

The surfactant solution is then spread over the air-water interface. After the solvent has evaporated, the monolayer is compressed, using an adjustable barrier, to form a condensed film, which is transferred to the polymer substrate by immersing and withdrawing the substrate through the solution, maintaining a constant horizontal pressure on the film.

The way in which the film is deposited on the substrate is dependent on the nature of the surfactant and the hydrophilicity/hydrophobicity of the substrate. If the substrate is hydrophilic, no monolayer is transferred during the first immersion, but monolayers are added successively during each subsequent withdrawal and immersion. Fig 2.1.2 shows the commonest type of Langmuir-Blodgett deposition, with surfactant molecules stacked head-to-head and tail-to-tail.

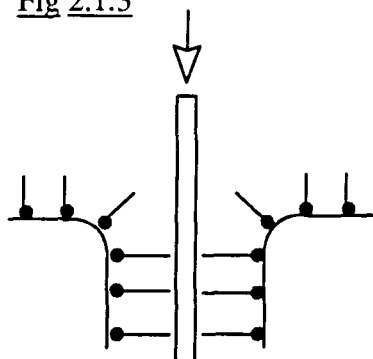
Fig 1.1.2



The thickness of the deposited film can be accurately controlled, being a function of the number of times the substrate is immersed and withdrawn through the solution.

If the substrate is hydrophobic, the first monolayer is added as the substrate is first immersed in the water (Fig 2.1.3).

Fig 2.1.3



Langmuir-Blodgett deposition on a hydrophobic polymer substrate

Although this is the type of deposition observed in most cases, some surfactants have been shown to stack in head-to-tail monolayers on a substrate⁸.

In some cases it is possible to use thermal or photo-excitation to form a polymerised Langmuir-Blodgett film, if the surfactant contains a polymerisable group, for example vinyl.

An advantage of the Langmuir-Blodgett technique is that it enables uniform, ordered films to be produced which can be as thin as one monolayer. Proposed applications of the Langmuir-Blodgett technique for polymer surface modifications include improvement of adhesive properties and lubrication.

(ii) Chemical Vapour Deposition (CVD)

CVD involves excitation of monomer molecules in the gas phase with plasma, thermal energy or by photo-excitation in a vacuum chamber to form radicals, followed by polymerisation at the surface of a substrate. The film thickness can be increased as a function of the reaction time and the gas flow rate through the chamber.

Section 2.2

Covalently-attached Coatings

This section covers grafting of polymers onto substrate surfaces by photo-initiation, radiation-initiation and chemical initiation.

Grafting onto a polymer surface involves the creation of macroradicals on the surface to be grafted (initiation). Grafting may be initiated by any of the following techniques:

(i) Photo-initiation

The surface to be grafted is irradiated with light in the visible or ultraviolet region of the spectrum, usually in the presence of a sensitiser⁹⁻¹². This is discussed in more detail in chapter 3.

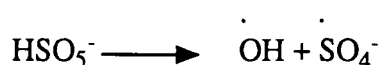
(ii) Radiation-initiation

Macroradicals are formed on the surface to be grafted by irradiating the surface with, for example, γ -rays from ^{60}Co ¹³⁻¹⁵.

In both photo-initiated and radiation-initiated grafting, either the pre-irradiation or the mutual irradiation techniques can be used. Pre-irradiation is where the polymer is exposed to the energy source before it is exposed to the monomer. For this method to work, the radicals involved must either be trapped or must have relatively long lifetimes. Mutual irradiation is where the polymer to be grafted is irradiated while it is in contact with monomer.

(iii) Chemical Initiation

This makes use of a redox system to produce macroradicals on the surface of the polymer to be grafted. An example of such a system is potassium monopersulphate/Fe(II), used by Giri et al.¹⁶ in the grafting of poly(acrylamide) onto wool fibres. It is believed that radicals are generated by the following redox reaction, and that these react with wool to form macroradicals on the surface of the fibres.



Section 2.3

Modification of the Original Surface

This section covers non-specific oxidation of surfaces by corona discharges, flame treatment, ozone treatment/photooxidation and oxidation by chromic acid; specific chemical modification: namely modification with sulphur and fuming sulphuric acid; and surface decomposition by ion bombardment.

Non-specific Surface Oxidation

(i) Corona Discharge

This has been carried out in a variety of gases by Briggs et al.^{17,18}. The treatment time is of the order of seconds. Autoadhesion was found to be enhanced by treatment in all the gases they used, with the exception of hydrogen. Oxygen functions were found to be incorporated into the polymer surface. Short treatment times resulted in the formation of carbonyl, hydroxy- and ether functionalities, whereas longer treatments led to more highly oxidised species such as carboxyl and ester functionalities. It is believed that adhesion is enhanced as a result of interaction through hydrogen-bonding.

A useful application of this form of oxidation is improvement of the printing characteristics of polymer films. This is done by treatment by corona discharge excited in air.

(ii) Flame Treatment

This technique is used commercially on plastic bottles, again to improve adhesion for printing onto the surface¹⁹. A natural gas-air mixture is used in the flame, and bottles are treated for 1.2 seconds in the oxidising area of the flame. Treated bottles were characterised by ESCA. Increased levels of oxidation were observed on the surface.

(iii) Ozone Treatment/Photooxidation

Surface modification of polyethylene and polystyrene by ozone treatment and by photooxidation have been studied by ESCA^{20,21}. Ozone treatment involved subjecting films to a flow of 0.5l/min of ozone gas generated in dry oxygen in a commercial reactor. Films were photooxidised by exposing them to radiation at 254nm from a mercury lamp in a dry oxygen atmosphere. Both treatments were found to result in the formation of ether, ketone and carboxyl groups on the surfaces of polyethylene and polystyrene. Several hours were required to produce fully oxidised surfaces. Comparison of the two techniques showed treatment by ozone to be a milder technique than photooxidation, which has been observed to initiate crosslinking and hydrogen abstraction, which can affect the bulk properties of the polymer as well as the surface

(iv) Oxidation by Chromic Acid

Polyethylene and polypropylene films have been etched by immersion in chromic acid²² (a mixture of $K_2Cr_2O_7$, H_2O and H_2SO_4 in the proportions 7:12:150 by weight) for a given time, usually of the order of hours, followed by washing in distilled water and drying under reduced pressure. The surfaces of treated films were characterised by XPS (or ESCA). Oxygen-containing species such as carboxyl, carbonyl and hydroxy were observed, also a sulphur-containing species, $-SO_3H$. The depths of oxidised layers were found to be more than 300Å, much greater than that observed for flame-treated surfaces. Again, this technique

can be used to improve adhesion.

Specific Chemical Modification

Polyethylene surfaces have been modified with atomic sulphur, generated by pyrolysis and photolysis of carbonyl sulphide and by sulphur vapours, and with fuming sulphuric acid²³⁻²⁵. It was established (using Multiple Internal Reflection Spectroscopy) that treatment with sulphur resulted in insertion into C-H bonds, forming surface thiols. Treatment with fuming sulphuric acid led to the formation of surface sulfonic acid groups.

Surface Decomposition by Argon Ion Bombardment

A polyimide (PIQ) has been modified by irradiation with argon ions²⁶. Characterisation of the surface by XPS (or ESCA) and direct recoil spectrometry showed that ion bombardment had caused decomposition of the surface to form a carbonaceous layer, which was found to be considerably more conductive than the original surface.

Section 2.4

Plasma Techniques

There are two main surface modification techniques involving plasma. These are distinguished by the nature of the gases used in the plasma. Most organic compounds, organosilicons and organometallics will polymerise in a plasma state to form a thin film on a polymer substrate. This is known as plasma polymerisation or grafting. Another form of plasma surface modification is plasma treatment or etching. This uses gases which will not polymerise in a plasma state. Some of these will not react at all with the polymer, for example helium, neon and argon, but can cause some chemical and physical reactions at the surface as a result of the highly energetic species formed in the plasma, and emission of UV radiation. Other gases, although not able to form polymers on their own in a plasma state, will react with and can be incorporated into substrate polymer chains. Examples

are hydrogen, nitrogen, oxygen and ammonia.

Advantages of using plasma techniques for surface modification is that they can be applied to nearly all polymers as very reactive, highly energetic species are created under plasma conditions. Plasma grafting produces a very thin surface layer, resulting in minimum alteration of the bulk properties. Grafted layers tend to be very dense, containing a large number of crosslinks, hence they are generally non-permeable. Bacteria are destroyed in plasma conditions, so treated films are sterile, which is desirable if the films are to be used for biomedical applications. Other applications of plasma treatment are in the improvement of dyeability of fibres²⁷ and enhancement of adhesive bonding.

Chapter 3

PHOTOGRAFTING

Basic Photochemistry: Background

(a) Absorption of Radiation

The first law of photochemistry (the Grotthus- Draper Law) states that a photochemical reaction can take place only if radiation is absorbed by the system.

The energy of a quantum of radiation (a photon) is given by the following equation:

$$E = h\nu \quad (3.1)$$

where h is Planck's constant (6.626×10^{-34} J s) and ν is the frequency of the radiation.

A molecule can absorb radiation only if the difference between two energy levels is exactly equal to that of the incident photon, ie. if

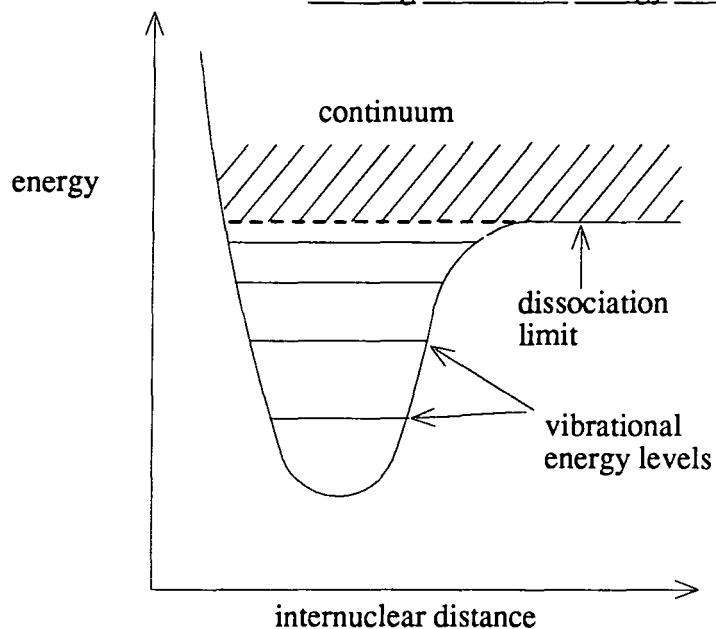
$$E_2 - E_1 = h\nu \quad (3.2)$$

where E_1 and E_2 are the energies of a molecule in the initial (lower level) and final (higher level) states respectively.

All photochemical reactions occur via electronically excited states which have specific energies, structures and lifetimes. Each electronic state has a series of discrete vibrational levels, which become closer together as they increase in energy, converging at the dissociation limit to form a continuum. (Fig 3.1).

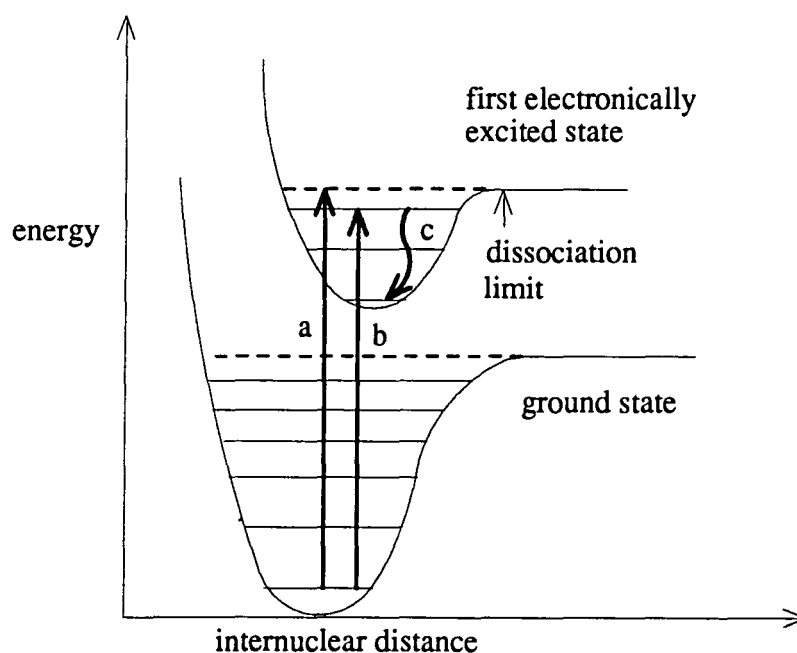
Fig 3.1

An Electronic Energy Level
showing Vibrational Energy Levels



Most photochemical reactions occur from the lowest vibrational level of the first electronically excited state. If a molecule is excited beyond the dissociation limit of an electronically excited state, bond dissociation occurs. Otherwise an excited state will be formed from which the molecule can return to the ground state by one of a number of radiative or non-radiative processes (Fig 3.2).

Fig 3.2



Key

- a: photodissociation
- b: excitation to an excited state which can lose energy by a radiative or non-radiative process to return to the ground state;
- c: return to the lowest vibrational level of the first excited state via a vibrational cascade.

Electronic levels can be categorised as follows:

- (i) Ground State, S_0 : the initial state of the molecule before excitation.
- (ii) Excited Singlet States, $S_1, S_2, S_3, \dots, S_n$ are formed after absorption of a photon. Electron spins are paired in these states. The majority of singlet photochemical processes occur from S_1 , since the rate of internal conversion (see later) from S_2, S_3, \dots, S_n to S_1 is very fast.

- (iii) Excited Triplet States, $T_1, T_2, T_3, \dots, T_n$:

The lowest excited triplet state, T_1 is formed mainly by a radiationless transition, intersystem crossing (see later) from S_1 . The higher triplet states, T_2, \dots, T_n , are formed by absorption of a photon from T_1 . Formation of a triplet state by direct absorption of a photon is a forbidden process. Electron spins are unpaired in triplet states.

Following absorption of radiation, and excitation, a molecule may return to the ground state by one of the following radiative or non-radiative processes:

Radiative Processes

Energy loss by a radiative process is known as luminescence, which includes emission by fluorescence and phosphorescence. Fluorescence, is a transition from the lowest excited singlet state, S_1 to the ground state, S_0 and phosphorescence is a transition from the lowest triplet state, T_1 to the ground state

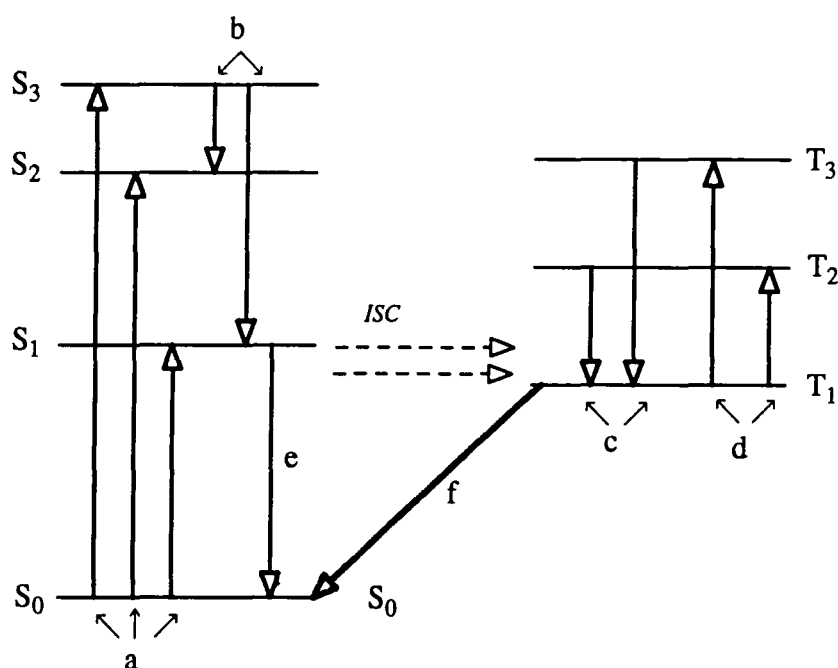
S_0 . Phosphorescence is a forbidden process so occurs much more slowly than fluorescence. Typical lifetimes of S_1 and T_1 states are in the ranges 10^{-9} to 10^{-6} seconds and 10^{-3} to ten seconds respectively³¹.

Non-radiative Processes

These are processes by which a molecule may return to the ground state with no emission of radiation. The molecule may move down through several singlet or triplet states until it reaches the ground state. Energy may be lost by collision with other molecules. These transitions are known as internal conversions. Alternatively, intersystem crossing may occur, whereby the molecule returns to the ground state via a transition from a singlet to a triplet state. This is known as intersystem crossing (ISC).

The Jablonski Diagram below shows the various types of photochemical processes mentioned in this chapter.

Jablonski Diagram showing Photochemical Processes

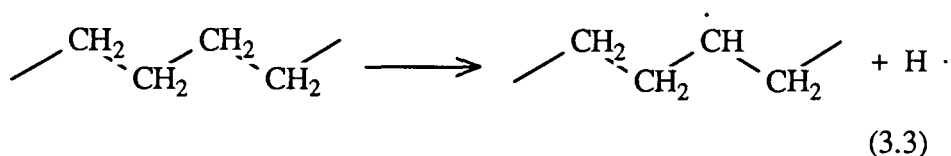


Key

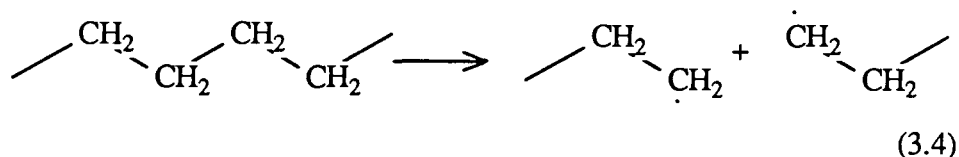
- a: absorption
- b: internal conversions
- c: triplet-triplet internal conversions
- d: triplet-triplet absorptions
- e: fluorescence
- f: phosphorescence

Photochemical Generation of Radicals on Polymer Surfaces

A radical may be produced on the surface of a polymer by direct absorption of a photon. For example in polyethylene, absorption of a photon can lead to homolysis of a C-H bond leading to the production of a secondary carbon radical (3.3)



or homolysis of a C-C bond leading to primary radicals via polymer chain scission (3.4).

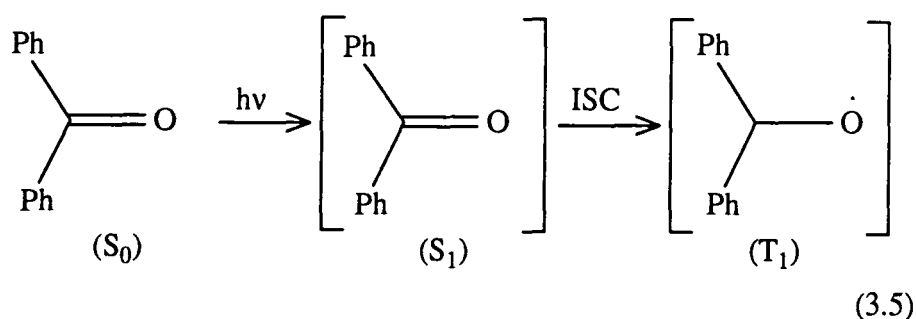


Obviously, chain scission is undesirable as it will result in lower molecular weight polymer at the surface, whereas C-H bond homolysis will give an active radical site where grafting can be initiated without degrading the polymer. The photoenergies necessary for these processes are require irradiation at wavelengths below 200nm, that is in the vacuum UV. Use of this type of radiation is not experimentally convenient and an alternative approach is to generate the required

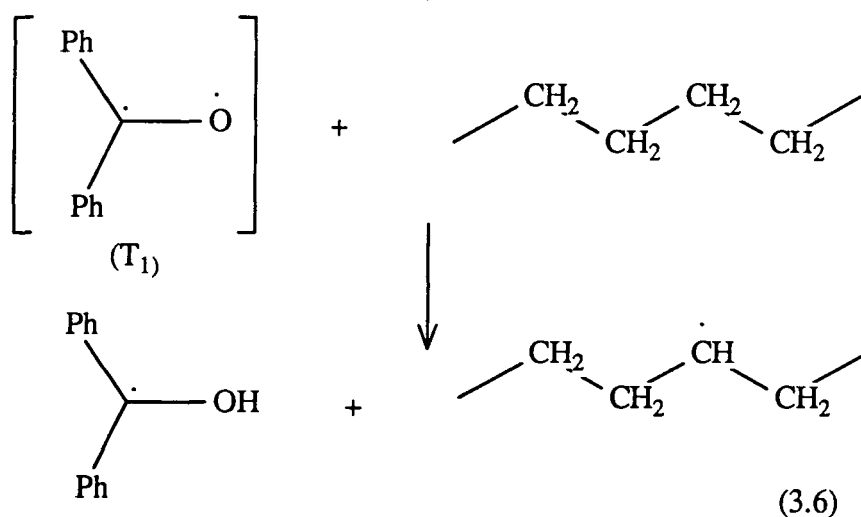
radical sites on the polymer surface via abstraction reactions using other photosensitive compounds.

Generation of Surface Radicals by Hydrogen Abstraction

The photosensitive compound used in this work is benzophenone, which absorbs at 345nm (λ_{\max})³⁰ and undergoes efficient intersystem crossing to the photochemically reactive lowest triplet state T_1 , which has a lifetime of 4.7×10^{-3} seconds.



This can then react with a polymer such as polyethylene by hydrogen abstraction to form a macroradical(3.6), and an inert diphenyl ketyl radical



Hence irradiation at 350 to 400nm of benzophenone in the presence of polyethylene gives selectively hydrogen abstraction, rather than chain scission.

The efficiency of the photochemically promoted abstraction process can be defined in terms of the quantum yield of radical formation, Φ_R (3.7).

$$\Phi_R = \frac{\text{number of radicals formed}}{\text{number of quanta absorbed by the system}} \quad (3.7)$$

Φ_R is wavelength-dependent, and for most polymers is very low, requiring dosages of long duration at short wavelength (below 300nm) to produce enough macroradicals to give a complete surface coverage of grafted polymer chains. Benzophenone has a high quantum yield of disappearance when irradiated with UV light so its use will cut down the intensity and duration of the dose required, involving less risk of extensive photodegradation of the bulk polymer.

Photografting Techniques

The method used in this work is a vapour-phase process developed by Rånby et. al.²⁸ Photografting is carried out in a purpose-built reaction cabinet, in a nitrogen atmosphere. The cabinet is equipped with a heating bath and a nitrogen supply. Benzophenone and monomer are evaporated from a solution in an open dish which is shielded from UV-radiation by aluminium foil. The sample is irradiated through a quartz window while exposed to a saturated vapour of solvent, benzophenone and vinyl monomer.

Vapour-phase photografting has also been carried out on a smaller scale in a sealed tube, also in a nitrogen atmosphere.²⁹

The equipment used for this work will be described in more detail in chapter five.

Another method developed by Rånby et. al.²⁸ is the continuous grafting process, also carried out in a purpose-built photografting device. The sample, in the form of a tape or fibre is passed through a presoaking solution of "photoinitiator" and monomer, through a reaction chamber where it is irradiated in a nitrogen atmosphere and onto a take-off roll.

Chapter 4

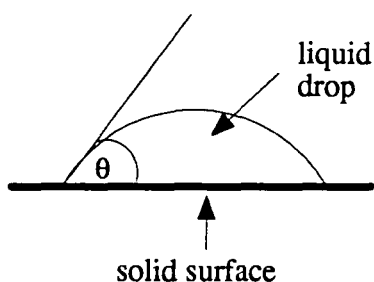
CHARACTERISATION OF TREATED FILMS

It is necessary to be able to quantify the effect of the treatments to which the films are exposed. In this work we have attempted to establish the effect of surface treatments on the films' surface free energies using contact angle measurements and on their elemental composition using ESCA. Tests for fouling propensity were carried out at BP Sunbury. Differential Scanning Calorimetry (DSC) was carried out on some untreated samples to determine the percentage crystallinity. This chapter sets out to describe the principles behind these methods of analysis, and their uses.

(a) Contact Angles

If a drop of a pure liquid is placed on a flat, solid surface, the drop surface will form a specific angle with the plane of the surface. This is known as the contact angle, θ .

Fig 4.1

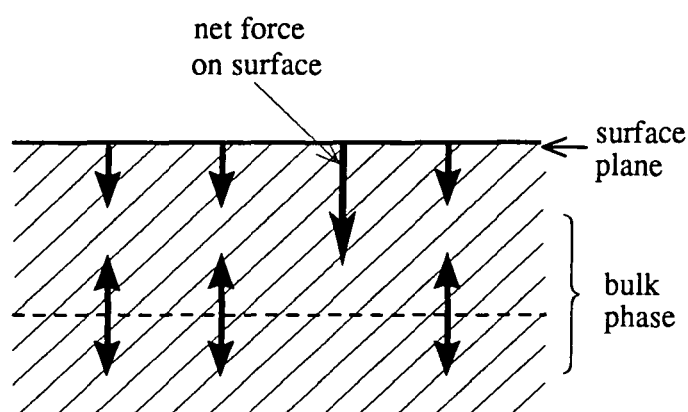


In order to understand how the contact angle relates to the surface free energy of a polymer film, it is first necessary to define what is meant by a surface. For the purposes of this work, a surface is considered to be a plane having a location and an area, but no volume. It is most useful to consider surface free energy changes in terms of the Helmholtz free energy, A , as all changes in the surface can take place at constant volume.

The properties of a surface differ from those of the bulk because surface

molecules are subjected to a different environment to bulk molecules. If we consider an isolated system, and imagine a hypothetical plane in the bulk, parallel to the surface, it can be shown that intermolecular forces on molecules in this plane cancel out, and that there is no net force in any direction on molecules in the bulk. It is evident that molecules in the surface plane will experience a net force downwards into the bulk, perpendicular to the plane.

Fig 4.2



This is the origin of surface energy. The excess force per unit length of a line in the surface is given the term "surface tension", γ . Surface tension can be related to surface energy as follows: by definition, the Helmholtz free energy, A , of a system is given by:

$$A = E - TS \quad (1)$$

where E is the total internal energy, T is the temperature of the system and S is the entropy. Hence a small change in the Helmholtz free energy, dA , is given by:

$$dA = dE - TdS - SdT \quad (2)$$

A small change in the total internal energy, dE , is given by:

$$dE = dq - dw + \sum_i \mu_i dN_i \quad (3)$$

where dq is a small heat input to the system and dw is work done by the system. If dV is a small change in volume of the system, and $d\Omega$ a small change in the surface area, (P is the pressure of the system), then

$$dw = PdV - \gamma d\Omega \quad (4)$$

since work can be done on the system by extending the surface against surface tension forces.

If $dq = TdS$, then

$$dE = TdS - PdV + \gamma d\Omega + \sum_i \mu_i dN_i \quad (5)$$

and

$$dA = \gamma d\Omega - PdV - SdT + \sum_i \mu_i dN_i \quad (6)$$

Surface tension can then be defined as

$$\gamma = \left(\frac{\delta A}{\delta \Omega} \right)_{V, T, N_i} \quad (7)$$

If two isolated surfaces (1) and (2) are put together across an interface, the surface tension at the interface, γ_{12} , will be less than the sum of the surface tensions of the isolated surfaces, γ_1 and γ_2 , due to intermolecular interactions between the two phases. This difference is termed the work of adhesion, w_a (equation 8).

$$w_a = \gamma_1 + \gamma_2 - \gamma_{12} \quad (8)$$

Fowkes³³ suggested that the work of adhesion between two phases across an interface is given by a simple summation of that due to each type of intermolecular interaction.

$$w_a = w_a^d + w_a^h + w_a^p + \dots \quad (9)$$

where the superscripts represent dispersion forces, hydrogen bonding and polar (dipole-dipole) interactions. Fowkes also suggested that the only significant interactions across an interface are those which are common to both phases, and that since dispersion forces are the only interactions common to all materials, w_a^d

is likely to be the dominant term.

$$w_a \approx w_a^d \quad (10)$$

Using a geometric mean approximation, this gives

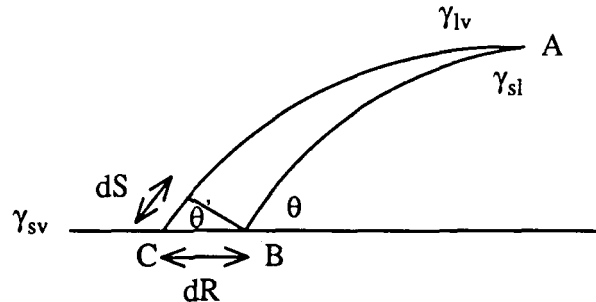
$$w_a^d = 2(\gamma_1^d \gamma_2^d)^{\frac{1}{2}} \quad (11)$$

for the work of adhesion due to dispersion forces alone. This gives

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{\frac{1}{2}} \quad (12)$$

To relate the contact angle to surface tension forces, we can consider what happens if a liquid drop in equilibrium on a planar surface undergoes a virtual displacement from the equilibrium position.³² For such a displacement, $\delta A = 0$.

Fig 4.3



where the subscripts lv, sv and sl denote the liquid-vapour, solid-vapour and solid-liquid interfaces. If $(\delta A)_i$ is the change in Helmholtz free energy of the system for a particular interface due to a change in the interfacial area, then

$$(\delta A)_i = -dw = \gamma_i d\Omega_i \quad (13)$$

and

$$\delta A = (\delta A)_{sv} + (\delta A)_{sl} + (\delta A)_{lv} \quad (14)$$

If the edge of the drop (the base of which is assumed to be a circle of radius R) is displaced from B to C so that the periphery of the drop becomes AC (from AB) then the change in energy is given by

$$\delta A = -2\pi R dR \gamma_{sv} + 2\pi R dR \gamma_{sl} + 2\pi R dS \gamma_{lv} \quad (15)$$

Since dS is equal to $dR \cos \theta'$ then

$$\delta A = 2\pi R dR (-\gamma_{sv} + \gamma_{sl} + \gamma_{lv} \cos \theta') \quad (16)$$

At equilibrium, $\delta A = 0$ and $\theta' = \theta$, so that

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \quad (17)$$

This is known as the Young-Dupré equation. Combining this with equation (12) gives

$$\cos \theta = \frac{2(\gamma_s^d \gamma_l^d)^{\frac{1}{2}}}{\gamma_{lv}} - \frac{\gamma_l}{\gamma_{lv}} \quad (18)$$

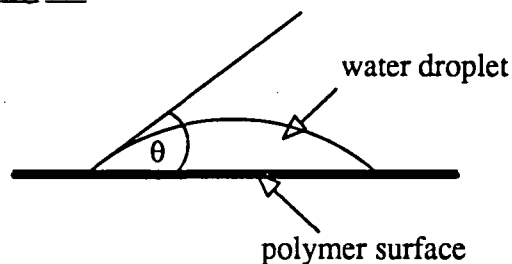
Since adsorption of its own vapour will not alter the surface energy of a liquid, $\gamma_l = \gamma_{lv}$ so that

$$\cos \theta = \frac{2(\gamma_s^d \gamma_l^d)^{\frac{1}{2}}}{\gamma_l} - 1 \quad (19)$$

In this work, contact angles have been measured with distilled water to give an indication of the water wettability of the treated polymer surfaces. Surfaces can be loosely classified as hydrophilic or hydrophobic.

(i) If $0 < \theta < 90^\circ$, the surface is said to be hydrophilic. If $\theta = 0$, complete spreading has taken place and the surface is completely wettable (Fig 4.4).

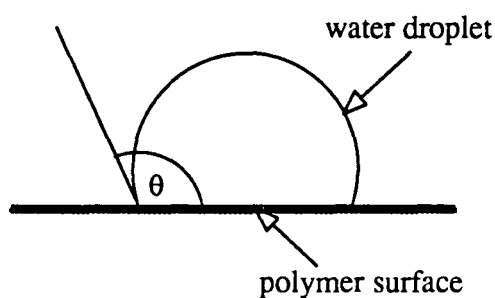
Fig 4.4



(ii) If $90^\circ < \theta < 180^\circ$, the surface is said to be hydrophobic; the water

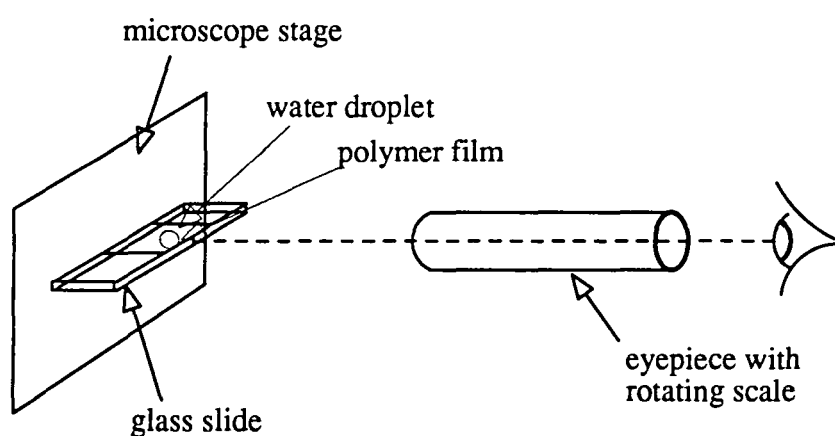
droplet tends to shrink away from the surface in order to minimise unfavourable interactions (Fig 4.5).

Fig 4.5



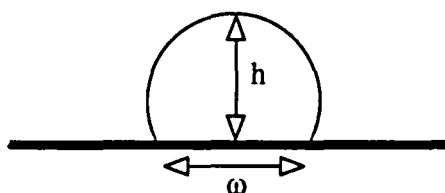
There are several methods used for measuring contact angles. In this work, the contact angle was calculated from the relative drop dimensions. The calculation assumes the polymer surface to be planar, and the water droplet to be a truncated sphere. A sample of the polymer film is fixed to a glass slide with a drop of water and a $2\mu\text{l}$ drop placed on the edge of the sample surface using a syringe. The slide is placed on the platform of a horizontal microscope with the water droplet nearest the eyepiece (Fig 4.6).

Fig 4.6



An eyepiece with rotating scale enables measurement of the relative height, h and base width, ω of the drop (Fig 4.7).

Fig 4.7



The contact angle is calculated as follows:

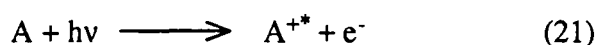
$$\tan\theta = \frac{2h}{\omega} \quad (20)$$

θ can be measured to an accuracy of $\pm 1^\circ$ to $\pm 2^\circ$ using this method.

(b) ESCA

(Electron Spectroscopy for Chemical Applications)

ESCA operates by irradiating the surface of a sample with a monoenergetic beam of X-rays and measuring the kinetic energies of ejected photoelectrons. The difference allows the computation of the electron binding energies.



where A is an atom of any element and * denotes an excited state.

All electrons from valence to core levels can be studied, and all elements except hydrogen and helium. In ESCA, the emphasis is on the study of core electrons, since these are localised on the atoms and have binding energies characteristic of a given element. The core levels also monitor closely the valence electron distribution, although they do not take part in bonding.

Equipment³⁵

An ESCA spectrometer consists of the following:

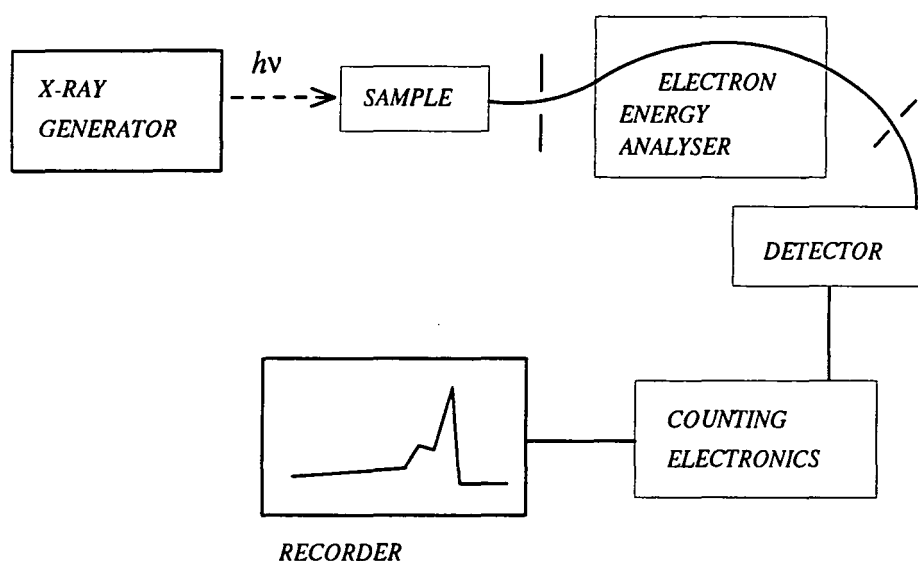
- (i) an X-ray generator and monochromator;

- (ii) a vacuum chamber: a high vacuum is required in order to prevent electrons from being scattered as they pass from the analyser to the detector. The chamber is evacuated to 10^{-7} torr or less by oil diffusion pumps backed by two-stage rotary oil pumps. Prepumped insertion locks and valves are used to introduce a sample, mounted on a probe, from the atmosphere into the spectrometer chamber.
- (iii) the photoelectrons are guided into an electron analyser. This produces signals which can be fed into a detector and amplifier, and from there to a computer for further processing of results.

A spectrum takes about ten minutes to record for a typical example.

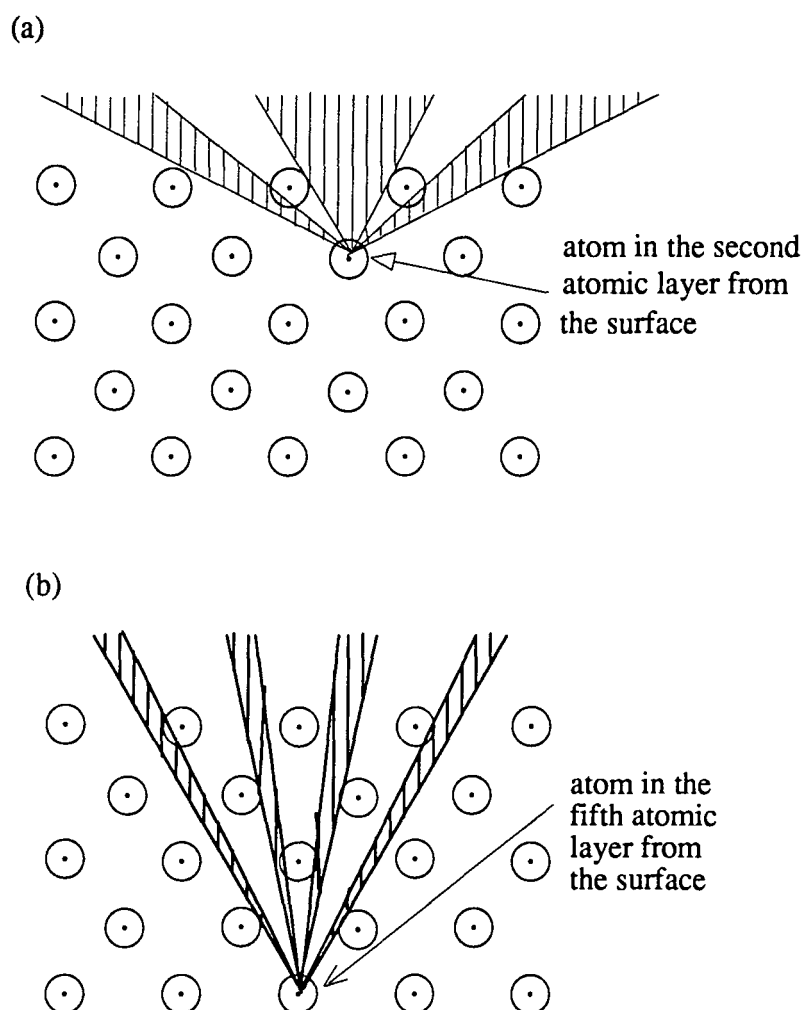
Fig 4.8

ESCA SPECTROMETER



ESCA is a surface technique, since atoms closer to the surface of the sample give a larger fraction of an ESCA signal than those further down in the bulk. This can be rationalised as follows:

Fig 4.9



Shaded areas indicate paths which a photoelectron can take without being scattered by atoms in the lattice. An electron ejected from an atom in the second atomic layer below the surface (Fig 4.9a) has a much greater probability of reaching the surface than one ejected from an atom in the fifth atomic layer from the surface (Fig 4.9b), since it has a greater number of paths which it can take without passing close to an atom in the lattice. The sampling depth is generally in the range 5\AA to 50\AA , but depends on the energies of the incident X-ray photon and emitted electron, and on the take-off angle.

Information Obtainable

Signals can be obtained from all elements except hydrogen and helium, and

as signal intensities from all elements are of approximately the same order of magnitude, the same level of sensitivity can be used for all elements.

Relative intensities of signals can be used to measure relative concentrations of elements present in the surface, with multiplication by a sensitivity factor derived from the spectra of homogeneous samples.

Chemical shifts are observed, hence peaks can be correlated with oxidation state and atomic charge, giving information about the chemical binding state of an element. Relative concentrations of different oxidation states can be obtained from peak intensities.

In this work we used a Kratos ES-200 instrument, MgK α , at 10^{-7} torr, and a take-off angle of 35° , giving a sampling depth of $\sim 35\text{\AA}$ for carbon.

(c) Tests for Fouling Propensity

Fouling propensities with bovine serum albumin were determined at BP Research Centre, Sunbury. The method involves spinning discs of the polymer under test in a standard solution of radio isotope labelled protein. The extent of fouling is then determined in a counter and presented as a number on an arbitrary scale. All aspects of the test: size of disc, mounting, spinning speed, extent of isotopic label, depth and concentration of solution, are rigorously standardised and so samples can be confidently compared.

(d) Differential Scanning Calorimetry (DSC)

When a material undergoes a physical or chemical change, for example melting or decomposition, a change in enthalpy is observed. This is the basis of Differential Scanning Calorimetry.

DSC was used in this research to determine the percentage crystallinity of two different polyethylene samples.

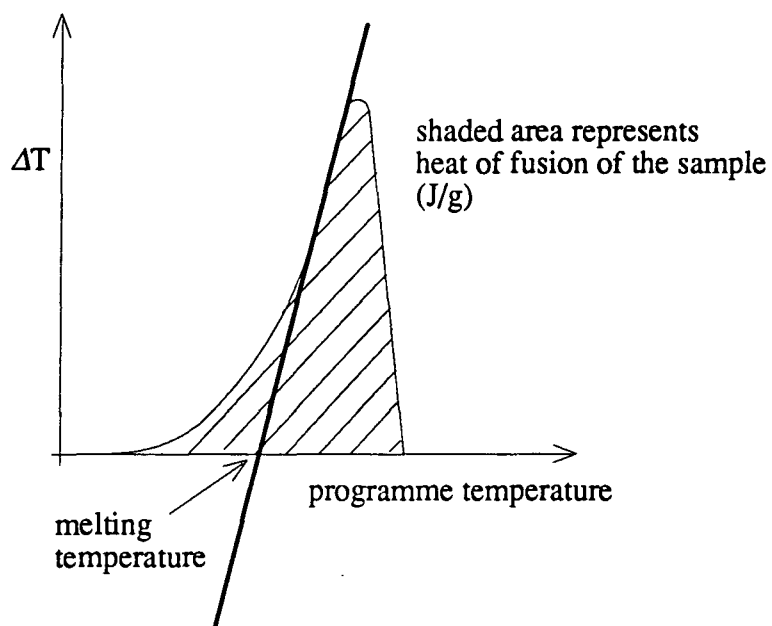
In DSC, a sample and a reference material are maintained at the same

temperature throughout a controlled temperature programme, in which the temperature of the sample and reference is changed at a constant rate. If the sample undergoes an endothermic or exothermic change, the energy supply to the sample or reference is increased by independent heating sources in order that both remain at the same temperature. Differences between the amount of electrical energy supplied to the sample and reference are recorded as a function of the programme temperature.

For this work, a Perkin-Elmer DSC7 instrument was used. The sample and reference material are contained in platinum sample holders within aluminium sample pans (provided that the programme temperature does not exceed 500°C) The sample pans used have lids which can be crimped on using a purpose-built press. The sample is weighed before recording the DSC by subtracting the mass of the empty sample pan from that of the filled sample pan. Generally, 3-8mg of material are used. Samples are usually in the form of a powder or small pieces of film if solid. DSC may also be recorded for samples in liquid form.

A wide range of information can be obtained about a material using DSC³⁴. In this work, we determined the melting temperature and the enthalpy of fusion, which allows computation of the percentage crystallinity of a material.

Heat of fusion (per gramme of polymer) was computed by integrating the area of the melting peak (Fig 4.10).

Fig 4.10

The melting temperature is found by drawing a line through the steepest point on the forward edge of the melting peak and extrapolating it to the temperature axis (Fig 4.10). The percentage crystallinity is calculated as the ratio of the heat of fusion (J/g) of the sample to that of a 100% crystalline material. An indication of the purity of the sample can be obtained from the melting range.

Chapter 5

EXPERIMENTAL WORK

Introduction

This chapter sets out to describe the experimental work done during this research project, and to discuss the results obtained. It is divided into six sections as follows:

1.The Grafting Procedure and Experimental Set-up

2.UV-Irradiation of Polyethylene Films

3.Grafting of Poly(acrylic Acid) onto Polyethylene

4.Grafting of Poly(HEMA) onto Polyethylene

5.Grafting of Poly(HEMA) onto Ultem Film

6.Grafting of Poly(HEMA) onto Ultem Membrane

7.Overall Conclusions

Section 1.

The Grafting Procedure and Experimental Set-up

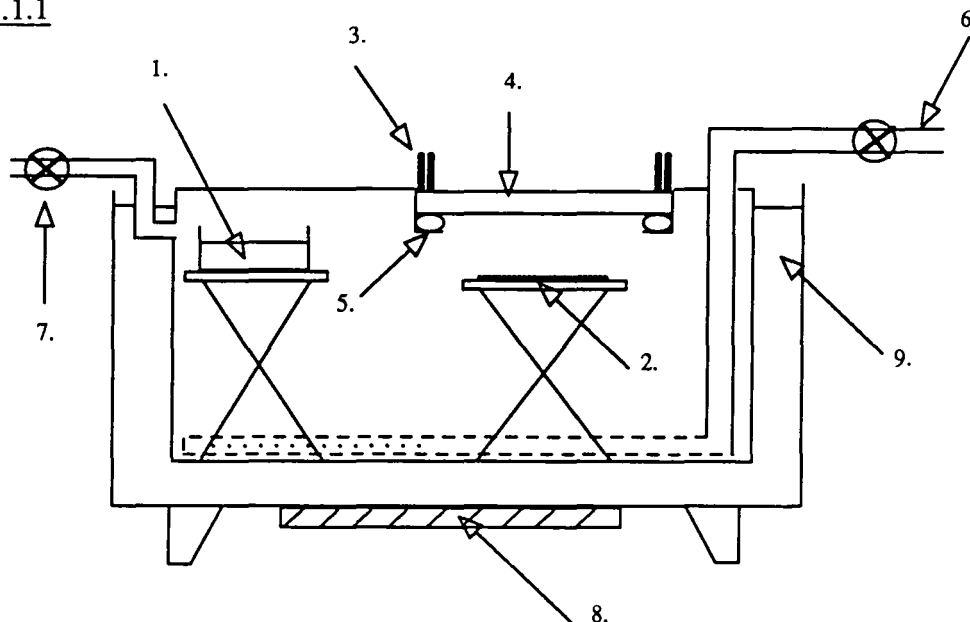
The Experimental Set-up

The vapour phase photografting technique developed by Rånby *et. al.*²⁹ has been adapted and used throughout this research project. The photografting cabinet in which the reactions have been carried out was made in the Chemistry Department workshops at Durham, and is adapted from that shown in a paper by Allmér, Hult and Rånby⁹ (see Fig.5.1.1).

It should be noted that grafting has followed a "learning curve" during this research, so the grafting procedure described here is that which was finally arrived at towards the end of the work after numerous modifications of the procedure followed at the start of the work. Any differences with respect to the procedure outlined here will be noted in the relevant sections of this chapter.

The photografting cabinet is made from sheet steel, and incorporates a quartz or Pyrex window. The cabinet is sealed to air by placing a sheet of quartz or Pyrex (quartz was used for all grafting work) on a ring of butyl rubber tubing, and weighing down with lead.

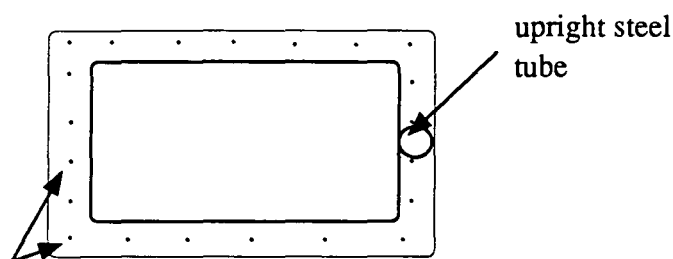
Fig 5.1.1

Key:

1. solution of sensitiser and monomer
2. polymer film to be grafted
3. lead weights
4. quartz (or Pyrex) window
5. airtight seal (butyl rubber tubing)
6. nitrogen inlet
7. nitrogen outlet
8. 9kW bar heater
9. water bath

The nitrogen inlet is connected to a supply of dry, high quality nitrogen and comprises a ring of perforated steel tube connected to an upright. (See Fig.5.1.2)

Fig 5.1.2 Plan View of Nitrogen Inlet



perforations

This allows entry of nitrogen over the whole perimeter of the cabinet, ensuring that it can be evenly purged. The cabinet is surrounded by a water bath which is heated by a 9kW bar heater welded to the underside of it. The heating circuit incorporates a contact thermometer, enabling the temperature to be controlled within $\pm 1^{\circ}\text{C}$ in the range 0° to 100°C .

The Grafting Procedure

The sample to be grafted is placed in the photografting cabinet, beneath the quartz window, with a crystallising dish containing a solution of vinyl monomer (2M) and benzophenone sensitiser (0.2M) in acetone. The solution is placed in the shaded half of the cabinet and shielded from UV radiation by wrapping the dish in aluminium foil. Dissolved oxygen is first removed from the solution by bubbling dry, high quality nitrogen through it for ten minutes before use.

The cabinet is then sealed as described earlier, purged with nitrogen for 45 minutes, heated to the required temperature by the surrounding water bath, allowed half an hour to equilibrate and irradiated for the required time through the quartz window. The lamp used throughout the work was a Hanovia UVS 1000 ultraviolet lamp.

Polymer samples were washed before grafting, to remove any dirt or grease which would prevent grafting onto the surface, and afterwards to remove homopolymer. Methods of cleaning vary according to the nature of the polymer in question, so these will be detailed in the relevant sections.

Grafted samples were characterised by some or all of the techniques

detailed in Chapter 4 (excluding DSC, which was used to characterise polyethylene prior to grafting).

Section 2.

UV-Irradiation of Polyethylene Films

These experiments were carried out in order to establish the validity of the analytical procedures used, and the suitability of the reaction cabinet. To this end, samples of polyethylene were irradiated under a variety of experimental conditions, and the effect on the surface character monitored by contact angle measurements with water, and by ESCA.

Experimental Details

At this stage of the work, the cabinet was sealed by placing the quartz or Pyrex window on a ring of "Weathershield" (an expanded domestic foam sealant) covered with a layer of vacuum grease and weighed down with lead. This was found to give a reasonably good seal when the system was put under positive pressure of nitrogen, but retrospectively, it is believed that this may have allowed a very slow leakage of oxygen into the system. (See Section 3.)

Samples of a high density polyethylene film were cleaned in "Micro" (a laboratory detergent solution) for 2-3 hours, rinsed in methanol then dried overnight in a desiccator over phosphorus pentoxide before irradiation. The origin and specification (provided from Stock in the ESCA laboratory by Mrs. S. Walker) of the film was unknown, therefore an attempt was made to characterise it with respect to crystallinity using Differential Scanning Calorimetry (DSC) (see appendix 1). It was found to be highly crystalline (54% crystallinity) with a melting point of 132°C. The percentage crystallinity was calculated assuming a heat of fusion value of 290J/g³⁴ for a 100% crystalline sample.

The samples were irradiated for one hour, at a distance of 0.4m from the lamp, under the following conditions:

- (i) in air, with no filter
- (ii) in air through quartz
- (iii) in air through Pyrex
- (iv) in nitrogen through quartz
- (v) in nitrogen through Pyrex

The irradiated samples were characterised by measuring the contact angle with water, and by ESCA, and were compared to a reference sample. Experimental data for these experiments can be found in Appendix 2.

The largest change in the contact angle with water was observed when the film was irradiated in air with no filter, which resulted in a decrease from 99° to 90°. The next largest decrease was observed when the film was irradiated in air through quartz; small decreases were observed for irradiation in air through Pyrex and in nitrogen through quartz, and no change was observed when samples were irradiated in nitrogen through Pyrex.

Due to temporary problems with the ESCA spectrometer, ESCA spectra are available only for films irradiated in air. Surprisingly, oxygen to carbon ratios calculated from the spectra show a decrease in oxygen content of the surface on irradiation.

Discussion

Since the UV absorption bands due to C-H and C-C bonds occur below 200nm³¹, and Pyrex cuts off at ~300nm⁴ no photo-processes involving these bonds are possible when polyethylene is irradiated through a Pyrex filter, but with quartz, which cuts off at 150nm³⁸ direct excitation is possible but unlikely in practice since the lamp is operating in air, which will absorb significantly at short wavelengths, and the UV output of the mercury lamp is negligible below 200nm.

Oxygen absorbs at wavelengths below 200nm, dissociating to form atoms
(5.2.1)



The atoms can recombine or react with further oxygen to form ozone
(5.2.2)



Ozone absorbs weakly in the visible region at $\sim 600\text{nm}$ and strongly in the ultraviolet region at 320nm . Both absorptions result in dissociation (5.2.3)



Hence for C-C and C-H absorption to occur, it would be necessary to exclude oxygen from the radiation path. Absorption of radiation by ozone would not be expected to interfere with photo-oxidation of polyethylene; but, of course, ozone is an oxidant (chapter 2.).

Charlesby and Partridge³⁷⁻⁴² found polyethylene displays phosphorescence bands in the region $450\text{-}500\text{nm}$. These were believed to be caused by carbonyl groups, occurring mainly as aldehydic groups located at chain ends. A fluorescence band was also observed at 375nm , again due to carbonyl functions. Both quartz and Pyrex will transmit wavelengths which can be absorbed by these functionalities, so in principle, photo-processes can occur when polyethylene is irradiated through both filters.

It was concluded from these experiments that irradiation in air with no filter has the greatest impact on the contact angle, irradiation through quartz the next largest effect and irradiation through Pyrex the least, which is consistent with reasonable expectation. Irradiation of polyethylene through both filters when the cabinet was purged with nitrogen resulted in no significant reduction in contact angle, again consistent with reasonable expectation.

The apparent contradiction between contact angle measurements, which indicated an increase in surface wettability after irradiation and the ESCA measurements which appeared to indicate a decrease in oxygen, ie. a decrease in hydrophilic groups, may be explained by at least two possibilities. Firstly, by

considering the physical conditions under which ESCA spectra are recorded (chapter 4.), namely, very low pressure, under these conditions relatively low mass oxidised fragments may evaporate, reducing the surface oxygen content. Alternatively, it is established that wettability attained via surface oxidations used to modify polymers for printing decays with time due to oxidised chain fragments migrating into the bulk, and under our experimental conditions the temperature may have been high enough to allow this to happen.

These experiments were conducted to familiarise the author with the use of the equipment and techniques. The results obtained were reproducible and could be rationalised, giving confidence in the methods and techniques adopted.

Section 3.

Grafting of Poly(Acrylic acid) to Polyethylene

These experiments were carried out in order to establish the suitability of the reaction cabinet for grafting. It has been shown by Allmér, Hult and Rånby that it is possible to graft poly(acrylic acid) onto polyethylene.⁹ This section is a repeat of some of the experiments carried out by Allmér, Hult and Rånby.

Grafted samples were characterised by contact angle measurements with water.

Experimental

Low density polyethylene was used, taken from new polyethylene bags supplied by Beveridge. The films have been characterised by DSC (appendix 1) and found to have a lower % crystallinity (32%) than the samples used in section 2 of the work. A less crystalline sample was used for grafting work as it had been reported⁹ that surface grafting was less successful on a highly crystalline sample. Films were extracted in toluene at 60°C in order to remove low molecular weight fractions and processing contaminants, then rinsed in acetone and ethanol and

dried in a vacuum oven (25°C, 0.05mm Hg) overnight before use.

Acrylic acid (Aldrich) was purified by vacuum transfer before use in order to remove inhibitor (hydroquinone monomethyl ether). Benzophenone was used as received after checking purity by measuring the melting point and recording the infrared spectrum. Acetone (May & Baker, Analar) was also used as received.

Procedure

The films to be grafted were placed in a reaction cabinet with a crystallising dish containing a solution of 2M acrylic acid and 0.2M benzophenone in acetone, as shown in Section 1, figure 1.

The solution was shielded from UV by wrapping the dish in aluminium foil. Dissolved oxygen was removed from the solution by bubbling high quality nitrogen through it for ten minutes before use. The grafting procedure was modified twice during this section of the work (methods 1,2 and 3).

Method 1

The cabinet was sealed, heated to 60°C by the surrounding water bath, purged with nitrogen for 30 minutes, and irradiated through the quartz window. The lamp to sample distance was varied between 20 and 40cm.

Method 2

The same procedure was followed, but the seal on the cabinet was changed from "Weathershield" to a ring of butyl rubber tubing as described in section 1. The vacuum grease was omitted. Samples were irradiated at a distance of 20cm from the lamp surface.

Possible disadvantages of methods one and two were considered to be that:

- (i) at the start of irradiation, the atmosphere in the cabinet would not be filled with acrylic acid and benzophenone vapour, since any evaporated solution would be carried out of the cabinet during purging with nitrogen;
- (ii) as the reaction cabinet was heated before purging with nitrogen, evaporation and removal of acrylic acid/benzophenone vapour would be substantial during

purging, hence the procedure was re-ordered:

Method 3

The cabinet was sealed and purged with nitrogen for 30 minutes, then heated to the required temperature (60°C for grafting with acrylic acid), allowed half an hour to reach an equilibrium vapour pressure and irradiated through the quartz window.

The treated films were extracted with aqueous 0.1M KOH at 60°C for 30 minutes then washed in 0.05M aqueous HCl at room temperature for another 30 minutes to remove homopolymer formed during grafting. The films were dried in a vacuum oven at room temperature overnight before characterisation by contact angle measurements with water. The treated samples were compared to a reference sample which was washed as described above but not irradiated. (See appendix 3 for experimental data.)

In spite of its shortcomings, characterisation of films grafted following method one showed that a decrease in the lamp to sample separation, and an increase in the time of irradiation resulted in a decrease in the contact angle with water. Decreasing the lamp to sample separation from 40 to 20cm decreased the mean contact angle from 86° to 59° for an irradiation time of 2 hours, and an increase in the irradiation time from 30 minutes to two hours decreased the contact angle from 91° to 59° at a lamp to sample separation of 20cm. These results are consistent with reasonable expectation in as much as a lower contact angle indicates increased grafting.

Films grafted following method two showed a steady increase in contact angle as a function of time, up to an irradiation time of three hours. Surprisingly, improving the quality of the seal on the box did not appear to improve the extent of grafting as indicated by contact angle measurements with water. A film was then irradiated for two hours following method 3. No significant decrease in the contact angle was observed initially, however, the contact angle was considerably reduced by heating in distilled water (from 70° to 55°). It seems probable that the grafted

surfaces could have reversibly lost their wettability during storage in the vacuum oven due to the grafted polymer chains migrating into the surface layers of the polyethylene film, or that the surface temperature during grafting was high enough to allow mobility. The hydrophilic surface was regained when immersed in hot water due to interaction of the grafted chains with water. These latest results suggest that it is possible that earlier experiments were also successful, but that the grafts "buried themselves" in the hydrophobic surface. These observations are self consistent and indicate a degree of mobility in the surface layers of the original polymer and the grafted material. It is reasonable that, if mobility allows, a heterogeneous system will organise itself to present as low a surface energy as possible when exposed to dry air.³²

Section 4

Grafting of Poly(HEMA) onto Polyethylene

As in section 3, low density polyethylene was used for these experiments. Before use, the films were extracted in toluene at 60°C for five minutes then rinsed in acetone and ethanol and dried in a vacuum oven (25°C, 0.05mm Hg) overnight before use.

Hydroxyethyl methacrylate (HEMA) (Aldrich) was purified by vacuum distillation (53°C, 7×10^{-2} mm Hg) in the presence of cuprous chloride then stored in a freezer at -15°C. Cuprous chloride was prepared by reducing cupric chloride (appendix 4). Benzophenone (Aldrich, 99%) was used as received after checking purity by measuring the melting point and recording the infrared spectrum. Acetone (May & Baker, Analar) was also used as received.

The grafting procedure followed was as for section 3, method 3. Samples were irradiated for two and three hours and characterised by contact angle measurements with water. A small reduction in contact angle (17-23°) was observed, the change being largest for the sample irradiated for 3 hours (appendix 5). After heating in distilled water at 60°C for 5 minutes, a further reduction in

contact angle (6°) was observed for the sample irradiated for two hours, but not for that irradiated for three hours.

In order to compare the difference in contact angle between the graft onto polyethylene and the pure homopolymer, poly(HEMA), a sample of poly(HEMA) was prepared as follows: a 2mm thick layer of inhibitor-free HEMA (purified as for grafting) was poured onto a teflon sheet, bent upwards at the edges to form a tray. The tray was placed 20mm away from the surface of the UV lamp, in the reaction cabinet and irradiated through the quartz window for one hour. The product was placed in a vacuum oven at room temperature overnight to evaporate any remaining free monomer, then rinsed with methanol and replaced in the vacuum oven for a further hour.

The polymer formed was soft (easily scratched), but fairly stiff and readily handled. The mean contact angle with water (taken from six measurements) was 43° with a standard deviation of 2° .

It can be concluded from these experiments that although the graft has been successful to a certain extent, it has not yet reached anything approaching a complete grafted layer. However, since the time remaining was fairly short, it was decided to proceed to section 5 of the work, since the object of the research was to graft onto Ultem.

Section 5

Grafting of Poly(HEMA) onto Ultem Film

Films of Ultem were prepared as follows: Ultem (in pellet form, supplied by BP) was dried overnight in a vacuum oven at 40°C , 0.1 atm., then dissolved in dichloromethane to give a 20 % solution. Dichloromethane was purified by repeated washing with conc. sulphuric acid until the acid layer remained colourless; then with distilled water, followed by a 5% solution of sodium carbonate, then with water again, followed by drying over anhydrous calcium chloride and finally distilling from phosphorus pentoxide. The films were cast

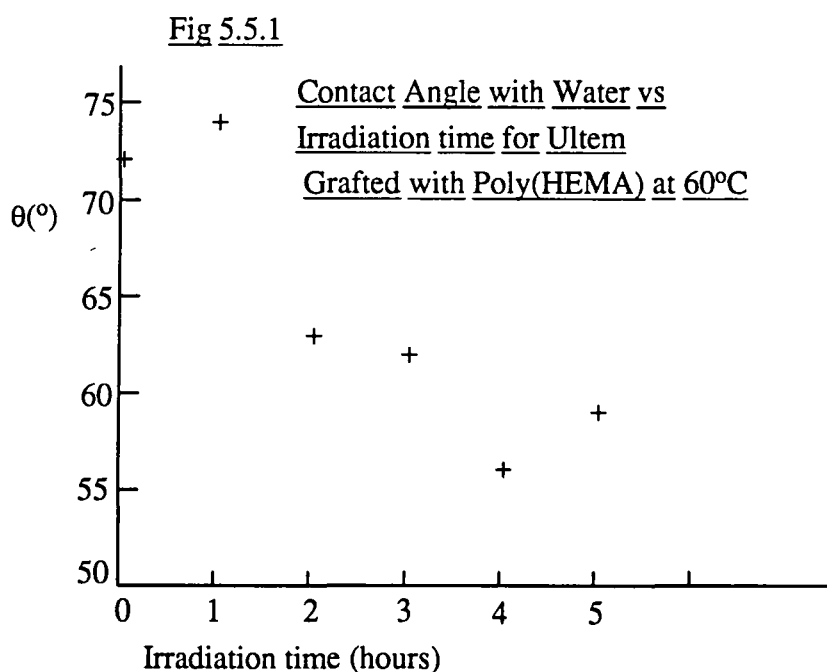
using a film former with a 200 μ m blade. Details of the casting process can be found in appendix 6. The films were washed before and after treatment, first in methanol at 60°C for ten minutes then in distilled water at room temperature for 30 minutes, followed by drying for several hours under reduced pressure (8×10^{-2} atm.)

HEMA was purified as described in section 4. Acetone (May & Baker, Analar) was purified by shaking for several hours with anhydrous calcium sulphate then decanting and distilling at room temperature through Linde type 4A molecular sieves.

Experimental data for this section can be found in appendix 7.

Grafting proceeded as described in section 4. Samples were irradiated for 1,2,3,4 and 5 hours. Characterisation was by contact angle measurements with water, and some of the samples were tested for fouling propensity.

The contact angles are summarised in Fig 5.5.1.

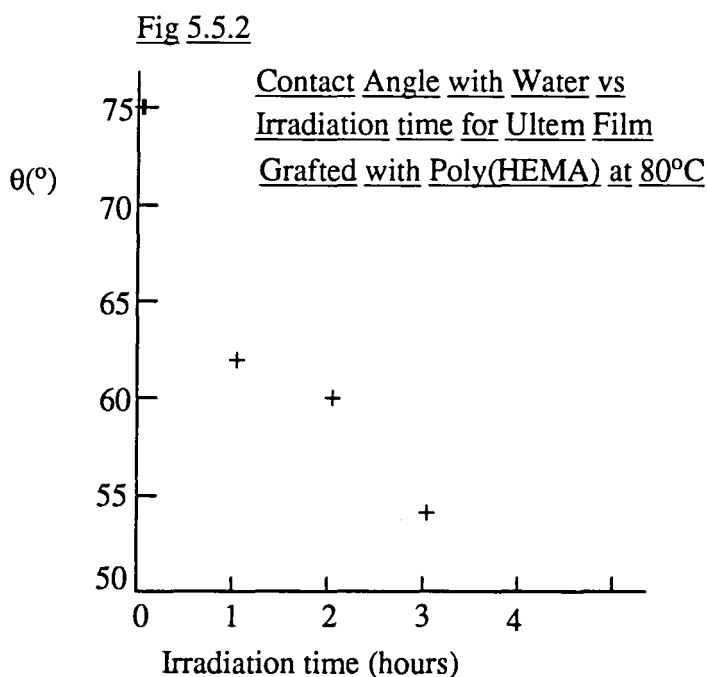


No line or curve has been drawn through the points since the relationship between contact angle and irradiation time is not known, and the author has not been able to construct a convincing mathematical model for what is a complex multistep process. The contact angle appears to reach a minimum after 3-4 hours, which is a

practically useful result.

The samples grafted for 4 and 5 hours were tested for fouling propensity. These were given as 22 and 14 units respectively, compared to a value of 40 to 50 units for an unmodified sample. This shows that grafting has considerably reduced fouling propensity, and that a longer time of irradiation has resulted in a larger decrease in the fouling propensity.

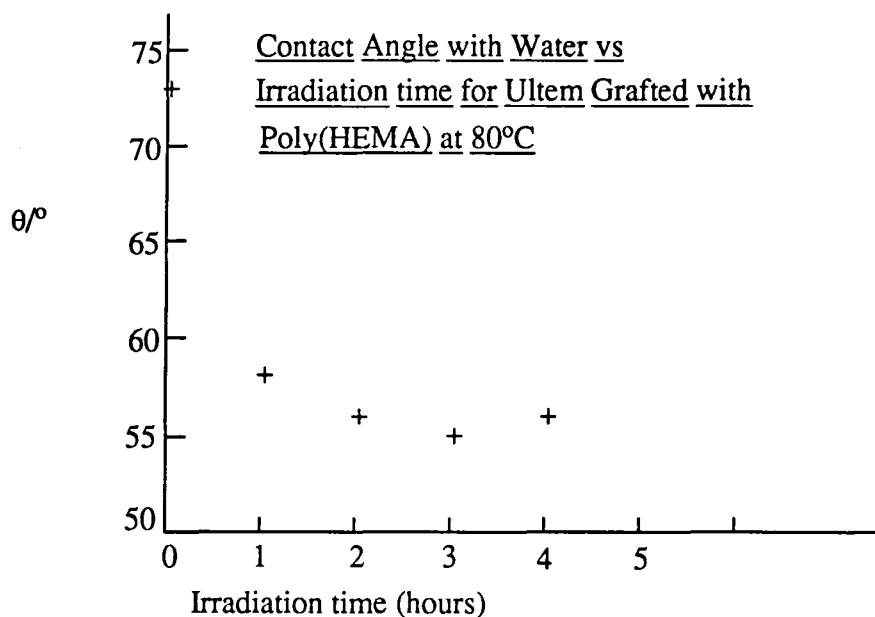
The temperature at which samples were grafted was increased to 80°C and samples irradiated for 1,2 and 3 hours (Fig. 5.1.2).



It appears from these results that grafting proceeds more quickly at the higher temperature as the contact angle falls much more quickly to a lower value. The sample grafted for three hours was tested for fouling propensity, and a value of 19 units was given, lower than for the sample grafted for four hours at 60°C.

At this stage the time during which the cabinet was purged with nitrogen was increased from 30 to 45 minutes. Samples were grafted for 1,2,3 and 4 hours at 80°C and characterised by contact angle measurements with water and by ESCA. The contact angles are summarised in Fig 5.5.3.

Fig 5.5.3

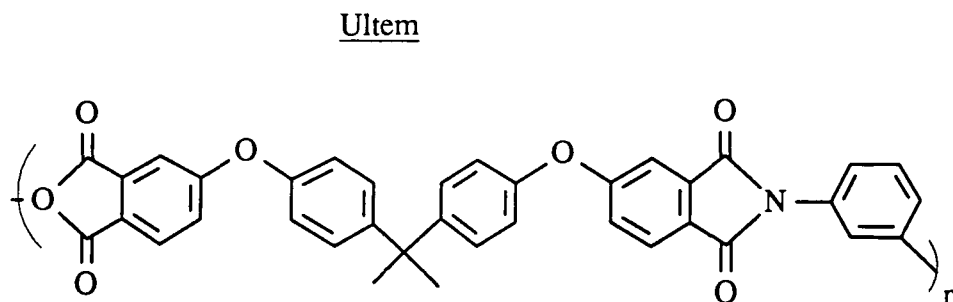


This appears to be beneficial to the grafting process, since a low contact angle (58-56°) is achieved after a shorter time. The form of the curve is much less ambiguous in this case showing a rapid decrease to a plateau value.

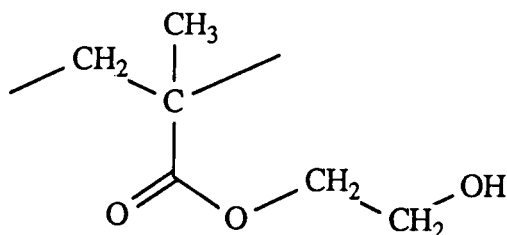
ESCA spectra were recorded for C1s, O1s and N1s electrons, and the amount of each element calculated as a percentage of the sum of carbon, nitrogen and oxygen. The relative amounts were compared to those calculated from the formula Ultem and poly(HEMA).

The structure of the repeating unit in Ultem is shown in Fig. 5.5.4.

Fig 5.5.4



This gives carbon : nitrogen : oxygen = 82.2:4.4:13.3. For poly(HEMA) the ratio is 66.7:0:33.3 as calculated from the structure of the repeat unit (Fig 5.5.5).

Fig 5.5.5Poly(HEMA) Monomer Residue

Hence we would expect that as the irradiation time is increased, the percentage graft will also increase; that the %C will decrease, %O will increase and %N will decrease. There are a few anomalies but generally, this is the case (see appendix 7).

Fouling propensities were given as 19 for the 1, 2 and 3 hour grafted samples and 23 for the sample grafted for 4 hours, compared to a value of 45 for an unmodified sample. Although these results do not decrease with increase in irradiation time, they do show that grafting has lowered the fouling propensity.

Conclusions

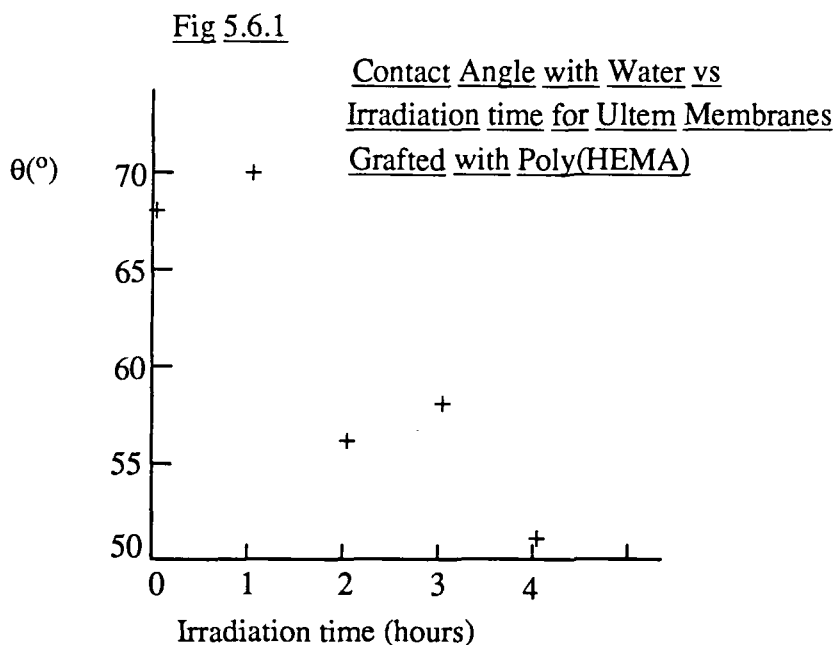
We can conclude from this part of the work that

- (a) it is possible to graft poly(HEMA) onto Ultem using this technique;
- (b) that the speed of grafting increases with temperature up to 80°C;
- (c) that the fouling propensity of Ultem is decreased by grafting of poly(HEMA) onto the surface and that
- (d) grafting is more successful when the system is thoroughly purged. One attempt to graft poly(HEMA) onto Ultem was unsuccessful when the nitrogen supply failed whilst purging the reaction cabinet. In fact measurement of the contact angle with water showed an increase from 82° to 92°, providing further evidence that the grafting process is inhibited by the presence of oxygen.

Section 6

Grafting of Poly(HEMA) onto Ultem Membrane

Ultem membrane was provided by BP Sunbury. Before and after grafting, membranes were washed in methanol at room temperature for 30 minutes and dried under reduced pressure (8×10^{-2} atm) for several hours. Membranes were grafted following the procedure described in section 5. The reaction cabinet was purged with nitrogen for 45 minutes beforehand and all reactions took place at 80°C . All experimental results for this section can be found in appendix 8. Samples were grafted for 1,2,3 and 4 hours. The results are summarised in Fig 5.6.1.



Calculations from ESCA spectra showed decreases in %C, increases in %O and decreases in %N successively with increase in irradiation time.

The grafted membranes, with the exception of that grafted for one hour, were tested for fouling propensity. Values of 26, 16 and 26 units were given for membranes grafted for 2,3 and 4 hours respectively, compares to a value of 31 for ungrafted membrane. Another membrane sample was grafted for 4 hours under the same conditions as previously. A contact angle of 43° was observed for this, with a fouling propensity of 16 units. ESCA spectra were not recorded for this sample.

We can conclude from contact angle measurements and ESCA results that

poly(HEMA) has been grafted onto Ultem membrane. Tests for fouling propensity have shown that the graft has a beneficial effect on the membranes with respect to reduction of fouling by proteins

Section 7

Overall Conclusions

The concepts discussed in the introductory sections of this thesis have been tested and established. In summary, it has been shown that the vapour-phase photografting technique developed by Rånby can be used to graft the water-compatible poly(HEMA) onto Ultem for both solid films and membranes. The process of grafting HEMA onto Ultem has a marked and beneficial effect on the hydrophilicity and the protein-fouling propensity of the surface. However, much work remains to be done.

Chapter 6

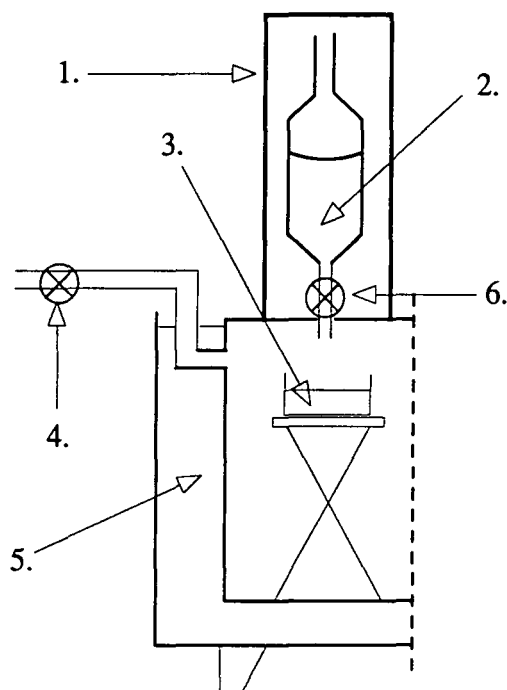
Suggestions for Further Work

Suggested Modifications to Grafting Setup

It has been observed that when poly(HEMA) is grafted to Ultem, the contact angle with water reaches a fairly constant value after 4-5 hours of irradiation (chapter 5, section 5). This is higher than the contact angle measured on the surface of pure poly(HEMA), suggesting that a complete grafted layer cannot be achieved using the present set-up. A possible cause of this is that after 4-5 hours, there is no more HEMA remaining to be evaporated from the solution. After 5 hours the crystallising dish which contained the grafting solution was found to contain only solid poly(HEMA). This could possibly be remedied by using a larger amount of grafting solution at the start of the experiment. However, a better solution to this would be to drill a hole in the shaded half of the cabinet and fit a tube connected to a stock solution of HEMA and benzophenone so that the solution in the crystallising dish is constantly replenished. The stock solution should be shaded from UV radiation by covering it with a box covered in aluminium foil (Fig 6.1). This ensures that the reaction chamber always contains unpolymerised HEMA.

At 80°C these grafting experiments were conducted well above the boiling point of acetone (56°C), the "carrier" solvent; while the higher temperature clearly will aid transport of benzophenone and monomer to the grafted surface, it seems that the influence of alternative carrier solvents would be worth investigating.

Fig 6.1



Key

1. box covered in black, UV-absorbing paper so that UV irradiation will not reach the stock solution of HEMA and benzophenone
2. stock solution of HEMA and benzophenone
3. crystallising dish containing a solution of HEMA and benzophenone in acetone
4. nitrogen outlet
5. water bath
6. tap set so that the stock solution drips slowly into the crystallising dish to replace grafting solution as it evaporates

Another possible limitation regarding the maximum time that the sample can usefully be irradiated for is that polymerisation occurs on the surface of the quartz window, which will decrease the amount of UV radiation reaching the sample. The extent of polymerisation was observed to increase with time of irradiation. This is obviously a more difficult problem to solve. It may be possible

to coat the quartz with an inhibitor of polymerisation which will:

- (a) not absorb UV at wavelengths shorter than the cut-off point of quartz (150nm);
- (b) remain localised on the quartz window so as not to inhibit polymerisation of HEMA onto the Ultem film;

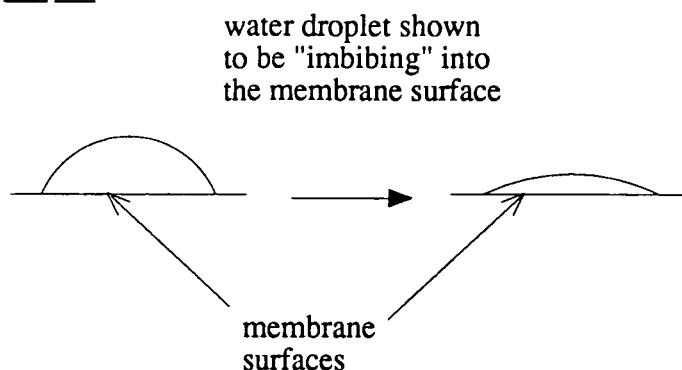
Suggested Further Experiments

It has been established when grafting poly(HEMA) to Ultem that a lower contact angle is achieved more quickly when grafting is carried out at 80°C than 60°C. However, the optimum temperature at which grafting takes place has not been found, so a useful experiment would be to graft samples as a function of temperature (at a constant irradiation time) to find whether grafting occurs more rapidly at still higher temperatures. An upper limit will obviously be imposed by the softening temperature of Ultem or the boiling point of water.

It would be of interest to investigate the change in contact angle after heating in distilled water for varying times. It is possible that the high temperature in the reaction cabinet has caused the grafted chains to migrate into the surface, causing the surface to reversibly lose its wettability. It would also be useful to investigate the stability of the grafted surface by measuring the contact angle as a function of time elapsed after grafting.

Although it has not yet been determined for certain whether grafting has occurred inside the pores of the membrane, we believe that this has taken place to some extent as water droplets placed on membranes grafted for three and four hours have been observed to be "imbibed" into the surface (Fig 6.1).

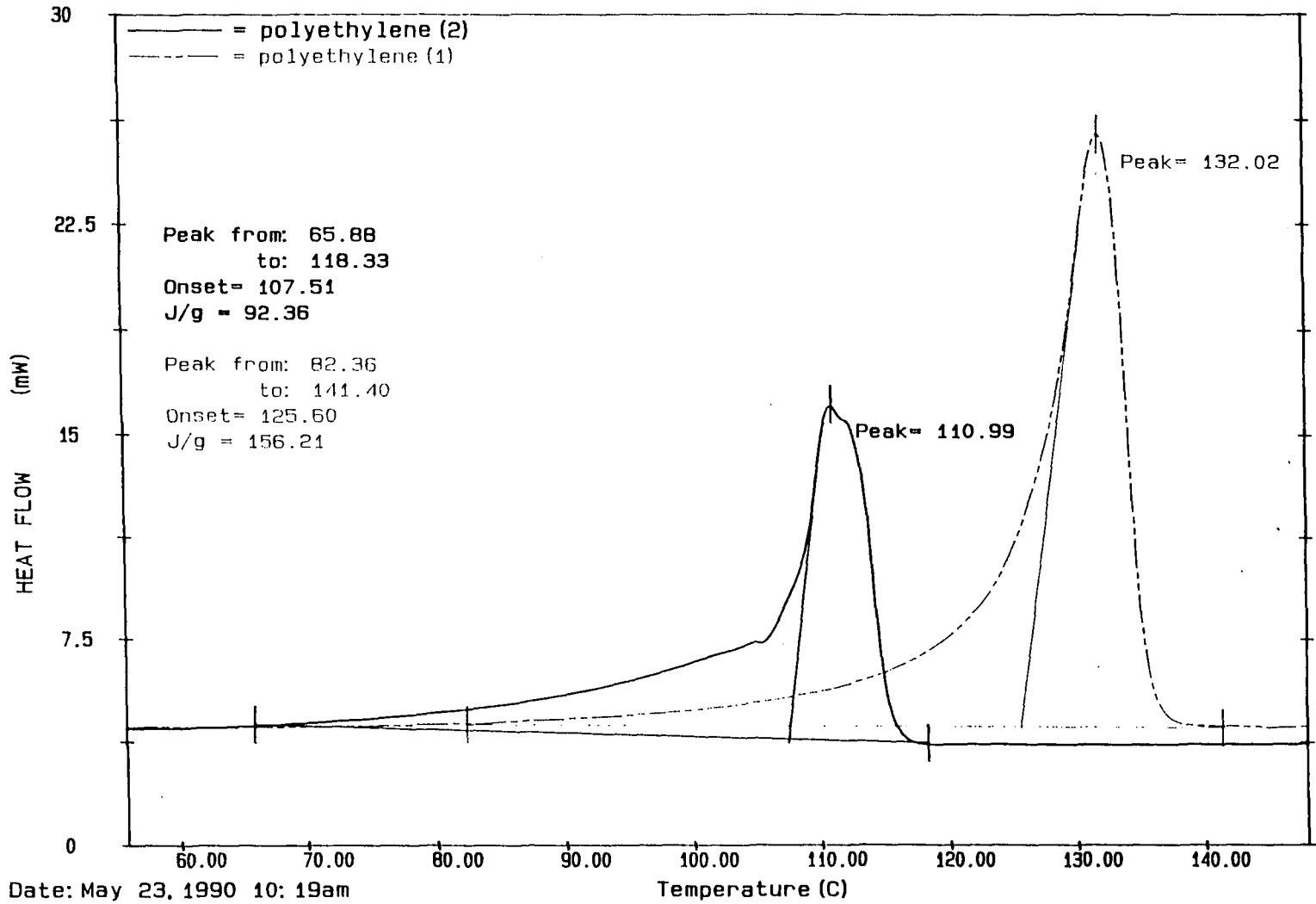
Fig 6.1



An alternative, more quantitative method which can be used to determine the extent of grafting inside the membrane pores is the Maximum Bubble Pressure Method. The pressure, P , at which a fluid is expelled from a cylindrical pore is related to the fluid surface tension, γ , the pore diameter, d , and the contact angle, θ , which the fluid makes with the pore surface by the Washburn equation (1).

$$P = \frac{4\gamma \cos\theta}{d} \quad (1)$$

If it is assumed that grafting changes only the surface contact angle, the extent of grafting in the pores can be determined by measuring the pressure at which gas begins to flow through the wetted membrane. It is recommended that the fluid used be a mixture of methanol and water.



Date: May 23, 1990 10:19am
 Scanning Rate: 20.0 C/min
 Sample Wt: 4.192 mg Path: \PE\
 File: PE2C LINDA

IRC DURHAM

Appendix 2**Irradiation of Polyethylene in Air and in Nitrogen Atmospheres: ESCA data and Mean Contact Angles with Water**

This data refers to chapter 5, section 2. Table 2.1 shows the carbon to oxygen ratio calculated from ESCA spectra, the mean contact angle with water, θ , calculated from ten separate measurements and the root mean square standard deviation from the mean, σ .

Table 2.1

Experimental Conditions	C : O (ESCA)	θ	σ
untreated	0.10	99	1.0
irradiated in air (no filter)	0.06	90	1.3
irradiated in air (quartz)	0.07	95	1.4
irradiated in air (Pyrex)	0.07	97	2.2
irradiated in N ₂ (quartz)	-	97	1.5
irradiated in N ₂ (Pyrex)	-	99	1.1

Appendix 3**Grafting of Poly(acrylic Acid) to Polyethylene:****Mean Contact Angles with Water**

This data refers to chapter 5, section 3. Table 3.1 gives the mean contact angle with water, θ , taken from ten separate measurements and the root mean square standard deviation from the mean, σ , for samples grafted using method 1.

Table 3.1

Irradiation time (minutes)	Lamp to sample separation (cm)	θ	σ
0	-	102	1.1
30	20	91	4.4
30	40	94	2.4
120	20	59	6.1
120	40	86	1.2

Table 3.2 gives the mean contact angle and root mean square deviation from the mean for samples grafted using method 2.

Table 3.2

Irradiation time (hours)	Lamp to sample separation (cm)	θ	σ
0	-	104	0.9
1	20	83	1.4
2	20	68	8.9
3	20	61	13.8

3.3 gives the mean contact angle and root mean square deviation from the mean for samples grafted using method 3. All experiments referred to here were done at a lamp to sample separation of 20cm.

Table 3.3

Experimental Conditions	θ	σ
Untreated	103	1.0
Irradiated for two hours	70	5.7
As above, followed by washing in water at 60°C for 5 mins	55	5.8

Appendix 4

Preparation of Cuprous Chloride⁴³

This refers to chapter 5. section 4.

The following solutions were prepared:

- (a) a 10% solution of sodium sulphite (by weight) (50ml);
- (b) a 52% solution of cupric chloride (25ml);
- (c) a solution of sulphurous acid, prepared by dissolving 1g sodium sulphite in distilled water and adding 12ml 2M hydrochloric acid.

The sodium sulphite was slowly added to the cupric chloride solution, while stirring. The suspension of cuprous chloride formed was diluted with half of the sulphurous acid solution; the precipitate was allowed to settle and most of the supernatant solution decanted. The solid was filtered by suction on a sintered glass disc, washing it onto the sinter with the remaining sulphurous acid solution. It is important that the precipitate is always covered by solution during filtration, as oxidation to copper(II) is rapid if exposed to moist air. The product was washed with glacial acetic acid, ethanol and diethyl ether then dried in a warm oven and stored at room temperature in an airtight container.

Appendix 5**Grafting of Poly(HEMA) onto Polyethylene:****Mean Contact Angles with Water**

This data refers to chapter 5, section 4. Table 5.1 shows the mean contact angle, θ , and root mean square deviation from the mean, σ .

Table 5.1

Experimental Conditions	θ	σ
untreated	104	1.0
irradiated for 2 hours	87	1.4
as above, followed by washing in water at 60°C for 5 mins	81	1.7
irradiated for 3 hours	83	1.0
as above, followed by washing in water at 60°C for 5 mins	84	0.8

Appendix 6

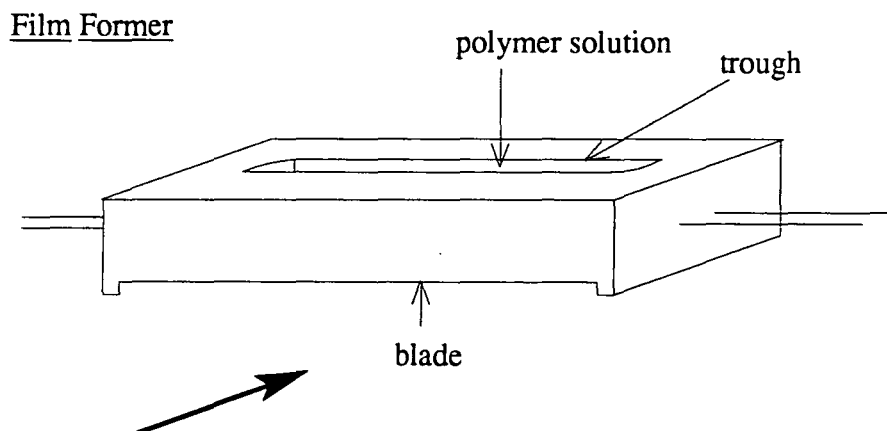
Casting of Ultem Film

Pellets of Ultem were dried overnight at 45°C then dissolved in dichloromethane to make a 20% solution by weight.

Dichloromethane was first purified by repeated washing with conc. sulphuric acid until the acid layer remained colourless, washing with distilled water, then with a 5% solution of Na_2CO_3 , then with water again; dried with anhydrous CaCl_2 then distilled from phosphorus pentoxide.

The solution was made up from freshly distilled dichloromethane and the films cast 24 hours after the solution was made up to allow any air bubbles formed during dissolution to be expelled.

The films were cast using a film former with a 200 μm blade (see below).



The film former is placed on a clean film of Mylar (about 20 x 30cm). The trough is filled to about 2mm depth with polymer solution, and the former drawn across the Mylar in the direction of the arrow.

It is estimated that the average thickness of a film cast with a 200 μm blade will be 40 μm after evaporation has been taken into account. This value may be decreased still further depending on the speed with which the film of Ultem solution is formed on the Mylar substrate.

Appendix 7**Grafting of Poly(HEMA) onto Ultem Film:****ESCA data and Mean Contact Angles with Water**

This data refers to chapter 5, section 5. Table 7.1 shows the mean contact angle with water, θ , the root mean square deviation, σ , and the fouling propensities for samples grafted at 60°C.

Table 7.1

Irradiation time (hours)	θ	σ	Fouling propensity
0	72	3.1	40-50
1	74	4.0	-
2	63	4.7	-
3	62	1.2	-
4	56	3.2	22
5	59	3.7	14

Table 7.2 shows the mean contact angle with water, θ , the root mean square deviation, σ , and the fouling propensity for samples grafted at 80°C.

Table 7.2

Irradiation time (hours)	θ	σ	Fouling propensity
0	75	2.2	40-50
1	62	4.9	-
2	60	4.6	-
3	55	2.3	19

Table 7.3 shows ESCA data, the mean contact angle with water, θ , the root mean square deviation from the mean contact angle, σ , and the fouling propensities for samples grafted at 80°C after increasing the time during which the cabinet was purged to 45 minutes. The percentages of carbon, nitrogen and oxygen are given as a percentage of the sum total of carbon + nitrogen + oxygen as calculated from ESCA spectra. t is the irradiation time in hours.

Table 7.3

t	θ	σ	%C	%N	%O	Fouling propensity
0	73	1.3	78.1	3.0	18.9	45
1	58	2.2	78.3	2.2	19.5	19
2	56	1.3	76.0	1.3	22.7	19
3	55	0.8	77.3	2.0	20.7	19
4	56	1.6	76.6	0.1	23.3	23

Appendix 8**Grafting of Poly(HEMA) onto Ultem Membrane: ESCA data and Mean Contact Angles with Water**

This data refers to chapter 5, section 6. Table 8.1 shows ESCA data, the mean contact angle with water, θ , and the root mean square deviation from the mean contact angle, σ . The percentages of carbon, nitrogen and oxygen are given as a percentage of the sum total of carbon + nitrogen + oxygen as calculated from ESCA spectra. ESCA results are not available for the sample grafted for one hour.

Table 8.1

t	θ	σ	%C	%N	%O	Fouling propensity
0	68	6.5	83.2	4.6	12.2	31
1	70	1.3	-	-	-	-
2	56	2.2	77.7	1.6	20.6	26
3	58	4.0	76.0	0.1	23.9	16
4	51	2.7	71.8	1.6	26.6	26
4	43	-	-	-	-	16

Bibliography

1. A.C. Wilbraham & M.S. Matta; Introduction to Organic and Biological Chemistry, Chapter 9; Benjamin Cummings Publishing Company, California, (1984)
2. E.A. MacGregor & C.T. Greenwood; Polymers in Nature; John Wiley & Sons Ltd. (1980)
3. I. Lundström, B. Ivarsson, U. Jönsson, H. Elwing; Protein Adsorption and Interaction at Solid Surfaces, in Polymer Surfaces and Interfaces, Ed. W.J. Feast & H.S. Munro, John Wiley & Sons Ltd. (1987)
4. W. Norde, F. MacRitchie, G. Nowicka & J. Lyklema; Protein Adsorption Solid-Liquid Interfaces: Reversibility and Conformation Aspects; J. Colloid & Interface Sci. 112(2), 447-456 (1986)
5. M.D. Bale, S.J. Danielson, J.L. Daiss, K.E. Goppert R.C. Sutton; Influence of Copolymer Composition on Protein Adsorption and Structural Rearrangements at the Polymer Surface; J. Colloid & Interface Sci. 132(1), 176-187 (1989)
6. R.K. Scopes; Protein Purification: Principles and Practice; 2nd Edn., Springer-Verlag New York inc.

(1987)

7. B.D. Ratner; Biomedical Applications of Synthetic Polymers, in Comprehensive Polymer Science: The Synthesis, Characterisation, Reactions and Applications of Polymers, Vol 7, Ed. G. Allen, J.C. Bevington, S.L. Aggerval; Pergamon Press (1989)
8. M.C. Petty; Molecular Engineering using the Langmuir-Blodgett Technique, in Polymer Surfaces and Interfaces, Ed. W.J. Feast & H.S. Munro; John Wiley & Sons Ltd. (1987) 163-187
9. K. Allmér, A. Hult, B. Rånby; Surface Modification of Polymers I: Vapour Phase Photografting with Acrylic Acid; J. Polym. Sci.; Polymer Chem. Ed., 26, 2099 (1988)
10. K. Allmér, A. Hult, B. Rånby; Surface Modification of Polymers II: Grafting with Glycidyl Acrylates and the Reactions of the Grafted Surfaces with Amines; J. Polym. Sci.; Polymer Chem. Ed., 27, 1641-1652 (1989)
11. H. Kubota, Y. Murata, Y. Ogiwara; Effects of Solvent in Photoinduced Graft Copolymerisation of Vinyl Monomers on Cellulose; J. Polym. Sci.; Polymer Chem. Ed., 2, 485-492 (1973)

12. C.H. Ang, J.L. Garnett, R. Levot, M.A. Long, N.T. Yen; Photosensitised Grafting of Styrene, 4-Vinylpyridine and Methyl Methacrylate to Polypropylene; J. Polym. Sci.; Polymer Lett. Ed., 18, 471-475 (1980)
13. K. Kaji; Grafting of Poly(acrylic Acid) onto Polyethylene Filament and its Distribution; J. Appl. Polym. Sci., 28, 3767-3777 (1983)
14. K. Kaji; Distribution of Grafted Poly(acrylic Acid) in Polyethylene Film; J. Appl. Polym. Sci., 32, 4405-4422 (1986)
15. T. Momose, H. Yoshioka, I. Ishigaki, J. Okamoto; Radiation Grafting of α,β,β -Trifluorostyrene onto Poly(ethylene-tetrafluoroethylene) Film by Pre-irradiation Method. I. Effects of Pre-irradiation Dose, Monomer Concentration, Reaction Temperature and Film Thickness; J. Appl. Polym. Sci., 37, 2817-2826 (1989)
16. G. Giri, P.K. Sahoo, R.K. Samal; Graft Copolymerisation onto Wool Fibres: Grafting of Acrylamide onto Wool Fibres Initiated by Potassium Monopersulphate/ Fe(II) Redox System; J. Appl. Polym. Sci., 40, 471 (1990)
17. A.R. Blyth, D. Briggs, C.R. Kendall, D.G. Rance,

- V.J.I. Zichy; Surface Modification of Polyethylene by Electrical Discharge Treatment and the Mechanism of Autoadhesion; Polymer, 19, 1273 (1978)
18. D. Briggs & C.R. Kendall; Chemical Basis of Adhesion to Electrical Discharge Treated Polyethylene; Polymer, 20, 1053-1054 (1979)
19. D. Briggs, D.M. Brewis & M.B. Konieczko; X-Ray Photoelectron Spectroscopy Studies of Polymer Surfaces. Part 3. Flame Treatment of Polyethylene; J. Materials Sci., 14, 1344-1348 (1979)
20. J. Peeling & D.T. Clark; Surface Ozonisation and Photooxidation of Polyethylene Film; J. Polym. Sci.; Polymer Chem. Ed., 21, 2047-2055 (1983)
21. J. Peeling, S.J. Mohammed, D.T. Clark; An ESCA Study of the Surface Ozonisation of Polystyrene Film; J. Polym. Sci.; Polymer Chem. Ed., 20, 1797 (1982)
22. D. Briggs, D.M. Brewis & M.B. Konieczko; X-ray Photoelectron Spectroscopy Studies of Polymer Surfaces. Part I. Chromic Acid Etching of Polyolefins. J. Materials Sci., 11, 1270-1277 (1976)
23. D.A. Olsen & A.J. Osteraas; Sulfur Modification of Polyethylene Surfaces. I. Insertion of Sulfur into

- Polyethylene Surfaces; J. Polym. Sci. A-1, 7, 1913-1920 (1969)
24. D.A. Olsen & A.J. Ostersaas; Sulfur Modification of Polyethylene Surfaces. II. Modification of PE Surfaces with Fuming Sulfuric Acid; J. Polym. Sci. A-1, 7, 1921-1926 (1969)
25. D.A. Olsen & A.J. Ostersaas; Sulfur Modification of Polyethylene Surfaces. II. Frustrated Multiple Internal Reflection Spectroscopy of Sulfonated PE Surfaces; J. Polym. Sci. A-1, 7, 1927-1932 (1969)
26. S. Contarini, J.A. Schultz, S. Tachi, Y.S. Jo, J.W. Rabalais; Ion Bombardment Induced Decomposition of Polyimide (PIQ) Studied by X-Ray Photoelectron Spectroscopy (XPS) and Direct Recoil (DR) Spectrometry; Applied Surface Science, 28, 291-301 (1987)
27. Y. Iriyama, T. Yasuda, D.L. Cho, H. Yasuda; Plasma Surface Treatment on Nylon Fabric by Fluorocarbon Compounds; J. Appl. Polym. Sci., 39, 249-264 (1990)
28. B. Rånby, Z.M. Gao, A. Hult, P.Y. Zhang; Modification of Polymer Surfaces by Photoinduced Graft Copolymerisation; ACS Symposium Series, 364, 168-186 (1988);

29. Y. Ogiwara, M. Kanda, M. Takumi, H. Kubota;
Photosensitised Grafting on Polyolefin Films in
Vapour and Liquid Phases; J. Polymer Sci.; Polymer
Lett. Ed., 19, 457
(1981)
30. J.G. Calvert & J.N. Pitts; Photochemistry,
Wiley(1966)
31. B. Rånby & J.F. Rabek; Photodegradation,
Photo-oxidation and Photostabilisation of Polymers:
Principles and Applications; John Wiley & Sons
Ltd.,(1975)
32. B.W. Cherry; Polymer Surfaces; Cambridge University
Press (1981)
33. D. Briggs, D.G. Rance & B.J. Briscoe, Surface
Properties, in Comprehensive Polymer Science,
vol II, ed. G. Allen & J.C Bevington, Pergamon
Press, Oxford (1989)
34. M.E. Brown, Introduction to Thermal Analysis,
Chapman & Hall Ltd., London (1988)
35. D.T. Clark & W.J. Feast; Application of Electron
Spectroscopy for Chemical Applications (ESCA) to
Studies of Structure and Bonding in Polymeric
Systems; J. Macromol.Sci - Revs. Macromol. Chem.,

C12(2), 191-286 (1975)

36. A. Schönberg; Preparative Organic Photochemistry; Springer-Verlag, (1968) p490
37. A. Charlesby & R.H. Partridge, The Thermoluminescence of Irradiated Polyethylene and Other Polymers; Proc. Roy. Soc. A., 271, 170 (1963)
38. A. Charlesby & R.H. Partridge; The Effect of Oxygen on the Thermoluminescence of Irradiated Polyethylene; Proc. Roy. Soc. A., 271, 188 (1963)
39. A. Charlesby & R.H. Partridge; The Identification of Luminescence Centres in Polyethylene and Other Polymers; Proc. Roy. Soc. A., 283, 312 (1965)
40. Charlesby & R.H. Partridge; Thermoluminescence and Phosphorescence Under Ultraviolet Irradiation; Proc. Roy. Soc. A., 283, 329 (1965)
41. R.H. Partridge; Electron Traps in Polyethylene; J. Polym. Sci., A-1, 3, 2817 (1965)
42. R.H. Partridge; Exciton Interpretation of the Vacuum-Ultraviolet Absorption Spectra of Saturated Organic Polymers; J. Chem. Phys., 49, 3656 (1968)

43. G. Pass & H. Sutcliffe; Practical Organic
Chemistry; John Wiley & Sons (1973)

