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## SYNTHESIS AND CHARACTERISATION OF POLYETHYLENE GRAFT COPOLYMERS.

by

Mohammad Azam MSc, MPhil

### A doctoral thesis

submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the Loughborough University of Technology.

October 1992

Supervisor: Professor John V. Dawkins BSc, PhD, DSc, CChem, FRSC

Department of Chemistry

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## **ORIGINALITY**

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

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#### ABSTRACT

Graft copolymers based on a non-polar polyethylene backbone and polar poly(methyl methacrylate) (PMMA), poly(phenyl ethyl methacrylate) (PPHETMA) and poly(butyl acrylate) (PBA) side chains were synthesised by non-ionic grafting onto method. Carboxyl terminated prepolymers and hydroxyl group containing backbones were synthesised and characterised separately and then condensed in a common solvent to form a graft copolymer. Carboxyl terminated prepolymers PMMA, PPHETMA and PBA of molar masses in the range of 1400 to 4400 g mol<sup>-1</sup> were prepared by free-radical polymerisation using 4, 4-azobis (4-cyanovaleric acid) (ACVA) as initiator and thioglycollic acid (TGA) as chain transfer agent. Backbones containing hydroxyl groups were synthesised by hydrolysing ethylene-vinyl acetate (EVA) copolymers to ethylene-vinyl alcohol (EVOH) copolymer with a VOH content of 9.8 mole %, with a VOH content of 21 mole % and a partially hydrolysed terpolymer ethylene-vinyl alcohol-vinyl acetate with a VOH content of 8.0 mole %.

Synthesised graft copolymers were characterised by gel permeation chromatography (GPC) by comparing the retention volumes of the precursor and the product. Molar masses determined from a polystyrene calibration curve supported the conclusion obtained from the comparison of retention volumes. Further characterisations were performed by infra-red (IR) and nuclear magnetic resonance (NMR) spectroscopy. IR and NMR were also used for the determination of composition of graft copolymers and they were compared with the theoretical values.

Differential scanning calorimetry (DSC), wide angle x-ray scattering (WAXS) and dynamic mechanical thermal analysis (DMTA) of the graft copolymers showed their amorphous behaviour, which indicated that the morphology of the crystalline EVOH copolymer backbone was disrupted after the grafting of prepolymer side chains.

Blends of a graft copolymer system poly(ethylene-vinyl alcohol)-g-PMMA were prepared with poly(vinyl chloride) (PVC) in different proportions. DMTA analysis of the blends showed some miscibility between graft copolymers and PVC.

Solution properties of poly(ethylene-vinyl alcohol)-g-PMMA graft copolymer were investigated in toluene and tetrahydrofuran (THF) at 25  $^{0}$ C. which indicated that graft copolymers can aggregate in dilute solution in toluene and THF.

# CHAPTER 1

# INTRODUCTION

#### 1.1 Graft copolymers definitions and structure.

In a report (1) by the International Union of Pure and Applied Chemistry, graft copolymers are defined as high polymers, the molecules of which consist of two or more polymeric parts of different chemical composition, chemically united together. A graft copolymer may be produced in a number of ways, for example, by polymerising a monomer in the presence of another kind of polymer. Alternatively, the union of two different polymers by chemical reaction between their molecular end groups or by a reaction producing cross linking between the different polymers would also produce a graft copolymer. Later, in another report (2), the definition of a graft copolymer appears as a polymer comprising molecules with one (or more) species of blocks connected to the main chain as a side chains, having constitutional or configuration features that differ from those in the main chain. The simple case of a graft copolymer can be represented by the structure below.

MAAAAAXAAAAA
ξ
B
В
B
В
В
В
Ş

where a sequence of `A` monomer units is referred to as the main chain or backbone to which the grafts are attached. `B`units are a sequence of monomer units referred to as the side chain and `X` is a linking point of the side chain and the backbone. In a graft copolymer the backbone and side chains may both be homopolymeric. The backbone may be homopolymeric and the side chains copolymeric, or vice versa; or both backbone and side chains may be copolymeric but with different chemical composition.

#### 1.2 <u>Properties and applications.</u>

Interest in graft copolymers has increased over the years owing to their diverse applications as emulsifiers, surface coating agents, coating materials and compatibilisers in polymer blends. A graft copolymer consisting of a backbone and a side chain of different chemical nature shows interesting physical properties and offers a number of applications. For example, natural rubber grafted with styrene is claimed to be a reinforcing resin for natural rubber (3). Grafting methyl methacrylate onto natural rubber improves adhesion to a film (4). Dying and dye retention in fibers such as poly(acrylonitrile) are improved by grafting. Strength, abrasion resistance, crease resistance and crease retention of cotton are increased by grafting with vinyl monomers using gamma irradiation (5-10). Graft formation introduces tolerance towards non-solvents, for example a polystyrene graft cellulose acetate in a solvent tolerates a large addition of toluene or similar hydrocarbon. This characteristic property can be used in formulating adhesive or coating compositions (11). Grafting also improves compatibility, for example, cellulose acetate is incompatible with polystyrene. Even a few percent of one polymer mixed with another gives a white opaque film upon casting from solvent but addition of even a small amount of a graft copolymer results in a clear transparent film (6). To the colloid scientist, graft copolymers are very important since in principle they offer the means by which macromolecular surface active agents of precisely-tailored architecture can be prepared for any particular use. In favourable cases graft copolymers of controlled structure and composition can be relatively easily prepared. Also, graft copolymers offer the possibility of providing a wide range of properties depending upon the amphipathic nature of the segments, such as polar non-polar, soft-hard for use as surfaceactive agents and as simple dispersents

Graft copolymerisation is a common method of modifying polymer properties (12,13). The physical properties of a specific graft copolymer are of great importance. A polymeric backbone exhibiting certain structural characteristics can be changed by side chains of a different chemical nature as result of grafting reactions. For example, a non-

polar backbone with polar side chains, or a crystalline backbone with amorphous side chains and vice versa, lead to interesting properties in solution and in the solid state.

In solution, graft copolymers may possess colloidal-type properties. A selective solvent, that is a solvent for one type of sequence and at the same time a precipitant for the other types of sequence, may lead to the formation of structures in which unlike copolymer sequences are micro-separated. In concentrated solution, various more or less rigid organised structures can be formed depending on the nature of the copolymer and the solvent (12). In dilute solutions particles are formed which in analogy to soaps are called micelles. If they are dispersed in solution molecularly, they are termed monomolecular micelles, and if they are associated they are termed as polymolecular micelles.

In the solid state, graft copolymers show properties characteristic of each of the components rather than an average of the individual components. In thermodynamic terms two components in a graft copolymer are mutually compatible with each other only if their free energy of interaction is favourable, that is negative. Since the mixing of sequences of polymers, like the mixing of simple liquids in the majority of cases is endothermic, incompatibility of chemically dissimilar sequences is often observed. For graft copolymers exhibiting a two phase morphology their spatial arrangement will be dependent on the concentration and nature of the components. The component present in the larger concentration will normally form a continuous phase and thereby greatly influence the physical properties of the graft copolymers. Components differing in chemical nature tend to separate and this tendency becomes much more pronounced if the graft copolymers are composed of mutually insoluble components.

Due to their interesting properties and wide applications a variety of graft copolymers have been prepared by a number of different methods, including free-radical, cationic, anionic and non-ionic techniques. These methods are classified (14) into three categories: grafting from, grafting through and grafting onto. In the grafting from method active sites on a pre-formed polymer backbone are used to initiate the polymerisation of a second monomer to produce grafted polymer segments. Since this method involves generation of grafts from a

polymer backbone having active sites by a monomer the resulting graft copolymer is highly contaminated with homopolymer. The grafting through method involves generation of branches or grafts from pendant unsaturation on a polymer chain or of a macromonomer. Grafting through between two polymer chains with unsaturation may result in a cross linked polymer. Synthesis of graft copolymers by grafting onto methods involves the reaction between a polymer chain (backbone) carrying randomly or regularly distributed reactive functions with another polymer carrying an antagonist function located selectively at its chain end. Grafting onto offers a clear advantage over the other two methods. Since the backbone and prepolymer are prepared separately, it is easier to characterise both prior to any grafting reaction. Knowing the properties of precursors, it is easier to purify and characterise a newly formed grafted product. Moreover, it is possible to identify changes in the properties of covalently linked precursors after grafting reactions. Grafting onto from polymeric species carrying functions capable of results undergoing reactions and these functions may be of ionic or non-ionic nature. In the literature not many examples are available which involve a non-ionic grafting onto method. Several examples quoted (15-23) involved synthesis of graft copolymers by a coupling reaction between a polymer chain with a terminal functional group and a polymer backbone having reactive functional groups. In these nonionic grafting onto methods synthesis of polymer chains with a terminal functional group by free-radical polymerisation are not commonly used, because of the difficulties involved in achieving monofunctional chains by free-radical polymerisation in which all chains have a terminal functional group and desired functionality. The non-ionic grafting onto method described in this work involved the use of a matched chain transfer agent and an initiator to produce polymer chains by free-radical polymerisation with terminal functional groups and desired functionality.

#### 1.3 <u>Aim of the present work.</u>

The purpose of this project was to produce a graft copolymer system with a non-polar backbone and polar branches by a non-ionic grafting onto method. Attempts were made to synthesise such graft copolymers, first, by preparing a copolymer backbone with reactive functional

groups distributed randomly and prepolymers with terminal functional groups, and second, condensing copolymer and prepolymer in a common solvent. Graft copolymers consisting of non-polar polyethylene backbone and polar side chains of poly(methyl methacrylate) (PMMA), poly(phenyl ethyl methacrylate) (PPHETMA) and poly(butyl acrylate) (PBA) were prepared. Since polyethylene consists of non-polar ethylene units and the prepolymers consist of polar units, these graft copolymers will have interesting physical properties. In order to have polyethylene as backbone in the graft copolymers, ethylene-vinyl alcohol (EVOH) copolymer was chosen. This copolymer has pendant hydroxyl groups and can be reacted with polymer bearing carboxyl groups at the chain ends. After replacing the hydroxyl groups by side chains the resultant graft copolymers will have a polyethylene backbone and prepolymer side chains. The EVOH backbone copolymers were prepared by hydrolysing ethylene-vinyl acetate (EVA) copolymers to achieve VOH contents of 9.8 mole % and 21 mole % and a terpolymer of ethylene-vinyl alcohol-vinyl acetate with a VOH content of 8.0 mole %. The carboxylic terminated prepolymers were prepared by free-radical solution polymerisation using the initiator 4,4-azobis(4-cyanovaleric acid) (ACVA) and the chain transfer agent thioglycollic acid (TGA). The pendant hydroxyl groups on the copolymer backbone were reacted with terminal carboxyl groups after converting to acid chloride of prepolymer PMMA, PPHETMA and PBA of molar masses in the range of 1400-4400 g mol<sup>-1</sup> by simple coupling reactions.

The synthesised graft copolymers were characterised by GPC. The characterisation by GPC was considered by comparing the change in the retention volume on GPC chromatograms of precursor EVA and the graft copolymer. The change in the molar masses of the precursor and the product can be judged by comparing their chromatograms and this change can clearly be seen in the shift of retention volume peaks. This shift in peaks can be supported by the molar masses obtained from a calibration curve.

The characterisation of the graft copolymer by spectroscopic techniques IR and NMR was considered to be useful, since precursor backbone and prepolymers consist of functional groups which have characteristic bands in the IR region and important chemical shifts due to various

protons in <sup>1</sup>H NMR. Moreover, these techniques offer an easy way to elucidate the composition of the graft copolymers.

Since EVOH copolymer is crystalline, replacement of hydroxyl groups as a result of grafting reactions will disturb the regular arrangement of ethylene units and this disturbance will be pronounced when prepolymer chains replace hydroxyl groups. The grafting of prepolymer side chains onto an EVOH backbone can be established by studying the morphology of the grafted product by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and wide angle x-ray scattering (WAX). The qualitative information based on these techniques can help to elucidate the crystalline or amorphous behaviour of the precursor and the product, which will provide confirmation of grafting reactions onto the precursor copolymer backbone.

Owing to the different chemical structure of the backbone and the side chain, these graft copolymers show interesting behaviour in solution. The solution behaviour of a graft copolymer system poly(ethylenevinyl alcohol)-g-PMMA in toluene and tetrahydrofuran (THF) was investigated by determining the intrinsic viscosities at 25 °C. Attempts were made to produced miscible blends of poly(ethylene-vinyl alcohol)-g-PMMA graft copolymers with poly(vinyl chloride) (PVC) in different proportions. Miscibility of the blends was studied by DMTA analysis.

# CHAPTER 2

# THEORY AND BACKGROUND

### 2.1 <u>Methods of preparation.</u>

Adkin and Hultz (24) first produced a graft polymer when they polymerised styrene in the presence of polystyrene. Viscosity measurements of the product concluded that the new styrene units were attached to the polystyrene backbone. Flory (25) proposed a theory suggesting that branched vinyl polymers could result from chain transfer reactions involving polymer molecules and a growing polymer chain. La Bras and Campagnon (26,27) reported the grafting of acrylonitrile on natural rubber. Interest in graft copolymer synthesis was increased when Mesrobian and co-workers (28) introduced the use of radiation to the synthesis of graft copolymers. In the literature a number of methods are reported for the synthesis of graft copolymers. Kennedy and Marechal (14) classified these into three main categories.

#### 2.1.1 Grafting from method.

In the grafting from method a polymer backbone having active sites or functions capable of generating such sites, are used to initiate the polymerisation of a second monomer. A simple scheme of such a method is given below.



#### Active site.

This method is quite efficient but has the disadvantage that it does not provides an accurate knowledge of molecular structure of a graft copolymer formed. The number of grafts is not accessible experimentally and their length may fluctuate very much within a sample. Moreover, the graft copolymer often contains a fair amount of both homopolymers. The sites created on the backbone can be freeradical, anionic or cationic in nature.

#### A. <u>Free-radical grafting from.</u>

Several methods are reported (29-31) for the generation of free-radical sites on the polymer backbone and from which grafts were grown by the addition of monomer. Eastmond (29) and Bamford (31) have used the reaction of halogen containing polymers with a metal carbonyl such as molybdenum hexacarbonyl to generate free radical sites.



A polymer backbone having hydroxyl groups can be used to create active sites by oxidising with metal ion. For example, a backbone containing hydroxyl groups can be oxidised by metal ions cobalt ( $Co^{3+}$ ), cerium (Ce <sup>4+</sup>), manganese (Mn<sup>3+</sup>), vanadium (V<sup>5+</sup>) and iron from which vinyl monomer may be grafted (32-34).



Smets et al (35,36) used the perester functions to generate active sites on poly(methyl methacrylate) (PMMA) containing acryloyl chloride. t-Butyl hydroperoxide after reacting with the acryloyl chloride of PMMA, formed a perester with the elimination of HCl. When a polymer solution was heated in presence of a monomer grafts, were generated from the thermal cleavage of the perester, .



Chapiro (37,38) has used irradiation to generate the free-radical sites on the polymer backbone from which grafts were grown. A typical scheme of creating such sites by irradiation is given below.



#### B. <u>Anionic grafting from.</u>

Metallation of a polymer backbone can be used as an active site for the growing of grafts with a suitable monomer. The major problem with this method is to find a satisfactory way to obtain a macromolecule with carbanion sites distributed randomly. The metallation of a polymer can be done by an addition reaction, substitution of labile hydrogen and by a metal halogen exchange reaction.

Allyl halides can be added to a polymer bearing unsaturation. Under well defined conditions the resultant metallated backbone can be used subsequently as initiator for the polymerisation of another monomer, for example, butyl lithium in benzene added to p-diisopropenyl benzene (PDIB) at a temperature chosen such as to avoid propagation (39).



Metallation of a polymer backbone to generate carbanion grafting sites by replacement of labile hydrogen was achieved by butyl lithium (40-42), which was used either alone or as a complex with tetramethyl ethylenediamine (TMEDA) to metallate polydienes, polystyrene (PS) or poly(phenylene oxide) (PPO).



Halogenated polymer backbones can react with metal to generate carbanion sites for grafting from reactions (43). Poly p-chlorostyrene was metallated with sodium naphthalene. The activated backbone was used to initiate the graft copolymerisation of acrylonitrile, vinyl pyridine, methyl methacrylate and styrene (44).



M-M~

### C. <u>Cationic grafting from.</u>

The cationic sites are created on various halogenated backbones by Lewis acids  $(CH_3CH_2)_3Al$ ,  $(CH_3)_3Al$  and BCl<sub>3</sub> (45,46). Several halogenated polymer backbones such as poly(chloroprene) (48-54), chlorinated styrene-butadiene rubber (SBR) (51,55,56), chlorinated (50,57-59), and brominated butyl rubber (51,60), chlorosulfonated polyethylene (61), and chlorinated butadiene (51) were used to create cationic sites by Lewis acids. The monomers grafted on such sites include styrene, alkyl vinyl ethers, tetrahydrofuran and isobutylene.



Kennedy used a tertiary alcohol to initiate the cationic site for a grafting from process (62-64). The polystyrene backbone was brominated via some tertiary carbon atoms by n-bromo succinamide (NBS) followed by alkaline hydrolysis to yield the tertiary alcohol functions. Grafts of poly(isobutene) (PIB) were grown from that backbone in the presence of BCl<sub>3</sub>.

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#### 2.1.2 Grafting through.

A grafting through process involves the polymerisation of a monomer to a polymer backbone carrying pendant unsaturation. A typical scheme for grafting through is as follows,



Smets and Schmets (65) copolymerised small amounts of ethylidene dimethacrylate with methyl methacrylate to form a soluble polymer with pendant unsaturation. Polymerisation of styrene or ethyl acrylate in the presence of this unsaturated polymer produced a graft copolymer.

The major drawback of these reactions involves formation of links between individual molecules. If growing sites happen to incorporate unsaturation belonging to two different backbones, this results in a cross linked material. This difficulty can be overcome by controlled grafting through by using a macromonomer. It involves firstly, the synthesis of a polymer species with terminal polymerisable unsaturation and referred to as a macromonomer. In the second step, the copolymerisation of these species with a suitable monomer in the presence of a free-radical initiator allows easy access to a graft copolymer with little homopolymer backbone contamination.



Having realised the utility of macromonomers, considerable work has been done to study the methods of their synthesis and subsequent copolymerisation to graft copolymers. The synthesis of macromonomers has been reported by anionic, cationic and free-radical methods.

#### A. <u>Anionic method</u>.

Induced deactivation of living ionic sites is one of the major routes for the synthesis of a macromonomer. This method reduces the chances of a spontaneous transfer or a termination reaction on the polymerisable terminal unsaturation. For example, a macromonomer with terminal styryl or with a methacrylic ester function can be synthesised upon deactivation of living anionic polymers by means of p-chloromethyl styrene or methacryloyl chloride (66-69). Deactivation of a living poly(ethylene oxide) (prepared by anionic polymerisation) by pchloromethyl styrene leads to a macromonomer.



#### B. <u>Cationic method.</u>

Kennedy has introduced cationic polymerisation for macromonomer synthesis (70). In order to avoid side reactions, he used vinyl benzyl chloride/CH<sub>3</sub>Al/H<sub>2</sub>O as an initiator for the synthesis of poly(isobutylene) macromonomer (71). However, it has the disadvantage that the loss of head group functionality in some of the polymer chains can result during synthesis. It was overcome by the use of a initiator  $p(\beta$ -bromo ethyl cumyl chloride) to a saturated group (72). Finally unsaturation was generated by a dehydrohalogenation reaction.



#### C. <u>Free-radical methods</u>.

Synthesis of macromonomers by free-radical methods has been studied extensively by several workers (41, 73-77). These methods involve two steps. In the first step, polymer chains with terminal carboxylic acid, hydroxyl or amino functional groups were synthesised by using a chain transfer agent having the desired functional groups in conjunction with an initiator having the corresponding functional groups. In the second step, the condensation of these functional groups with a monomer containing reactive functional groups yielded macromonomers. For example, condensation of a terminal carboxyl group in a carboxyl terminated polystyrene prepared by free-radical polymerisation with a epoxide in glycidyl methacrylate leads to a macromonomer.



#### 2.1.3 Grafting onto.

A grafting onto process results from the reaction of a polymer carrying a reactive site at the chain end and another polymer with attached functional groups distributed randomly along its chain. A simple scheme for such a reaction is presented as follows,



Backbone

prepolymer

Graft copolymer

where X and Y are reactive sites on a backbone and at the chain end. They may be electrophilic or nucleophilic in nature.

An advantage of these methods is that they allow an easy way to structural characterisation of the graft copolymers formed, since precursor polymers and graft copolymer are made separately so they can be characterised individually. Knowing the molar masses of each of them and the overall composition of the graft copolymer, it is possible to evaluate the number of grafts per chain and the average distances

between two successive grafts along the backbone. In grafting onto if reacting polymers have ionic functions such as an anion or cation it is termed ionic grafting onto and if reacting polymers carry functional groups liable to react such as hydroxyl or carboxyl then it is termed non-ionic grafting onto.

#### A. Ionic grafting onto.

Ionic methods are further subdivided into anionic and cationic grafting onto.

#### i) <u>Anionic grafting onto methods</u>.

In this method a polymer having a strong nucleophilic carbanion, is grafted onto a polymer backbone containing electrophilic functions such as ester, anhydride, halide, nitrile and pyridine.(78,79).Graft copolymers were prepared from a polymer with nucleophilic carbanion by grafting onto a polymer backbone containing reactive halogen or epoxide functions with 80-90 % grafting efficiencies (80-84).



It has been found that with alkyl halides such as PVC, side reactions, for example elimination, may occur, which may compete if a strong nucleophile is used (85). It has also been reported that benzylic and allylic halides are far more satisfactory, since elimination is impossible in such reactions(83,86).

#### ii) <u>Cationic grafting onto methods</u>.

In these methods a polymer chain carrying strong electrophilic species is grafted onto a polymer backbone having a nucleophilic function. Amine (87), benzene nucleus (88), and hydroxyl (89,90) functional groups on a polymer backbone were reacted with living poly(tetrahydrofuran) (PTHF) (87,89,90) and living poly(dioxalone) (88). Amines are best studied by this method as they yield ammonium salts.



#### B. <u>Non-ionic grafting onto methods.</u>

A polymer backbone containing hydroxyl,, amino, thiol and several other groups can undergo a condensation reaction with a polymer having reactive functional groups to produce graft copolymers.



where X and Y are reactive functional groups. This method involves two steps. First, the synthesis of a polymer backbone with functional groups distributed randomly along the chain and second, the synthesis of prepolymer chains with terminal functional groups.

### i). <u>Prepolymers with terminal functional groups.</u>

Synthesis of polymer chains with terminal functional groups via freeradical polymerisation was first reported by Bamford (91). He used the initiator 4,4-azobis (4-cyanovaleric acid) (ACVA) to produced carboxyl terminated polystyrene and poly(methyl methacrylate) (PMMA), and obtained a mixture of polymer species, which is illustrated using a simplified scheme.

Initiation	Initiator (I)	$k_d \rightarrow 2R$
	Monomer (M) $+ \hat{R}$	——— R— M
Propagation	R - M + M	$k_p \qquad R - M - M$
· · · ·	R → (M) → M + M	$\stackrel{k_p}{\longrightarrow} R - (M)_{n+1} M$
	i.e. $P_n + M$	$k_p P_{n+1}$
Termination	$ \begin{array}{c} \bullet & \bullet \\ \mathbf{P}_{\mathbf{X}}^{T} & \bullet & \mathbf{P}_{\mathbf{y}} \end{array} $	$k_{t,C} \rightarrow P_{(X+Y)}$
	$\mathbf{P}_{\mathbf{X}} + \mathbf{P}_{\mathbf{Y}}$	

where  $k_d$ ,  $k_p$  and  $k_t$  are rate constants for initiation, propagation and termination respectively.  $k_{t,c}$  and  $k_{t,d}$  are individual rate constants for termination by combination and disproportionation respectively.

Thus, for polymerisation initiated by ACVA and terminated by combination, a polymer chain with carboxyl groups at both ends is produced, while termination by disproportionation produces two types of polymer chains, one possessing a carboxyl group at one end and a double bond at the other end, while the other possess a carboxyl group at one end and a hydrogen atom at the other end. A polymeric radical can stop adding monomer without simultaneous termination of the kinetic chain. This process involves chain transfer during which a growing polymeric radical abstracts an atom from another molecule so further monomer addition cannot occur. However, simultaneously as a result of this process a new radical is generated which can add monomer so that the kinetic chain can be maintained. The molecules to which chain transfer can occur include solvent (S), initiator (I), monomer (M) or some other added substance called a chain transfer agent (X). Thus, a growing polymer chain can abstract a hydrogen atom from a chain transfer agent (X) leading to a dead polymer chain and transfer the ability to add monomer to the chain transfer agent and can be represented as follows,

 $\stackrel{\bullet}{P}$  + X  $\xrightarrow{k_{tr'}x}$  PH + X

where  $k_{tr}$  is the rate constant for the chain transfer reaction between the polymeric radical P and X defined by,

 $k_{tr,x} = k_p C_x$ 

where  $C_x$  is the chain transfer constant for the substance X. Aliphatic mercaptans are suitable transfer agents for several monomers. Chain transfer agents with transfer constants near unity are quite useful in depressing molar mass in polymerisation reactions. A transfer constant near unity ensures that the transfer agent is consumed at the same rate as the monomer so that the concentrations of transfer agent and monomer remain constant throughout the reaction which results in a low molar mass polymer with narrow distribution. Large quantities of chain transfer agents are needed when the constant is much lower than unity, and agents with transfer constants greater than about 5 are used up too early in the reaction resulting in a higher molar mass polymer with a broad distribution.

In order to obtain a polymer chain with carboxyl end groups, Waite and Thompson (92) used the chain transfer agent and initiator possessing the desired functional groups which is termed as a matched chain transfer process. A simplified scheme for a typical matched chain transfer agent polymerisation is given in figure (2.1) where (M) represents a monomer, (ACVA) the initiator and (TGA) thioglycollic acid as the chain transfer agent. The scheme is incomplete because it omits all other possible transfer reactions to monomer, solvent, initiator and polymer. However, it does show that for transfer agents such as TGA, one end of the polymer chain will arise from the transfer agent. If the amount of transfer agent present is such that the normal kinetic processes of termination, governed by kt,c and kt,d are not significant, then a large proportion of the polymer chains produced will have a hydrogen atom at one end and a -SCH<sub>2</sub>COOH group at the other end. Only those polymer molecules derived directly by initiation via initiator fragments or by transfer to solvent molecules will not possess a -SCH<sub>2</sub>COOH group at one end and a hydrogen atom at the other end. However, if the initiator fragments also have the desired functional group then a large proportion of the polymer chains formed will possess the desired terminal functional groups.
# Figure 2.1 <u>Free-radical polymerisation scheme of a monomer in the presence</u> of a matched chain transfer agent (TGA) and initiator (ACVA).



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Similarly, to produce polymer chains containing a terminal hydroxyl, amine or substituted amine, matched chain transfer agents and initiators containing the desired functional groups can be used to obtain a polymer chain with the desired terminal functional groups. A list of such initiators and chain transfer agents is given in table 2.1.

# ii) <u>Copolymer backbones with functional groups</u>.

A copolymer backbone with the desired functional groups can be prepare either by free-radical copolymerisation of two monomers with one containing the desired functional group or by chemical modification of the functional groups on a polymer backbone. For example, the copolymerisation of 2-hydroxyethyl methacrylate (HEMA) with various monomers was used by many workers to prepared polymer backbones with pendant hydroxyl groups (93-97). A copolymer backbone with pendant epoxide groups was prepared by the free-radical copolymerisation of glycidyl methacrylate with monomers such as styrene, acrylonitrile (97), and methyl methacrylate (98,99). Yocum and Nyquist (100) have published a detail of functional monomers that can be used for the preparation of a copolymer backbone with the desired functional groups.

In the free-radical copolymerisation of two monomers the composition of the copolymer formed may differ from the feed. This difference of composition in the feed and the copolymer is due to the reactivity of the two monomers to each other and to the growing free-radical .Thus, two monomers  $M_1$  and  $M_2$  will lead to radicals  $M_1$  and  $M_2$ , and there are four possible way by which these monomers can add to each other.

$\mathbf{M}_1 + \mathbf{M}_1$	► M <sub>1</sub>	• k <sub>11</sub> [M <sub>1</sub> ] [M <sub>1</sub> ]
$M_1 + M_2$	<u>k<sub>12</sub></u> M <sub>2</sub>	$k_{12} [M_1] [M_2]$
$M_2 + M_1$	<u>k<sub>21</sub></u> M <sub>1</sub>	$k_{21} [M_2] [M_1]$
$M_2 + M_2$	<u>k<sub>22</sub></u> M <sub>2</sub>	• k <sub>22</sub> [M <sub>2</sub> ] [M <sub>2</sub> ]

#### Reaction.

Rate.

where k is a rate constant characteristic of each propagation step.

Table 2.1 List of initiators and match chain transfer agents which canbe used for free-radical polymerisation to produce polymerchains with terminal functional groups.

Initiator

Chain transfer agent

γ,γ–αzobis (γ–cyano–n– pentanol)

 $\alpha, \alpha$ -azobis ( $\gamma$ -amino- $\alpha, \gamma$ dimethyl valeronitrile)

α,α–azobis(γ–alkylamino–α,γ– dimethyl valeronitrile)

 $\alpha, \alpha'-\alpha$ zobis ( $\gamma$ -dialkylamino- $\alpha$ ,  $\gamma$ -dimethyl valeronitrile) 2-mercapto ethanol

 $\beta$ -mercapto ethylamine HCl

N(β-mercapto ethyl )-Nalkylamine HCl

N(β-mercapto ethyl )-N, Ndialkylamine HCl and 2,3 or 4 mercapto N:Ndialkylaniline HCl The rate of disappearances of two types of monomer are given by equations (2.1) and (2.2) respectively.

$$- \frac{d[M_1]}{dt} = k_{11} [M_1] [M_1] + k_{21} [M_2] [M_1] \dots (2.1)$$
$$- \frac{d[M_2]}{dt} = k_{12} [M_1] [M_2] + k_{22} [M_2] [M_2] \dots (2.2)$$

dividing equation (2.1) by (2.2) gives the copolymer composition,

$$- \frac{d[M_1]}{d[M_2]} = \frac{k_{11} [M_1] [M_1] + k_{21} [M_2] [M_1]}{k_{12} [M_1] [M_2] + k_{22} [M_2] [M_2]} \dots (2.3)$$

where  $\frac{d[M_1]}{d[M_2]}$  is the ratio of the rates of entry of monomer M<sub>1</sub> and M<sub>2</sub> into the copolymer.

Assuming that a steady-state concentration exists for both  $M_1$  and  $M_2$  then

$$k_{21} [M_2] [M_1] = k_{12} [M_1] [M_2] \dots (2.4)$$

Thus, rearranging for  $[M_1]$  and substituting into equation (2.4) gives the copolymer composition equation (2.5).

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] (r_1[M_1] + [M_2])}{[M_2] ([M_1] + r_2[M_2])}.....(2.5)$$

where  $d[M_1]/d[M_2]$  expresses the molar ratio of the two species in the copolymer while the right hand side of the equation relates to the concentrations of monomers in the feed.

 $r_1$  and  $r_2$  are reactivity ratios of monomer  $M_1$  and monomer  $M_2$  defined as,

$$r_1 = \frac{k_{11}}{k_{12}}$$
 and  $r_2 = \frac{k_{22}}{k_{21}}$ .....(2.6)

Reactivity ratios are the ratio of the rate constant for a given radical adding to its own monomer to the rate constant for it adding to the other monomer. Thus  $r_1 > 1$  means that radical  $M_1$  prefers to add  $M_1$ ;  $r_1$ 

< 1 means that it prefers to add M<sub>2</sub>. The values of the reactivity ratios indicate the type of copolymer formed which are usually of two types; ideal or alternating. A copolymer is said to be ideal if the two radicals are equally reactive to the two monomers present. In this case  $k_{11}/k_{12} = k_{21}/k_{22}$  or another words  $r_1 = 1/r_2$ . The two types of units are arranged randomly along the chain, the relative amounts of which are determined by the composition of the feed and the relative reactivities of the two monomers. In alternating copolymerisation each radical prefers to react exclusively with the other monomer and  $r_1 = r_2 = 0$ . In most cases  $r_1$  and  $r_2$  are both more than zero, which does not give a complete alternating copolymer but a tendency towards alternating copolymers. Another possibility is if  $r_1$  and  $r_2$  are both greater than unity. In this case growing radicals prefer to react with their own monomers which results in blocks of each units within the chain.

Polymers or copolymers may also be chemically modified to have reactive groups and enable them to function as polymeric backbones for grafting onto reactions. For example, acetate groups on a polymer or copolymer backbone can be hydrolysed to hydroxyl groups. Similarly, reactive amino, carboxyl, cyano, isocyano and several other groups can be created on a polymer or copolymer backbone by corresponding chemical modification and can be used as a backbone for possible grafting onto reactions.

In the literature several examples are reported for the synthesis of graft copolymers by the condensation of terminal groups of a prepolymer chain onto a backbone containing antagonist functional groups (15-23). Melville and co-workers (15) synthesised branched poly(vinyl acetate). They first synthesised a poly(vinyl acetate) prepolymer with terminal carboxyl acid groups, converted it to acid chloride and then grafted it onto a poly(vinyl alcohol) backbone by coupling reactions. Graham (16) synthesised a graft copolymer by grafting amino terminated polystyrene prepolymers onto a polymer backbone containing  $\beta$ -isocyanoethyl methacrylate.



Ikada and co-workers (17) have synthesised a graft copolymer by coupling reactions between polystyrene containing terminal acyl chloride groups and poly(vinyl acetate) containing amino groups along the chains. Gomes (101) synthesised poly(methyl methacrylate-gurethane) graft copolymers by a coupling reaction of poly(methyl methacrylate-2-hydroxy ethylmethacrylate) and polyurethane. This reaction involved condensation of hydroxyl groups on a copolymer backbone with terminal isocyanate groups of polyurethane prepolymers.

The major factors involved in grafting onto reactions are the reactivity of a functional group on the polymer substrate and its accessibility. The reactivity of functional groups on a high molar mass substrate is generally considered to be the same as that of their low molar mass homologues. Compared to a low molar mass homologue, a polymer is

a long chain molecule with a sequence of pendant functional groups strung along a backbone. In solution and in the solid state, polymer chain behaviour may be entirely different compared to a small molecule, because of the difference in amorphous and crystalline content, orientation of groups on the polymer chain and their solubility and compatibility. These greatly influence the interchain interaction and accessibility of the reactive sites which effect the grafting onto reactions.

#### A. <u>Crystallinity and orientation.</u>

In the solid state polymer chains may be in one of the following forms: amorphous and unoriented, amorphous and oriented, crystalline and unoriented, or crystalline and oriented. Polymers do not exist in any of these forms exclusively and the degree of crystallinity and orientation may vary not only from one sample to another, but also from one bundle of chains to another. It has been demonstrated that the attack of a chemical reagent on an amorphous structure occurs more readily than on a crystalline structure. However, the degree of penetration of the reagent and the extent of reaction are dependent upon the degree of orientation of the chains, number and complexity of chain entanglements and the temperature of the reaction in relation to the glass transition temperature of the polymer. In crystalline polymers the oriented chains act as a unit and therefore have a low surface area for chemical reaction. The penetration of a reagent is restricted to the periphery of the oriented areas.

# B. <u>Solubility.</u>

A solvent that is inert from the point of view of a particular chemical reaction under investigation may be a poor solvent for the polymer undergoing reaction. As a result the polymer chains may be present as tight coils and the reactive sites may be inaccessible. Coiled polymer chains in a solvent are therefore not necessarily more available or reactive than the chain in molten or solid state. The choice of a solvent is not only dictated by inertness to the chemical reagent but also by solvent reagent interactions, which determine the course of reaction. The most desirable solvent for achieving a specific interaction may be a poor solvent for the polymer; consequently the reaction may result in a heterogeneous product. The choice of solvent for the starting polymer may produce high solubility, and therefore uniform reaction, but if the reaction product is insoluble at low levels of reaction, then a nonuniform reaction may result.

#### C. <u>Compatibility.</u>

The chief difficulty in a grafting onto process arises from the incompatibility between polymers of a different chemical nature. When solutions of these polymers in the same solvent are mixed two phases are formed. As a result, a polymer carrying one type of functional group will not react easily with other groups attached to a different chain molecule. Compatibility becomes a significant factor when chemical reactions are carried out on polymers, as a result of the difference in structure between the starting polymer and the reaction product.

# 2.2 Properties of graft copolymers.

Interest in and applications of graft copolymers depend to a great extent on whether they offer any advantages over physical blends. Generally a graft copolymer should offer a clear advantage over a physical blend when a high degree of incompatibility exists between the component parts. It is difficult to make a well dispersed blend of polymers which have poor insolubility in one another. Even if this can be done, migration and separation will occur under stress because of poor adhesion and the combination will have low strength properties. On the other hand in a graft copolymer the components are tied by chemical bonds and will necessarily be in a highly dispersed state, or may in turn give rise to an organised structure.

Since graft copolymers consist of two different component polymers or copolymers having different chemical structure, then these components joined by a chemical bond as a result of grafting reaction should produce a product with interesting physical properties. The behaviour of the component polymers is greatly influenced by the solution properties if they are polar/polar or non-polar/polar systems. Similarly, the solid state properties are effected greatly if the constituent polymers have a different set of structural arrangements, that is amorphous/amorphous, amorphous/crystalline, or vice versa. Following this general outline the solution and the solid state properties of graft copolymers will be described in the following section.

# 2.2.1 Solution properties.

It is well established that the solution properties of graft copolymers are affected by the interaction between chemically unlike sequences (102-103). The behaviour of each sequence of a polymer chain in a solvent will be different; depending on the nature of the solvent, each sequence will solvate in a different manner. A solvent which is good for both sequences of polymer chains will have good solubility for the graft copolymer. A selective solvent for one of the sequences will lead to different behaviours of a graft copolymer in concentrated and dilute solution. The solubility of the graft copolymer greatly depends upon the interaction of each sequence with the solvent. The interaction of solvents with graft copolymers is a complex phenomena strongly dependent upon composition and structure of the species. To study this interaction block and graft copolymers should be treated simultaneously, since a block copolymer in its simplest form is a type of graft copolymer with the grafted chain tagged onto the end of a backbone. In studies of the solution properties some investigators reported (105-106) that the average chain dimensions of a block copolymer are larger than those of a homopolymer of equal molar mass, whereas the results of other investigators (107-109), indicated that the block dimensions are smaller. Inagaki and co-workers (110) reported that the copolymer chain may assume a conformation similar to that of the corresponding homopolymer in a poor solvent for the block sequence. Merrett (111) prepared graft copolymers by grafting PMMA onto rubber. When this graft copolymer was dissolved in benzene both chains were expanded to a relatively large extent due to a large solvent solute interaction. When methanol was added a white colloidal solution was formed, which indicated that the rubber chains collapsed to give colloidal particles which were stabilised by soluble PMMA chains. It appears that in a good solvent for both components, chains existed in a fully expanded form, and in a solvent only good for one of the components, polymer chains existed in an expanded and compact form. The same type of behaviour was observed by Battared (112) for poly(vinyl chloride-g-methyl methacrylate), poly(vinyl chloride-g-ethyl acrylate) and poly(vinyl chloride-g-vinyl acetate).

The behaviour of a graft copolymer in solution is also effected by the interaction between two dissimilar polymer chains which results in incompatibility, phase separation and configuration effects. This incompatibility between the composing homopolymer chains of block and graft copolymers is the predominant feature not encountered in simple homopolymers or random copolymers. A homopolymer has a large number of degrees of freedom; by grafting this number is multiplied considerably by possible variations in chemical composition, number, position, length and structure of grafted chains as well as inter and intra-chain configuration effects. Due to the incompatibility, preferential interaction will occur in solution resulting in structure formation (113). This on a molecular scale is different for an extremely dilute solution or on a macroscopic scale for concentrated solution and will be described in the following section.

# 2.2.1.1 <u>Behaviour in dilute solution.</u>

The dilute solution behaviour, of graft copolymers is mostly investigated in common solvents, that is a good solvent for each of the sequences in the graft copolymer. In a selective solvent, a good solvent for one of the sequences in the graft copolymer, colloidal behaviour is observed.

# A. <u>Dilute solution in selective solvents</u>,

Graft copolymers in a selective solvent, that is a solvent for one type of sequence and non-solvent for the other type of sequence form micelles. The core of such micelles consist of insoluble sequence of the graft copolymers. The external shell is formed by solvated sequences which prevent macroscopic flocculation of the copolymer. It is generally believed that such micelles, formed through a closed association process, are spherical with a narrow size distribution , but may change shape and distribution under certain conditions. Micelles of block and graft copolymers have been treated as monomolecular and multimolecular micelles (114) (figure 2.2). Sadron (115), who first suggested the term monomolecular micelle, assumed that the









Sketch of a monomolecular micelle in a diblock polymer. (reproduced from ref. 114). molecules of diblock copolymer in very dilute solution in a selective solvent would exhibit microseparation, in such a way that the a swollen peripheral soluble block provides a shell for the insoluble block. With increasing concentration of copolymer there would occur association of copolymer molecules to yield multimolecular spherical structures. Sadron put forward an assumption that the formation of a monomolecular micelle occurs as a result of different solvation of the copolymer blocks, and their incompatibility. A number of workers studied microphase separation or segregation in graft or block. copolymers due to incompatibility of sequences in the copolymer. Bresler et al (116) studied the mechanical and hydrodynamic behaviour of a nine-block copolymer with alternating sequence of polystyrene and polyisoprene. From the relationship between intrinsic viscosity, radius of gyration and the diffusion coefficient, he concluded that in a selective solvent molecules existed in monomolecular micelles. In their core, there were microseparated blocks protected by a solvated block from macroscopic flocculation (figure 2.3). Gallot and co-workers (117) investigated graft poly(methyl methacrylate/styrene) copolymers. They found conditions under which the impaired quality of solvent for polystyrene (mixture dioxane/cyclohexane) lead to a marked decrease in intrinsic viscosity and radius of gyration without any increase in molecular weight. They assumed the formation of monomolecular micelles in which the insoluble poly(methyl methacrylate) backbone collapsed to a negligible volume, and the respective graft formed some kind of polystyrene tails. Dondos et al (118,119) found that graft copolymers of poly(diphenyl-3, 3-propane-1/styrene) and poly(diphenyl-3,3-propane-1-methyl methacrylate) formed multimolecular or monomolecular micelles in selective solvents depending on the number of grafts.

Multimolecular micelles have been found to be formed by an equilibrium association process analogous to that of surfactant micelles (115). Multimolecular micelles in dilute solution have a spherical shape and are rather compact (figure 2.2.). Their weight (or particle weight in a given solution) decreases with increasing number of block or solvated grafts and increases with impairing quality of the solvent toward one type of block or towards the backbone. In those cases where a sufficient protection of the micelle core is guaranteed (multiblock

copolymers, graft copolymer with a large number of branches), the micelles formed have a lower weight.

The formation of monomolecular and multimolecular micelles effects the behaviour of the graft copolymer in solution. For multimolecular micelles both osmometry and light scattering show elevated molar masses, while for monomolecular micelles no change in molar mass was recorded (114). The transition from a molecular into micelle state is observed by the decrease in intrinsic viscosity irrespective of the type of micelle formed (114).

# B. <u>Dilute solution in good (common) solvents.</u>

Dilute solutions of graft and block copolymers in good solvents exhibit characteristic behaviour resulting from thermodynamic interaction of sub-chains with solvent molecules and each other. Two conformations for block copolymers in solution have been proposed (120). The segregated model, which has few hetrocontacts, where the molecular size of the blocks in solution is close to that expected for comparable homopolymer chains. The pseudo-Gausian or random structure model, in which different blocks overlap to some extent resulting in hetrocontacts which expand the component coils because of the additional repulsive forces between unlike segments. It has become clear that the chain configuration is mainly influenced by preferential interaction between like elements. In general, chains of graft copolymers are therefore more compact in solution. Depending on the interaction of the two sequences of the chain with solvent and interaction between the chains themselves, one of the components of the grafts may be more or less expanded compared to the other.

#### 2.2.1.2 <u>Behaviour in concentrated solutions.</u>

Graft and block copolymers in a dilute solution consisting of a gel particle of precipitated polymer solubilized by the soluble part of the molecule are called multimolecular micelle. The insoluble part or globular part (figure 2.4 ) does not necessarily have to be in a random configuration, but could take up a more regular pattern such as a helix (121,122). In concentrated solutions multimolecular micelles occur, while in more concentrated solutions, structures can be formed



Figure 2.4 <u>A cylindrical structure of mesomorphic gels in graft copolymer. A-</u> insoluble backbone, B-soluble side chains and circles solvent.



Figure 2.5 <u>Leaflike structure of meomorphic gels in graft copolymers</u>. <u>A-insoluble</u> <u>backbone</u>, <u>B-soluble side chains and circles solvents</u>.

analogous to those found in concentrated soap solutions (123,124). When multimolecular micelles of chains and block copolymers, with constituent chains of widely different solubility characteristics, agglomerate to form gels with order configurations over distances that are long compared with the molecule size, they are mesomorphic and amphipolar (112). Mesomorphic gels can occur in two structures cylindrical, (nematic). (figure 2.4) or leaflike (Semitic) (figure 2.5). Skoulios (125,126) identified these structures for a system of poly(styrene-b-ethylene glycol)-butyl phthalate or nitromethane. Gallot (117) observed these structures for the system poly(styrene-boxyethylene glycol)-ethyl benzene and reported that these structures can equally apply to graft copolymers.

# 2.2.2 Bulk properties.

A large number of publications have appeared in the literature dealing with the synthesis of graft copolymers, but the literature dealing with bulk properties of graft copolymers is very restricted. These properties of graft copolymers are not fully understood and no coherent theory has been developed to allow the test of a systematic approach against experimental results. Ceresa (127) discussed in detail only natural rubber-g-PMMA and poly(butadiene)-g-styrene. Burlant and Hoffman (128) did not discuss bulk properties of graft copolymers to any extent. Since a graft copolymer consists of a backbone and side chains which are chemically linked together, it will either behave as a miscible blend of two corresponding homopolymers or as two phases if two components are incompatible. Tobolsky (129) stated that graft and block copolymers are just another way of achieving a successful blend, with the only restriction being that the polymer constituents of the blend and the corresponding polymer must be amorphous and remain amorphous when strained. Nielson (130) described graft copolymers similar to polymer blends in their dynamic behaviour. Stein (131) observed a major change in the bulk properties of graft copolymers by phase reversal, that is, the continuous matrix is formed either by the backbone or grafted chains. This suggested that graft copolymers show phase separations, and the polymer usually consists of sequences of one constituent chain precipitated as droplets in a matrix of the other constituent. The size of the precipitated droplets depends upon the length of the graft as well as upon the interaction energy between the

chemical constituents. Such a two phase system will show physical properties analogous to a mechanical mixture of two different polymers. Each phase will show its normal or near normal glass transition. However, not all the literature data agree with these general statements and some interesting effects can be achieved.

A number of workers (132-134) have postulated intermolecular phase separation within molecules of block and graft copolymers. Block and graft copolymers have sequences of different homopolymers in the same molecule and are of different physical and chemical nature which will greatly effect the behaviour of the graft copolymers in bulk. To study the phase separation of graft copolymers first, the basic concepts which hold for homopolymers will be described and this treatment will be extended to graft copolymers in which the homopolymer sequences are joined by chemical bonds.

# A. <u>Phase separation in a crystalline system</u>

The mixing of homopolymers with each other depends upon the morphology of the components. In crystalline homopolymers a high degree of chemical and structural regularity along the chain is important. Under normal circumstances crystallisation of homopolymers results in a two phase material containing crystalline and amorphous regions. The content of the crystalline and amorphous regions depends upon the chemical nature of the homopolymer and conditions of crystallisation. In a highly crystalline homopolymer the matrix may consist of crystalline regions with the surface of aggregated lamella crystals as amorphous regions, whereas in a low crystalline polymer the crystallites are dispersed in the continuous amorphous phase.

The behaviour of graft copolymers in bulk will depend upon the chemical nature and the conditions which govern the crystallisation of the sequences of polymers joined by chemical bonds. If sequences of polymers are crystalline then the phase separation of graft copolymers will depend on the factors which govern the crystallisation of homopolymers.

# B. <u>Phase separation in an amorphous system.</u>

The process of mixing of two pure polymers at constant temperature and pressure can be presented as a change in the free energy by equation (2.7)

$$\Delta G = \Delta H - T \Delta S \cdots (2.7)$$

where  $\Delta H$  is the change in enthalpy and  $\Delta S$  the change in entropy which occurs in the process and T the absolute temperature. Two polymers will be soluble in each other if  $\Delta G$  is negative and the mixing process is thermodynamically favoured. If  $\Delta G$  is positive a two phase system is stable. Mixing increases the randomness or disorder of the system. Thus a change in entropy is always positive for a mixing process. With the positive absolute temperature, it is seen that the entropy contribution to the free energy change,  $-T\Delta S$  always favours the solution process. The entropy to be gained by intermixing the polymer molecules would be very small owing to the small numbers of molecules involved (135). A segment of a polymer molecule is always constrained to a position between its neighbours in the chain, greatly limiting its configuration possibilities in a mixture. As a result of this small contribution of the entropy terms, in order that the overall  $\Delta G$  be negative, the change in enthalpy upon mixing must be a very small positive value essentially zero or negative for mixing to occur (136-137).

The solubility of two polymers in each other can be predicted by the use of solubility parameters. Solubility parameters are related to the cohesive energy density, which was introduced by Hildebrand (138). The polymers have a great tendency to be soluble in each other if the solubility parameters of the polymers are the same. For non-polar liquids the internal change upon solution is given by

$$\Delta E = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \cdots (2.8)$$

where  $\phi_1 \phi_2$  are the volume fraction and  $\delta_1 \delta_2$  are the solubility parameters of the components respectively. Realising that amorphous polymers are essentially liquids and assuming that the volume change upon mixing is negligible, this is an expression for the change in enthalpy of solution. Since  $\Delta H = \Delta E$  for a constant volume, constant pressure process, the equation always results in a positive  $\Delta H$ , indicating that for non-polar high polymers, where the T $\Delta S$  term is small polymers will not be miscible unless  $\delta$  values are perfectly matched and phase separation will occur even if  $\delta_1$  and  $\delta_2$  are slightly different (139).

Experiments with polymer-polymer systems have indicated that complete compatibility is an exception rather than the rule (140-142). There is only one rubber-glass pair for which adequate evidence has been presented to show complete solubility in the bulk phase, the poly(vinyl chloride)-butadiene/acrylonitrile system where compatibility results due to strong interaction between the polar chloride and nitrile groups, but even then some evidence has shown that the solubility is attained only over limited ranges of molar mass and rubber composition (143-144). Thus, in almost all cases two polymer systems will consist of two phases: one polymer in large excess will form a continuous phase while the second in less concentration will form a dispersed phase.

From the mixing behaviour of non-crystalline homopolymers the following conclusions for graft copolymers can be drawn:

i) The phase separation in graft copolymers consisting of amorphous sequences will be governed by the same principle as in the mixing of two homopolymers. Phase separation will occur as a consequence of the interactions between two sequences of the polymer which result in a positive change in enthalpy just as in the case of a mixture of homopolymers.

ii) The components will be mutually incompatible if they have appreciable differences in chemical structure and composition.

iii) The difference in solubility parameters will also affect the phase separation, higher the difference greater the probability of phase separation.

iv) The morphology of graft copolymers with amorphous components depends upon the segmental ratio (i.e. volume fraction of the two components). The major component will normally exist as a continuous phase, with the minor component present as discrete domains. When the two phases are present in equal volume fractions they can exist in a co-continuous phase with lamellar structures. However, selection of a casting solvent will affect the morphology of the graft copolymer in the solid state. The component least soluble (i.e. most contracted) in the casting solvent utilised will tend to be the first to precipitate during solvent evaporation. This component will form discrete domains which will be dispersed in a continuous matrix of the second expanded component.

# 2.2.2.1 Glass transition temperature (Tg).

When an amorphous high molar mass polymer is cooled through the glass transition region its properties change from those of a soft flexible rubber to those of a hard brittle glass. As a result a change in many physical properties including coefficients of thermal expansion, heat capacity, refractive index, mechanical damping, nuclear magnetic resonance behaviour and electrical properties occur (130). The glass transition temperature can be defined as the temperature at the point of intersection of the extrapolated curves for the melt and the glass phase when any of the quantities such as volume and enthalpy, are plotted against temperature. A typical volume temperature relationship is given in figure (2.6). In terms of molecular behaviour Tg is defined as the temperature above which the polymer has acquired sufficient thermal energy for conformational changes due to rotation about most of the bonds in the backbone of the molecule occur. Although segmental motion does occur within the glassy state, which can be seen by sub Tg transitions, it tends to be subject to serve restriction and occurs on a much more limited scale than above Tg. Thus at the glass transition chain segments of polymer molecules begin to participate in the general kinetic agitation; the coefficient of thermal expansion and the increment of the refractive index changes sharply. Fox and Flory (145), Ueberreiter and Kanig (146) have suggested that since the free volume increases with rising temperature due to thermal expansion, the glass transition temperature will occur when the fraction of the total volume which is free volume reaches a certain critical value. This suggests that the transition temperature and the free volume fraction are intimately connected, and any factor which controls the free volume of a polymer at constant temperature affects







the value of Tg. Such factors can be either chemical or physical in nature. Grafting of a polymer onto a backbone brings structural changes to the backbone and contributes to factors which can effect the glass transition of polymers. In the following section the effect of these changes on the glass transition temperature of a graft copolymer will be described.

# A. <u>Structure of the grafted chain.</u>

Tg is affected by the size and the polarity of the side groups and the mobility of the chains. Any factor disturbing the closest packing of the main chain will lower the Tg. Similarly any factor stiffening or increasing the interaction between chains will increase the Tg. These general principles should equally apply to graft copolymers. However, the majority of these polymers have relatively few graft chains, insufficient to effect the free volume available to the backbone. Therefore the Tg of the backbone will initially be the same as for the homopolymer.

# B. <u>Compatibility of the component polymer chains.</u>

Kargin (147) studied in detail the glass transition of graft copolymers in which the two components were either compatible or incompatible with each other. The glass transition behaviour of graft copolymer systems of starch with polystyrene, PMMA or poly(vinyl alcohol) and poly(acrylic acid) with polystyrene were investigated. Starch/styrene graft copolymers showed a glass transition temperature at the same position as that observed for polystyrene. Similarly, for starch-methyl methacrylate graft copolymers the softening temperatures were practically the same as that for pure poly(methyl methacrylate). Analogous behaviour for poly(vinyl alcohol) and polystyrene graft copolymers were obtained. These graft copolymer systems are composed of components differing sharply in their properties, one of the components being soluble in water and the other in hydrocarbons. This means that the component polymers of the graft copolymer are completely insoluble in each other and the homogeneity of the system is maintained only by the chemical bond between two types of polymer chains. Since two component polymers are of a different nature and are insoluble in each other then these two components must tend to

separate, and any structural process must result first of all in an inhomogeneity of the system giving rise to a very peculiar phenomena of microseparation. The postulate of microseparation as demonstrated in solution is not difficult to maintain in a solid system, and the apparent retention of component properties is mainly due to this process. Kargin (147) further investigated the limit of this additivity by dilution with a plasticiser for one or the other of the components such as tetraline and glycerine for poly(vinyl alcohol-g- styrene). The glass transitions of either the polystyrene or poly(vinyl alcohol) chains change with plasticiser content as if the opposing component is not present. This suggests that in such a system microseparation exists among each component, since they are joined by a chemical bond which prevents them showing a marked separation under ordinary conditions, and addition of plasticiser enhanced it. After studying the glass transition behaviour of pure and plasticised graft copolymers one reaches the conclusion that the transition temperatures characteristic of the individual components in the graft copolymers are retained. This behaviour is characteristic only of such graft copolymers composed of components sharply differing in their properties. With those components whose properties differ less markedly the graft copolymer becomes more like a simple mixture of polymers. For example the glass transition temperature of graft copolymers of nitro-cellulose with poly(methyl methacrylate) and a physical mixture of two component polymers showed practically no difference

# 2.2.2.2 Dynamic mechanical properties.

The dynamic mechanical behaviour of polymers is of great interest. Damping is often the most sensitive indicator of all kinds of molecular motion which are going on in a material even in the solid state. Recently, a large number of high polymers and copolymers of different types have been investigated by dynamic mechanical methods with very interesting results. However, not much work has been done in the field of graft copolymers. The time-temperature variation of the complex modulus, like the dynamic storage (E) or dynamic mechanical loss (tan $\delta$ ), in graft copolymers and block copolymers is influenced by the types of coupling between the sequences of chains, which in turn, depends on the morphology of the system. The typical variation of the



# Typical dynamic mechanical curves for a two phase system.



dynamic mechanical loss curves is shown in figure (2.7) for a system polyA-block-polyB having micro domains in the amorphous state. The first transition at temperature  $T_1$  corresponds to the onset of segmental motion in phase A. The second transition at temperature  $T_2$ corresponds to the glass transition of microphase B. Graft copolymers shows a similar behaviour where two sequence of chains retain their properties. Shinohara (148) studied the dynamic mechanical behaviour of nylon-6 graft copolymers with vinyl monomers including methyl methacrylate (MMA), acrylic acid (AA), acrylonitrile (AN), vinyl acetate (VA), methyl acrylate (MA) and ethyl acrylate (EA) and measured the rigidity and tan  $\delta$  as a function of temperature. Two relaxation peaks one at 80 °C characteristic of nylon-6 and another peak at a position corresponding to vinyl homopolymer were observed and it was concluded that the two peaks for graft copolymers are due to the onset of segmental motion of the backbone nylon polymer and the grafted vinyl polymer respectively. Baccaredde and co-workers (149) investigated the dynamic mechanical behaviour of poly(styreneacrylonitrile)-g-(butadiene-acrylonitrile) in some detail. Dynamic mechanical properties (sound velocity and damping factor) were determined in samples of different polymeric mixtures and of the corresponding grafted copolymers, at the same frequencies of the order of 10 kHz over a wide temperature range. In the mixtures the same relaxation phenomena, characteristic of each component, were found and were located at the same temperature as the pure components. In the grafted materials, if the degree of branching was sufficiently high, the relaxation phenomena relative to the base components was shifted toward lower temperatures, compared with the corresponding phenomena relative to the same components in the pure state or in a mixture with the grafted components. These shifts were much more marked when the base components were characterised by polar chains or by hydrogen bridges between macromolecules.

39.

# CHAPTER 3

# **EXPERIMENTAL**

# 3.1 List of chemicals used with abbreviations

Acetone, SLR grade was used as supplied by Carless solvents.  $4\dot{A}$ -Azobis (isobutyronitrile) (AIBN) was used as supplied.

4,4-Azobis(4-cyanovaleric acid) (ACVA) was used as supplied by Fluka Chemie AG.

Benzoic acid, 99+% purity, was used as supplied by Aldrich Chemical Company Ltd.

Butanethiol, was used as supplied by Aldrich Chemical Company Ltd.

Tetrabutyl ammonium hydroxide (TBAH) was used as supplied by Aldrich Chemical Company Ltd, 1.0M solution in methanol.

Butyl acrylate, (BA), supplied by Aldrich, was inhibited with 10-55 ppm hydroquinone monoethyl ether and was purified by vacuum distillation at room temperature.

Calcium hydride, 95+% (CaH<sub>2</sub>), was used as supplied by Aldrich Chemical Company Ltd, as a coarse ground powder.

Chloroform (CHCl<sub>3</sub>), SLR grade was used as supplied by Carless solvents.

Cyclohexane, SLR grade was used as supplied by Carless solvents.

Ethanol, SLR grade, was used as supplied by Carless solvents.

2-Ethoxyethanol, 99% pure, was used as supplied by Aldrich Chemical Company Ltd.

Ethyl acetate, SLR grade, was used as supplied by Carless solvents.

2-Hydroxyethyl methacrylate, (HEMA) was supplied by Aldrich Chemical Company Ltd, in 97% purity, inhibited with 300 ppm hydroquinone monoethyl ether. This was dried over anhydrous magnesium sulphate before use.

Propan-2-ol (isopropanol), AR grade, was used as supplied by Fisons plc.

Anhydrous magnesium sulphate (Mg SO<sub>4</sub>) was used as supplied by Fisons plc.

Methanol, SLR grade, was used as supplied by Carless solvents.

4-Methyl pentan-2-one (methyl isobutyl ketone) (MIBK), AR grade was used as supplied by Fisons plc.

Methyl methacrylate (MMA), was obtained from Aldrich Chemical Company Ltd, 99% pure and inhibited with 100 ppm hydroquinone monoethyl ether. This was purified by vacuum distillation at room temperature before use.

Oxalyl chloride, 98% pure, was supplied by Aldrich Chemical Company Ltd and was used as supplied.

Petroleum ether (40:60), SLR grade was used as supplied by Carless solvents.

Phenyl ethyl methacrylate (PHETMA), was obtained from Polysciences Inc. inhibited with 200 ppm hydroquinone monoethyl ether. This was purified by passing through an inhibitor remover column.

Phenolphthalein, primary standard reagent, was used as supplied by Aldrich Chemical Company Ltd.

Potassium hydroxide (KOH) pellets, 97+% pure were used as supplied by BDH Chemicals Ltd.

Potassium hydrogen phthalate, primary standard grade was used as supplied by Aldrich Chemical Company Ltd.

Silica gel, self indicating granules, was used as supplied by Fisons plc.

Styrene(Sty), was obtained from Aldrich Chemical Company Ltd, 99% pure, inhibited with 10-15 ppm 4-ter-butyl catechol. This was purified by vacuum distillation at room temperature before use.

Sodium hydroxide (NaOH) pellets, 97% pure, were used as supplied by BDH Chemicals Ltd.

Mercaptoacetic acid, (thioglycollic acid, TGA), 95% pure was used as supplied by Aldrich Chemical Company Ltd.

Tetrahydrofuran (THF), unstabilised AR grade, was used as supplied by Fisons plc.

Thymol blue, ACS reagent, was supplied by Aldrich Chemical Company Ltd. This was used as a 2%(w/v) solution in methanol.

Toluene, SLR grade, was supplied by Carless solvents. It was dried over CaH<sub>2</sub> before use.

Para toluene sulphonic acid (PTSA), obtained from Aldrich Chemical Company Ltd, was used as supplied.

Xylene, AR grade, supplied by Fisons plc was dried over sodium wires before use.

# 3.2 Synthesis of carboxyl terminated prepolymers.

The carboxyl terminated prepolymers of MMA, PHETMA and BA were synthesised by free-radical solution polymerisation. ACVA and TGA were used as matched free-radical initiator and chain transfer agent, respectively. In a three necked round bottom flask (250ml) containing nitrogen inlet and reflux condenser, monomer mixed with TGA was added in ethyl acetate as polymerisation solvent. After purging with nitrogen for 15 minutes ACVA was added and the flask was transferred to a thermostated water bath maintained at 80°C. The polymerisation time was 2 hours for MMA, 4 hours for PHETMA and 3 hours for BA. The procedure for isolating and purifying the polymers was as follows.

# (a) <u>PMMA.</u>

The polymer was isolated by evaporating the ethyl acetate solution. Impure polymer was dissolved in a minimum amount of methanol and was precipitated in an excess of distilled water. PMMA was precipitated as a white viscous material. Further purification was carried out by redissolving polymer in a minimum quantity of hot methanol and reprecipitation in distilled water which was repeated two further times.

# (b) <u>PPHETMA.</u>

Impure PPHETMA was isolated by evaporating the ethyl acetate solution. The resultant polymer was dissolved in a minimum amount of chloroform and was precipitated in chilled methanol. Redissolution/reprecipitation steps were repeated two further times.

# (c) <u>PBA.</u>

The ethyl acetate was evaporated off and impure polymer was dissolved in petroleum ether (40:60). This petroleum ether solution was cooled with liquid nitrogen. The polymer was sedimented at the bottom of beaker and petroleum ether was discarded. Remaining traces of petroleum ether were evaporated off by leaving the beaker in the fume cupboard for several hours. The impure polymer was dissolved in methanol and poured into water. The polymer separated as a

viscous liquid on the surface which was removed, redissolved in a minimum amount of hot methanol and poured into distilled water. This procedure was repeated three times.

Finally, all the purified polymers were dried in a vacuum oven with a solvent trap, initially at 100°C for 2-3 hours to removed traces of water, and then at 60°C overnight. The pure polymers were characterised by end group analysis, gel permeation chromatography, NMR and IR.

# 3.2.1 <u>Conversion of carboxyl terminated prepolymers to acid chloride.</u>

The carboxyl terminated prepolymers were converted to acid chloride by reaction with oxalyl chloride. Oxalyl chloride was preferred to thionyl chloride since it is less reactive (150). The prepolymer (equal to the moles of HEMA present in a Sty-HEMA copolymer backbone for the synthesis of poly(Sty-HEMA)-g-PMMA or equal to the moles of VOH present in EVOH copolymer backbone for the synthesis of poly(ethylene-vinyl alcohol) graft copolymers) was dissolved in dry toluene and this solution placed in a three necked round bottom flask (100ml), equipped with a silica-gel drying tube. The oxalyl chloride twice the required molar concentration of the polymer was added. The solution in a flask was first cooled in an ice bath followed by stirring at room temperature for 24 hours. The unreacted oxalyl chloride was distilled off under vacuum at room temperature. The conversion of carboxyl group to acid chloride was confirmed by IR.

# 3.3 <u>Synthesis of poly(Sty-HEMA)-g-PMMA graft</u> copolymers.

# 3.3.1 Synthesis of Sty-HEMA copolymers .

The monomers Sty and HEMA were copolymerised in 2-ethoxyethanol using AIBN as initiator. In a three necked round bottom flask (250ml) equipped with nitrogen inlet and reflux condenser, the monomers were mixed and added to the polymerising solvent 2-ethoxyethanol. The nitrogen purge was for five minutes, and the flask was transferred to a thermostated water bath maintained at 60°C .The polymerisation was allowed to proceed for 6 hours. After the polymerisation the reaction mixture was cooled and poured into chilled petroleum ether

(40:60). The copolymer was isolated as a viscous liquid which settled at the bottom of the flask. The petroleum ether was decanted off. The copolymer was purified by dissolution in a minimum amount of toluene and precipitated in chilled cyclohexane. Further purification was performed by redissolving copolymer in a minimum amount of chloroform and reprecipitating in chilled methanol. This procedure was repeated three times. Finally, the pure copolymer was dried in a vacuum oven at 60°C overnight.

# 3.3.2 <u>Condensation of PMMA acid chloride with Sty-HEMA</u> <u>copolymer.</u>

A 5% w/v solution of PMMA acid chloride (synthesised in section 3.2.1) in dry toluene was prepared. This solution was placed in a three necked round bottom flask (250ml) fitted with reflux condenser and silica gel drying tube. A 2% w/v solution of Sty-HEMA copolymer in dry toluene was added to the PMMA acid chloride solution with a dropping funnel. This mixture was allowed to reflux for 24 hours at 110°C with nitrogen bubbling through the reaction mixture. After the reaction the mixture was cooled and impure graft copolymer was isolated by pouring into chilled n-hexane. The unreacted PMMA was removed by dissolving impure graft copolymer in a minimum quantity of chloroform and precipitating in chilled methanol. This redissolution/precipitation procedure was repeated five times. The purified graft copolymer was dried in a vacuum oven at 60°C for 24 hours.

A parallel experiment was performed to check transesterification during the condensation reaction of PMMA acid chloride with the Sty-HEMA copolymer backbone. A prepolymer with no carboxyl end group was synthesised For this purpose butanethiol as chain transfer agent and AIBN as free-radical initiator were used. The polymerisation, polymer isolation and purification methods were the same as described in section 3.2.

A 5%w/v solution of butanethiol terminated PMMA in dry toluene was prepared and was placed in a three necked round bottom flask (250ml) fitted with reflux condenser and silica gel drying tube. A 2%w/v solution of Sty-HEMA copolymer in dry toluene was added to the PMMA solution with a dropping funnel. Para toluene sulphonic acid (PTSA), equivalent to the total moles of HCl which could be produced during the condensation of PMMA acid chloride with the Sty-HEMA backbone was added to the reaction mixture. The reaction mixture was allowed to reflux by bubbling nitrogen through the solution for 24 hours at 110°C. The isolation and purification of the components from the reaction mixture were the same as described above, except that the unreacted PTSA was removed from the components by washing thoroughly with acetone. The pure components were dried in a vacuum oven at 60°C for 24 hours.

# 3.4 <u>Synthesis of poly(ethylene-vinyl alcohol) graft copolymers.</u>

# 3.4.1 <u>Complete hydrolysis of ethylene vinyl acetate copolymers</u>.

Two different grades of commercial EVA copolymers supplied by Dr D.E. Higgins, ICI Petrochemicals and Polymers Division were used. EVA copolymers with VA contents of 9.8 mole % and 21 mole % were hydrolysed to EVOH copolymer products. A 20 % w/v solution of EVA copolymer in xylene was prepared. The required amounts of EVA and xylene were placed in a three necked round bottom flask (500ml) fitted with a reflux condenser and nitrogen inlet. The flask was placed on an oil bath having a magnetic stirrer. The mixture was allowed to reflux for 2-3 hours with constant stirring, so that EVA copolymer completely dissolved. In a separate flask KOH was dissolved in ethanol. An excess of three to four times the stoichiometric amount of KOH was used for complete hydrolysis of EVA copolymers. The required amount of KOH was dissolved by refluxing in ethanol in the ratio 1:3 by volume of xylene used for the EVA solution. The EVA solution temperature was maintained at 65°C. The KOH solution was added slowly by dropping funnel to an EVA solution with vigorous stirring. After the complete addition of the KOH solution, the reaction mixture was allowed to reflux for 24 hours. It was removed from the oil bath and cooled to room temperature. The product was isolated by pouring the reaction mixture into excess methanol. The copolymer precipitated as a whitish powder and sedimented at the bottom of a beaker after allowing the mixture to stand for several hours. The methanol was decanted and the remaining methanol was removed by filtration. The product was washed with methanol several times to remove traces of xylene, followed by washing with acetone. The inorganic salts were removed from the product by washing thoroughly with distilled water. Finally, the product was washed with methanol and acetone. The purified copolymer product obtained was dried in a vacuum oven at 60°C for 24 hours.

# 3.4.2 Partial hydrolysis of ethylene vinyl acetate copolymer.

The EVA copolymer containing 21 mole % VA was partially hydrolysed to a terpolymer of ethylene-vinyl acetate-vinyl alcohol. The required amounts of EVA and KOH were dissolved in xylene and ethanol, respectively by the same procedure as described in section 3.4.1. For the partial hydrolysis of EVA the KOH was used as half the molar amount of VA present in EVA. The EVA solution was placed in a round bottom flask (500ml) fitted with reflux condenser and nitrogen inlet. It was stirred on an oil bath and the temperature was maintained at 65°C. The KOH solution was added to the EVA solution slowly with vigorous stirring. After the complete addition of KOH solution the reaction mixture was allowed to reflux for 24 hours. The product was isolated and purified by the same method as described in section 3.4.1.

# 3.4.3 <u>Condensation of carboxyl terminated prepolymer with ethylene-</u> <u>vinyl alcohol copolymer</u>.

The conversion of carboxyl terminated prepolymers PMMA, PPHETMA and PBA to acid chloride is describe in section 3.2.1. For the condensation reactions moles of acid chloride terminated prepolymer equal to the moles of VOH present in the EVOH copolymer were used. A 2 % w/v solution of EVOH copolymer in dry xylene was prepared. The required amount of EVOH was placed in a three necked round bottom flask with reflux condenser and nitrogen inlet. Dry xylene was added to the EVOH copolymer and the mixture was allowed to reflux for one hour under nitrogen. A 10 % w/v solution of acid chloride terminated prepolymer in dry xylene was prepared separately and then added to the EVOH solution slowly with a dropping funnel. The mixture was allowed to reflux at 140°C for 24 hours under a constant stream of nitrogen. After the reaction, the mixture was cooled down to room temperature. Graft copolymers were isolated in two steps. First, unreacted polymer backbone was removed, which because of its insolubility in xylene at room temperature can be separated by filtering the reaction mixture. Second, the resulting filtrate was added to excess methanol in order to precipitate the graft copolymer product with unreacted prepolymer remaining dissolved. Further purification was carried out by redissolving the graft product in chloroform and precipitating in methanol. After at least six redissolution/reprecipitation steps the methanol filtrate was poured into n-hexane to check any traces of unreacted prepolymer present in the methanol solution. At each purification/filtration step the methanol solution was evaporated off and the product was analysed by GPC to check the effectiveness of the purification step for removing unreacted prepolymer.

In order to check the possibility of any transesterification reactions during the condensation of carboxyl terminated prepolymer with the copolymer backbone a series of reactions was performed. First, prepolymers PMMA, PPHETMA and PBA with no carboxyl end group were synthesised by the procedure described in section 3.2. The monomers MMA, PHETMA and BA were polymerised in the presence of butanethiol as chain transfer agent and AIBN as initiator. The polymerisation conditions, the polymer isolation and purification procedures were the same as described in section 3.2.

A 2% w/v solution of copolymer in dry xylene and a 10% w/v solution of prepolymer in dry xylene were prepared as described earlier in this section. The two solutions were mixed together in a round bottom flask fitted with a reflux condenser and a nitrogen inlet. PTSA, equal to the total moles of HCl that can be produced during the condensation reaction of EVOH copolymer and acid chloride terminated prepolymer, was added to the reaction mixture which was allowed to reflux at 140°C under nitrogen for 24 hours. After the reaction, the mixture was allowed to cool down to room temperature. The components from the reaction mixture settled at the bottom of the flask, were removed by filtration and washed thoroughly with acetone to remove PTSA.

# 3.5 <u>Preparation of polymer blends.</u>

The blending of poly(ethylene-vinyl alcohol)-graft-PMMA graft copolymers with PVC was carried out using a mutual solvent method.

The blend constituents were dissolved independently in THF at a concentration in the range 0.01-0.03 g/ml on a shaker for 2-3 hours. These solutions were mixed in appropriate quantities to yield a solution of required composition. After mixing, the solutions were shaken for 4-5 hours to ensure homogeneity. The solution was then poured into a crystallisation dish and was left in a fume cupboard to permit evaporation of THF. The removal of last traces of solvent, most of which were trapped in the blend film was undertaken during the sample preparation for DMTA analysis. Samples were pressed between filter papers on a hydraulic press at 120  $^{0}$ C above the softening point of a graft copolymer and PVC for 5 minutes and then cooled to room temperature.

# 3.6 Characterisation.

#### 3.6.1 End group analysis.

The number average molar mass of carboxyl terminated prepolymers PMMA, PPHETMA and PBA was determined from end group titration data. The PMMA was analysed by aqueous titration. PPHETMA and PBA were analysed by non-aqueous titration. Both titration methods are described as follows.

# (a) <u>PMMA.</u>

A solution of NaOH (0.05M) was prepared in distilled water. It was standardised by a solution of potassium hydrogen phthalate (0.05M) using phenolphthalein as indicator to the end point light pink. 1.0g of PMMA was dissolved in 50ml of hot methanol. 10ml of polymer solution was placed in a conical flask and a few drops of indicator phenolphthalein were added. The solution was titrated against standard NaOH solution to the end point (light pink). For each polymer solution a minimum of three readings were taken and the average value was used to calculate the number average molar mass of polymer assuming one carboxyl end group per chain.

# (b) <u>PPHETMA and PBA.</u>

A solution of tertiary butyl ammonium hydroxide (TBAH) in isopropanol (0.04M) was prepared from a TBAH solution (1M) supplied in methanol. The resultant (TBAH) solution was standardised with a benzoic acid solution (0.04M) using thymol blue as indicator to the end point (light blue). 1.0g of polymer was dissolved in 25ml methyl iso butyl ketone (MIBK). 5ml of polymer solution was placed in a conical flask and few drops of indicator thymol blue were added. The solution was titrated against a standard solution of (TBAH) to the end point (light blue). For each polymer the titration was repeated at least three times and the average value was taken to calculate the number average molar mass of polymer assuming one carboxyl end group per chain.

# 3.6.2 Gel permeation chromatography(GPC).

The purity and molar mass distribution (MMD), of synthesised polymers were determined by gel permeation chromatography (GPC). The characterisation of carboxyl terminated prepolymers, Sty-HEMA copolymers, poly(Sty-HEMA)-g-PMMA graft copolymers and poly(ethylene-vinyl alcohol) graft copolymers by GPC were performed as described in the following section.

# 3.6.2.1 <u>Carboxyl terminated prepolymers.</u>

The low molar mass carboxyl terminated PMMA, PPHETMA and PBA samples were analysed by a GPC system having two columns (60 cm and 30 cm long) supplied by Polymer Laboratories Ltd. The columns were packed with crosslinked polystyrene beads of nominal pore size 500Å and 100Å. The solutions of polymer (0.15 % w/v) in THF with 5µl toluene as internal marker were used. Solutions were filtered through a Whatman micro fiber filter paper. A polymer solution was injected into the column system through a valve containing a 50µl loop. The samples were eluted with THF (HPLC grade) using a Knauer HPLC pump 64 with flow rate 1 ml per minute. The polymer concentration response in terms of refractive index was obtained with a Knauer differential refractometer, connected to a J.J chart recorder with a 100 mv range setting. The columns were calibrated with polystyrene



Figure 3.1 Analysis of GPC chromatogram.
### Figure 3.2 GPC calibration curve for polystyrene standards in THF for the 500 Å & 100 Å columns



% - Toluene

standards supplied by Polymer Laboratories Ltd. The refractive index chromatograms of polymer samples were analysed by dividing the chromatographic curves into a series of trace heights and elution volumes (retention volumes) at 1% intervals by taking the injection point as zero elution volume and toluene peak as complete elution (figure 3.1). By comparing the elution volumes with a polystyrene calibration curve which was constructed using a series of polystyrene standards with molar masses varying from Mp=164 to 22.0x 10<sup>3</sup> g.mol-1 and plotting log (peak molar mass) against elution volume(figure 3.2). A list of trace heights and molar masses was obtained. This information was analysed by a computer program as used by Croucher(151) in order to obtain the number average molar mass (Mn), the weight average molar mass(Mw), the peak average molar mass (Mp) and the polydispersity (Mw/Mn).

#### 3.6.2.2 Sty-HEMA copolymers and poly(Sty-HEMA)-g-PMMA

#### graft copolymers.

The GPC system used for the characterisation of these polymers consisted of a mixed gel column(60 cm long) supplied by Polymer Laboratories Ltd, packed with crosslinked polystyrene beads with a particle size of  $10\mu m$ . The 0.15% w/v polymer solution was filtered through a Whatman microfiber filter paper and was injected into the column through an injection valve with a 200  $\mu$ l loop. The samples were eluted with THF (HPLC grade) using a Knauer HPLC pump 64 at a flow rate of 1.0 ml per minute. The polymer concentration response was obtained both in terms of refractive index (RI) and ultraviolet (UV) absorption. For this purpose a Knauer 60 differential refractrometer and a Pye Unicam UV detector at a fixed wavelength of 267nm were used. The responses from RI and UV detectors as a function of elution volume were obtained with a two channel J.J chart recorder. Each chromatogram was obtained with the same experimental conditions (table 3.1) of the GPC system. The column was calibrated with polystyrene standards using a series of standards (supplied by Polymer Laboratories Ltd) with molar masses varying from Mp=1.25x10<sup>3</sup>to 2.1x10<sup>6</sup>g.mol<sup>-1</sup>. A calibration curve was plotted of log (peak molar mass) against elution volume (figure 3.3). The chromatogram was

Table 3.1 <u>GPC system experimental conditions used for the</u> <u>characterisation of Sty-HEMA copolymers, poly(Sty-HEMA)-g-</u> <u>PMMA and poly(ethylene-vinyl alcohol) graft copolymers.</u>

GPC system.	Poly(Sty-HEMA)- g-PMMA & St-	Poly(ethylene- vinyl alcohol)
	HEMA copolymers.	graft copolymers.
Column.	Mixed gel 60 cm long with particle size 10 µ	Mixed gel 10 cm long , particle size 10 µ
Solvent	HPLC grade THF.	0-Dichloro benzene with antioxidant BHT.
Temperature	Room temperature.	140 °C.
Detector	UV detector at wavelength 267 n m and RI detector.	IR detector at wavelength 3.42 micron.
Flow rate	1.0 ml per minute.	1.0 ml per minute.
Concentration.	0.15 % w/v	0.10 % w/v
Volume injected	0.15 ml.	0.20 ml.

Figure 3.3 GPC calibration curve for polystyrene standards in THF for the mixed gel column.



Toluené %

analysed by using this calibration curve in the same manner as described earlier (section 3.5.2.1) to calculate MMD.

#### 3.6.2.3 <u>Poly(ethylene-vinyl alcohol) graft copolymers.</u>

The characterisation of poly(ethylene-vinyl alcohol) graft copolymers was performed with a high temperature (140°C) GPC system with odichlorobenzene as solvent. It was carried out at RAPRA technology Limited Shrewsbury, Shropshire. A solution of graft copolymer was obtained by adding 50ml of boiling solvent to 50mg of sample through a glass fiber pad at 160°C. The filtered solutions were reheated to boiling immediately before the chromatography and each solution was run in duplicate. The chromatographic conditions are given in table 3.1. The results obtained were stored on computer software. The chromatogram was obtained in terms of retention volume and IR response of polymer concentration. This IR chromatogram was analysed by computer program which gave an overlay of molar mass distribution in terms of (log M) by comparing the retention volume and IR response with a polystyrene calibration curve. All results of molar mass for graft copolymers were based on polystyrene standards.

#### 3.6.3 Infra-red spectroscopy (IR).

The Nicolet 20 Dx FTIR spectrometer was used for the qualitative and quantitative analysis of synthesised polymers.

#### (a). <u>Qualitative analysis.</u>

The qualitative analysis of carboxyl terminated prepolymers, acid chloride terminated prepolymers, Sty-HEMA copolymers and poly(Sty-HEMA)-g-PMMA graft copolymers was performed by casting a polymer film on a sodium chloride disc. A polymer solution in chloroform (20% w/v) was used to cast a film. The solution was spread on a sodium chloride disc with the help of a glass rod. The chloroform was allowed to evaporate off leaving a polymer film on the disc. Prior to a sample run, a background spectrum for each run was recorded by placing the blank sodium chloride disc in the sample holder. Typically, 20 scans over the range of 4000-600 cm<sup>-1</sup> at resolution 2 cm<sup>-1</sup> were

performed. The computer recorded the sample spectrum on the software after subtracting, automatically a background spectrum.

#### (b) <u>Quantitative analysis.</u>

By a suitable calibration of the infra-red absorption of a group in a compound, the concentration of groups can be determined quantitatively. Absorption is given by Beer's law (152).

#### $A = \varepsilon bc \qquad (3.1)$

where A is the absorbance, b is the path length, c is the concentration and  $\varepsilon$  is the extinction coefficient. The chemical composition of the ethylene-vinyl acetate (EVA) copolymers were quantitatively determined from the carbonyl absorption of acetate units at 1743 cm<sup>-1</sup>. A calibration curve in toluene of absorbance versus concentration was established with solutions of commercial poly(vinyl acetate) (PVA), of Mw 9.0x 10<sup>4</sup> supplied by Polysciences Inc Warrington. Solutions of PVA were prepared in toluene in a volumetric flask. In order to obtain the spectrum for each solution, a sodium chloride solution cell (supplied by Perkin Elmer) was firstly, filled with neat toluene. The cell was placed in the sample compartment. 20 scans were taken from 4000-600 cm<sup>-1</sup>at a resolution of 4 cm<sup>-1</sup> and the spectrum was stored in the background file of the software. The cell was then removed, cleaned and filled with sample solution. The spectrum was determined as described above. The software automatically subtracted the background spectrum from the sample spectrum and gave the spectrum of the polymer. Peak absorbance at 1743  $cm^{-1}$  for each concentration was determined and a calibration curve of concentration versus absorption was plotted (figure 3.4). Solutions of EVA copolymers in toluene were then accurately prepared and spectra were measured in the same manner as described above. The absorbance of the carbonyl peaks in the EVA copolymer samples were then compared to the calibration curve in order to determine the concentration of acetate units.

The chemical composition of poly(ethylene-vinyl alcohol) graft copolymers were quantitatively determined from the carbonyl absorption of prepolymer units in the graft copolymer at 1732 cm<sup>-1</sup>. For each graft copolymer system a prepolymer with no carboxyl end group was synthesised using butanethiol chain transfer agent (see section





PVA conc % w/v

3.4.3). Solutions of butanethiol terminated prepolymers of various concentrations were prepared in CHCl<sub>3</sub> in volumetric flasks. The spectrum was determined for each solution as described above. Peak absorbancies at 1732 cm<sup>-1</sup> for butanethiol terminated prepolymers were determined and used to established a calibration curve, of concentration versus carbonyl absorption (figures 3.5-3.7). Solutions of graft copolymers in CHCl<sub>3</sub> were then accurately prepared and spectra were measured in the same manner as described above.

The absorbances of carbonyl peaks in the graft copolymer samples were then compared to the respective calibration curve in order to determine the concentration of prepolymer units in the graft copolymers.

#### 3.6.4 Nuclear Magnetic resonance spectroscopy (NMR).

A Bruker 250 MHz NMR was used for qualitative and quantitative analysis of synthesised polymers. The qualitative analysis of carboxyl terminated prepolymers was performed by dissolving 20mg of sample in 1 ml of deuterated CHCl<sub>3</sub> with TMS added as reference. The samples were filtered through a Whatman glass fiber filter paper. Typically, 500 scans for each sample were recorded for the range of 0-10  $\delta$  value.

The chemical composition of Sty-HEMA copolymers, poly(Sty-HEMA)g-PMMA and poly(ethylene-vinyl alcohol) graft copolymers was determined by dissolving 20mg of each polymer sample in 1 ml of deuterated CHCl<sub>3</sub> with TMS as reference. The procedures for the determination of composition are discussed for Sty-HEMA copolymers, and poly(Sty-HEMA)-g-PMMA graft copolymers in section 4.2 and for poly(ethylene-vinyl alcohol) graft copolymers in section 4.4.

#### 3.6.5 Differential Scanning Calorimetry (DSC) .

#### A. <u>Principle.</u>

Differential scanning calorimetry is a technique used for studying the thermal behaviour of materials as they undergo physical and chemical changes during heating or cooling. The sample to be examined is kept at the same temperature as a reference and the heat flow into each necessary to maintain the constant temperature is measured. This is



Figure 3.5 Butanethiol terminated PMMA calibration curve in chloroform.

Moles of MMA 10-4



# Figure 3.6 Butanethiol terminated PPHETMA calibration curve in chloroform.

Moles of PHETMA 10-4





Moles of BA 10-4

· .

achieved by placing separate heating elements in the sample and reference chambers; the rate of heating by these elements can be controlled and measured as desired. A typical DSC cell is shown in figure 3.8. It consist of the following components. The sample holder assembly which incorporates sample and reference container pans placed on the raised platform or thermoelectric disc which is made of constantan. The temperature programmer is capable of giving a wide range of heating and cooling rates and isotherm operating modes. A recording device incorporated an amplifier, which received the signal from the temperature sensor and differential temperature thermocouples. DSC plots are graphs of the differential rate of heating versus temperature (figure 3.9). The area under the peak is directly proportional to the heat evolved or absorbed by the change (endothermic or exothermic), and the height of the curve is directly proportional to the rate of reaction.

#### B. <u>DSC analysis.</u>

The thermal behaviour of EVA, EVOH copolymer samples and poly(ethylene-vinyl alcohol) graft copolymers were studied by using a Du Pont 2000 DSC fitted with cooling and computing accessories. The DSC cell contained sample and reference pans, heated at a constant rate. In the calorimetric mode the temperature difference between sample and reference was recorded against the temperature of the reference. The instrument was calibrated with indium (melting point 156.5 °C).

Samples were prepared by accurately weighing 10 mg into an aluminium pan and placing an aluminium lid on the top. The removing and placing of sample were performed at room temperature to avoid the accumulation of ice in the DSC cell. A sample was then cooled to 0 °C and was scanned under a nitrogen atmosphere over the temperature range of 0-130 °C. Cooling and heating rates of 10 °C per minute were used. For each sample endothermic and exothermic modes were recorded. The thermograms were stored on computer software. The endothermic and exothermic peaks on the thermograms were analysed by using a computer program, which determined the heat changes and the crystalline melting point of the sample.



## Figure 3.9

Differential scanning calorimetry out put from a instrumen showing thermal transitions in a polymer sample.

#### 3.6.6 <u>Wide angle x-ray scattering (WAXS).</u>

The method of x-ray diffraction is one of the oldest and most widely used techniques for the study of polymer structure. Crystalline polymers are arranged in a definite crystal lattice consisting of crystallographic planes. An incident x-ray beam is diffracted by these planes at different angles and intensities. Knowledge of these angles of diffraction and intensity of diffraction provide useful information regarding the structure of a polymer.

The reflection of electromagnetic radiation is governed by Bragg's law given by equation below,

$$n \lambda = 2d \sin \theta \dots (3.2)$$

where n is an integral denoting the order of diffraction,  $\lambda$  is the wavelength of the x-ray beam,  $\theta$  is the angle of incidence and reflection and d is the spacing between planes of atoms causing the reflection. To generate diffraction maxima from the planes with a given spacing d either  $\lambda$  or  $\theta$  should be varied. In the usual experiments it is  $\theta$  that is varied

The x-ray diffraction patterns of poly(ethylene-vinyl alcohol) graft copolymers were recorded using a x-ray powder diffractometer with symmetrical reflectance geometry and driven by a Hilterbrooks step scan motor, operating at 20 steps per second. A Philips 1130/00 x-ray generator was used. The x-ray beam used was nickel filtered CuK $\alpha$ radiation( $\lambda$ =1.54Å) generated at a tube voltage of 40 KV and tube current of 20 mA. Detection was by proportional counter with a pulse height analyser which sent reflection pulses to a ratemeter which was attached to a chart recorder at a speed of 20 mm per minutes.

The samples were cast films on a glass slide from chloroform solutions of poly(ethylene-vinyl alcohol)-g-PPHETMA and poly(ethylene-vinyl alcohol)-g-PBA. The poly(ethylene-vinyl alcohol)-g-PMMA samples were powdered and were prepared by the following procedure. Some wax was put on a glass slide on to which powder was sprinkled and another glass slide was put on top. The two were then gently pressed together to ensure that the sample was uniform with respect to the x-

ray beam. The samples were scanned at a rate of  $2\theta = 1^{\circ}$  per minute, in the range of  $2\theta = 5^{\circ}$  to 35°. The diffraction patterns were recorded as relative intensity versus 2 $\theta$ .

#### 3.6.7 Dynamic Mechanical Thermal Analysis (DMTA).

One of the most important techniques for studying the mechanical properties of polymers is dynamic mechanical thermal analysis, which involves impressing a small oscillating mechanical strain on a solid or viscoelastic liquid, and resolving stresses and strains into real and imaginary components. Changes in the state of molecular motion as temperature is scanned are detected. It is thus a most powerful technique for studying the effect of not only molecular structure, but also phase morphology, on physical properties.

#### A. <u>Principle</u>

Elastic materials obey Hooke's law, that is stress is directly proportional to the applied strain. Viscous liquids follow Newton's law of viscosity which states that stress is directly proportional to the rate of strain. On the other hand polymeric materials have properties which lies between these two and are termed as viscoelastic. In a dynamic mechanical test a sample is deformed by a stress which varies sinusoidally with time. The strain is neither in phase with the stress nor 90° out of phase but adopts an intermediate value. This phase lag results from the time necessary for molecular rearrangements and is associated with relaxation phenomena. The stress  $\sigma$  and strain  $\in$  can be expressed as follows:

where  $\omega$  is the angular frequency and  $\delta$  is the phase angle. Then,

 $\sigma = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta$ .....(3.5)

The stress can be considered to consist of two components, one in phase with strain ( $\sigma_0 \cos \delta$ ) and other 90° out of phase ( $\sigma_0 \sin \delta$ ). When these are divided by strain, the modules can be separated into





in-phase (real) and out-of-phase (imaginary) component. The relationships are

$$\sigma = \epsilon_0 E' \sin \omega t + \epsilon_0 E' \cos \omega t \dots (3.6)$$

where the storage modulus  $\vec{E}$  is equal to  $\left(\frac{\sigma_0}{\epsilon_0}\right)\cos\delta$  that is, the component of stress in-phase with the strain divided by the strain amplitude, and the loss modulus  $\vec{E}$  is equal to  $\left(\frac{\sigma_0}{\epsilon_0}\right)\sin\delta$ , that is the component of stress out-phase with strain divided by the strain amplitude. Dividing the loss modulus by storage modulus leads to the loss tangent  $\delta$  and is given by the equation below,

 $\frac{\overset{\prime}{E}}{\overset{\prime}{E'}} = \frac{\frac{\overset{\prime}{\Theta_{o}}}{\overset{\phantom{}}{\epsilon_{o}}} \sin \delta}{\frac{\overset{\phantom{}}{\Theta_{o}}}{\overset{\phantom{}}{\epsilon_{o}}} \cos \delta} = \tan \delta \qquad (3.7)$ 

The equation shows that  $\tan \delta$  is the ratio of the energy stored as potential energy to the energy lost as dissipation energy during a cycle.

The variation of E/E or tan  $\delta$  in the frequency plane and temperature plane for a typical homopolymer in the region of the glass transition is given in figure 3.10 At low temperature and high frequency storage modulus is characteristic of a glassy material. On increasing temperature and decreasing frequency, the storage modulus becomes characteristic of a rubbery material, the loss modulus in both cases has passed through its peak. The peak in tan  $\delta$  corresponds to the maximum in the damping and is interpreted as the glass transition temperature of the polymer.

#### B. **Dynamic mechanical measurements.**

The dynamic mechanical behaviour of EVA, EVOH copolymers and poly(ethylene-vinyl alcohol) graft copolymers and polymer blends of graft copolymer with poly(vinyl chloride) (PVC) were analysed with a Polymer Laboratories dynamic mechanical thermal analyser. It consisted of a DMTA head (figure 3.11) with a cooling coil, a microprocessor controlled temperature programmer and a computer accessory. The DMTA head required a rectangular sample clamped



### Figure 3.11

#### DMTA measuring head.



Figure 3.12

Dual cantilever clamping arrangements.

(figure 3.12) onto a fixed frame with bars at both ends. The sample was oscillated at its centre by a central clamp attached to a drive shaft linked to a mechanical oscillator. The frequency and amplitude (strain) of oscillation were pre-set on the instrument along with the temperature range and heating rate required. The resistance to the applied deformation was recorded as a function of the magnitude and phase of the sample displacement. The instrument converted the signals automatically to yield the dynamic storage (Young's) modulus (E) and the loss tangent.

The sample was prepared as an impregnated filter paper by pressing the polymer between filter paper on a hydraulic press at 120 °C for a few minutes at a pressure of 200 p.si. Samples were cooled to room temperature and left in a vacuum oven at 60 °C for 24 hours. The stability of the filter paper as an inert support was checked by analysing a blank filter paper under the same conditions. It did not show any significant behaviour over the temperature range studied. Samples with known thickness and breadth were clamped onto the clamping frame, which was cooled to -50 °C by pouring liquid nitrogen into the cooling coil of the DMTA head. A heating rate of 5 °C per minute and frequency of 1 Hz were used. The samples were analysed in the temperature range of -50 °C to 130 °C. The resultant data were stored on computer software. From the data thermograms in terms of modulus E/ versus tan  $\delta$  were plotted as function of temperature.

#### 3.6.8 Solution viscosity measurements.

Solution viscosities of poly(ethylene-vinyl alcohol)-g-PMMA graft copolymers were measured in a capillary suspended level Ubbelohde viscometer with efflux time well over 100 seconds. The viscosities of the solutions were determined relative to toluene or THF at 25 °C. A 1.0 % graft copolymer solution in toluene or THF was filtered through a Whatman glass micro fiber filter paper before placing in the viscometer. The solution was allowed to reach thermal equilibrium for ten minutes before measurements were taken . Measurements were repeated until efflux times agreed within 0.1 of a second. Dilution was carried out internally and was stirred with a magnetic bar to achieve thorough mixing. The viscometer was cleaned and dried after each

run. The relative viscosities were determined for at least five different concentrations to provide a relative viscosity in the range  $1.2 < n_r < 2.0$ .

# CHAPTER 4

# RESULTS AND DISCUSSION

#### 4.1 <u>Carboxyl-terminated prepolymers.</u>

Low molar mass samples of PMMA, PPHETMA and PBA were prepared. The molar mass control was achieved by using thioglycollic acid as chain transfer agent which also allowed the introduction of a carboxyl functional group at the end of a prepolymer chain. Polymerisation times of two hours for MMA monomer, four hours for PHETMA monomer, and three hours for BA monomer, were used corresponding to approximately 50 % monomer conversion. The polymerisation conditions for various prepolymer samples are shown in table 4.1. The characterisation of the prepolymers was performed by GPC, end group analysis, IR and NMR.

Typical GPC chromatograms of three purified prepolymers are given in figure 4.1. Separate methods were used for the purification of PMMA, PPHETMA and PBA (see section 3.2). All these methods removed the impurities of monomer, initiator, solvent and chain transfer agent. The number of purification steps was kept to a minimum to avoid fractionation of prepolymers. The chromatograms in figure 4.1 show a single main peak with no impurities remaining from the polymerised mixture and also show the separation of oligomers as indicated by the resolution of shoulders on the tail side of the main peak. The appearance of these shoulders on chromatograms for prepolymers of lowest molar mass was facilitated by performing GPC with 500 Å and 100 Å columns in series.

A comparison of molar masses obtained by GPC and end group analysis is shown in table 4.1. The molar masses obtained by GPC for prepolymers with carboxyl end groups may be lower than might be expected for conventional prepolymers with non-polar chain ends, because interactions involving polar end groups on oligomers with gels have generated retention in a GPC column for a longer time period (153). The molar masses by GPC are polystyrene equivalents obtained with a calibration curve established with polystyrene standards. It was reported (154) that calibration curves of polystyrene and PMMA are almost identical in GPC over a wide range of molar masses. Dawkins (154,155) used unperturbed dimensions per unit mass of different polymers for universal calibration. Since polystyrene and

# Table 4.1 Polymerisation conditions and molar mass results for prepolymers.

РММА	[M] mol dm <sup>-3</sup>	[TGA] mol dm <sup>-3</sup>	[ACVA] mol dm <sup>-3</sup>	Mn (GPC) g.mol <sup>-1</sup>	Mn (End group) g.mol <sup>-1</sup>	Mw/Mn
6HA	3.96	0.59	0.028	1350	1400	1.39
6J	3.96	0.32	0.028	1850	2000	1.34
6KA	3.96	0.19	0.028	2900	3000	1.25
5B	3.962	0.125	0.028	4400	4500	1.52
PPHETM A	[M] mol dm <sup>-3</sup>	[TGA] mol dm <sup>-3</sup>	[ACVA] mol dm <sup>-3</sup>	Mn (GPC) g mol <sup>-1</sup>	Mn (End group) g. mol <sup>-1</sup>	Mw/Mn
PhEt2	1.86	0.42	0.025	1700	1600	1.28
PhEt4B	1.86	0.21	0.025	1800	1900	1.31
PhET5A	1.86	0.10	0.025	2900	3100	1.42
PhEt8	1.86	0.05	0.025	4300	4500	1.57
РВА	[M] mol dm <sup>-3</sup>	[TGA] mol dm <sup>-3</sup>	[ACVA] mol dm <sup>-3</sup>	Mn (GPC) g. mol <sup>-1</sup>	Mn (End group) g. mol <sup>-1</sup>	Mw/Mn
BA5	3.08	0.36	0.044	1800	1700	1.52
BA6	3.08	0.16	0.044	3000	3100	1.68
BA6A	3.08	0.16	0.044	2860	3000	1.62
BA7	3.08	0.08	0.044	3800	4000	1.67

N.B. i) [M]

Monomer concentration.

- ii) [TGA] Chain transfer agent concentration.
- iii) [ACVA].Initiator concentration.



Figure 4.1 GPC chromatograms of purified prepolymers.

5<sup>410</sup> 1.1

PMMA have similar unperturbed dimensions, these polymers should have the same calibration curve. Values of the unperturbed dimensions for PBA and PPHETMA are not available, but values quoted (156) for other acrylic polymers indicated that PBA and PPHETMA should have similar unperturbed dimensions to polystyrene. Therefore, a polystyrene calibration curve was applied to all the prepolymers prepared and the Mn (GPC) values quoted in table 4.1 should not be far away from actual values.

Confirmation of the presence of carboxyl groups was obtained from end group analysis, which was performed as a simple acid -base titration and described in section (3.6.1). The IR spectrum of purified PMMA (6HA) in figure 4.2, PPHETMA (PhEt2) in figure 4.4, and PBA (BA5) in figure 4.6 are shown. The significant absorption due to carbonyl ester at 1732 cm<sup>-1</sup> in these spectra can easily be seen. A broad peak at 3300-3400 cm<sup>-1</sup> due to a hydroxyl O-H is also prominent in all spectra, suggesting the presence of a carboxyl end group in the prepolymers. However, the O-H peak was weaker in higher molar mass prepolymers, this was due to the long polymer chain having only one carboxyl group at the chain end representing a low fraction of the polymer chain and contributing very much less to the IR absorption.

The <sup>1</sup>H NMR spectra of the purified prepolymers are shown in figures 4.8-4.10. The NMR spectra were used to confirm the presence of carboxyl end groups in the prepolymers. Protons in the methylene -CH<sub>2</sub>-S- units of a thioglycollic acid residue in a carboxyl terminated polymer are reported (157) to resonate at  $\delta = 3.2$  ppm, and a single chemical shift was observed at this value in figures 4.8-410. However, this chemical shift for these protons was observed to be less intense in the higher molar mass prepolymers, which again suggests the polymer chain had a terminal carboxyl group which in a longer chain polymer represents only a small part of the molecule. The O-H proton of carboxyl group resonating (158) in TGA at  $\delta$ = 9.0 ppm was not observed. It has been reported that the detection of a carboxyl O-H proton in such a polymer is difficult (157). As the polymer has only one carboxyl O-H proton per chain, its concentration is very low and its resonance masked under the proton resonance of polymer repeat units in the chain.







Figure 4.3 IR spectrum of poly(methyl methacrylate) acid chloride (6HA).







<u>(PhEt\_2).</u>







## Figure 4.7 IR spectrum of poly(butyl acrylate) acid chloride (BA5).







Figure 4.9 <sup>1</sup><u>H NMR spectrum of poly(phenyl ethyl methacrylate) (PhEt 2).</u>





The matched chain transfer agent TGA in conjunction with the ACVA initiator was used for the introduction of a terminal functional group. Waite and Thompson (92) first introduced the concept of a matched chain transfer agent, using a chain transfer agent possessing the required functional group, with a free-radical initiator, having the same functional groups. The effect of a chain transfer agent on the average degree of polymerisation is given by the chain transfer equation (4.1), (159).

$$\frac{1}{Xn} = \frac{1}{(Xn)_0} + C_M + C_I \frac{[I]}{[M]} + C_S \frac{[S]}{[M]} + C_X \frac{[X]}{[M]} + C_P \frac{[P]}{[M]} \dots (4.1)$$

where Xn and  $(Xn)_0$  are the average degrees of polymerisation obtained in the presence and the absence of chain transfer reactions. [M], [I], [S], [X] and [P] are the molar concentrations of monomer initiator, solvent, chain transfer agent and polymer. Corner (159) suggested that the effect of undesirable transfer reactions on Xn can be reduced to negligible proportions if care is exercised in the choice of solvent and initiator, for which CS, CI and CP are small, or if the conversion of monomer to polymer is kept low. Values of these constants for transfer to solvent and initiator for MMA polymerisation in ethyl acetate at 80 °C are reported to be about 10<sup>-4</sup> or less (159). Values of these chain transfer constants for PHETMA and BA are not available in the literature, but values for other acrylate monomers are quoted (156) to be about  $10^{-4}$ , which indicates that the effects of undesirable transfer reactions on Xn in MMA, PHETMA and BA polymerisations are reduced to negligible proportions. Therefore equation (4.1) can be reduced to equation (4.2) assuming a low value of  $(C_M)$ .

 $\frac{1}{Xn} = \frac{1}{(Xn)_0} + C_X \frac{[X]}{[M]}$  .....(4.2)

Plots of 1/Xn versus [X]/[M] for polymerisations of MMA, PHETMA and BA in ethyl acetate are given in figure 4.11 which shows the effect of chain transfer agent concentration on average degree of polymerisation, (Xn calculated from Mn of end group analysis). The value of the chain transfer constant for the TGA chain transfer agent can be determined from the slopes of the straight lines. For a polymerisation of MMA with TGA in ethyl acetate at 80 °C the value of the chain transfer constant (C<sub>X</sub>) is reported (159) to be 0.63. The

Figure 4.11 Plots of reciprocal degree of polymerisation versus ratio of concentration of chain transfer agent to conentration of monomer.



[X]/[M] 10-2

values for PHETMA and BA are not available in the literature. The values of  $C_X$  determined were 0.61 for MMA, 0.71 for PHETMA and 0.67 for BA. The value of  $C_X$  for MMA obtained here was close to the reported value of 0.63. The values for PHETMA and BA are within the range of (0.5-2.0) as suggested by Corner (159) to obtain narrow distribution and desired functionality at the end of a polymer chain. If the chain transfer constant for an added chain transfer agent is low, ideally close to unity, then the ratio of the rates at which monomer and chain transfer agent are consumed by growing polymer radicals will be constant. Therefore, the polymer produced will have a narrow distribution of molar masses. When a chain transfer constant is not equal to unity, the transfer agent will be consumed at a rate either faster or slower than the monomer, and the ratio of [X]/[M] will change continuously throughout the polymerisation resulting in a broader distribution. The monomers used here have the chain transfer constants  $(C_x)$  within the expected range, and it is clear from figure 4.11 that the plot of  $1/(X_n)$  versus [X]/[M] gives a reasonable straight line for all three monomers. Therefore, the resulting polymers should have the desired functionality and a narrow molar mass distribution.

## 4.1.1 <u>Conversion of carboxyl-terminated prepolymers to acid</u> chloride.

The carboxyl terminated prepolymers were converted to an acid chloride prior to reacting with Sty-HEMA copolymer and ethylenevinyl alcohol (EVOH) copolymer backbones. The conversion was achieved by reacting the prepolymers with oxalyl chloride ( see section 3.2.1). The reaction involved an anhydride intermediate (160). The oxalic acid derivative is unstable producing carbon dioxide, carbon monoxide and hydrochloric acid, driving the equilibrium to the right hand side of equation (4.3).

$$\begin{array}{c} O & O & O \\ \parallel & \parallel & \parallel \\ R - C - OH + Cl - C - C - Cl \end{array} \qquad \qquad O & O & O \\ \blacksquare & \parallel & \parallel \\ R - C - Cl + [HO - C - C - Cl] \end{array}$$

The conversion was confirmed to be qualitative from IR by comparing figures 4.2, 4.4 and 4.6 with figures 4.3, 4.5 and 4.7 for typical carboxyl terminated prepolymers PMMA (6HA), PPHETMA (PhET2), and PBA (BA5) and the respective acid chlorides. The broad peak at 3400 cm<sup>-1</sup> due to O-H and a strong peak at 1732 cm<sup>-1</sup> due to ester carbonyl were observed. After conversion of carboxylic acid end groups to acid chloride groups the IR spectra exhibit the disappearance of the broad peak at 3400 cm<sup>-1</sup> due to acid chloride groups.

#### 4.2 Poly(Styrene-HEMA)-g-PMMA graft copolymers.

In order to develop a synthetic method for poly(ethylene-vinyl alcohol) graft copolymers, a graft copolymer system based on a Sty-HEMA copolymer backbone and PMMA side chains was investigated as a model experiment. This system was chosen because of good solubility of the copolymer backbone and prepolymer in common organic solvents, especially THF, which allowed the characterisation of precursors and graft copolymer product by GPC at room temperature. Acid chloride terminated PMMA prepolymers with molar masses in the range of 1500-4400 g mol<sup>-1</sup> were grafted onto the Sty-HEMA copolymer backbone of HEMA content 11.5 mole %. The synthesis and characterisation of carboxyl terminated PMMA and conversion to acid chloride terminated prepolymers is described in section 4.1. In the following section characterisation of Sty-HEMA backbone and poly(Sty-HEMA)-g-PMMA graft copolymers will be described.

#### 4.2.1 <u>Sty-HEMA copolymers.</u>

Copolymer backbones having hydroxyl groups distributed randomly were synthesised by copolymerising styrene and HEMA monomers. The monomer feed ratio was determined from the copolymer equation (2.5). The monomer reactivity ratios of styrene 0.68 and HEMA 0.64 in 2-ethoxy ethanol at 60  $^{0}$ C have been reported (161). Since the monomer reactivity ratios of both monomers are <1, this shows that each radical has a preference to react with the other monomer rather than its own, therefore the copolymer composition should not be very far from the monomer feed composition. Sty-HEMA copolymers of different compositions were synthesised and are presented in table 4.2. The

# Table 4.2 Comparison of mole fraction of monomer units in the monomerfeed and in the copolymer.

Sample	mole	mole	mole	mole
oumpio	fraction	fraction	fraction	fraction
	(Sty)	(Sty)	(HEMA)	(HEMA)
	in feed	in	in feed	in
		copolymer		copolymer
		by NMR		by NMR
SHA	0.80	0.73	0.20	0.27
SHB	0.80	0.70	0.20	0.30
SHC	0.90	0.83	0.10	0.17
SHD	0.90	0.885	0.10	0.115
synthesis procedure is described in section 3.3.1. Pure copolymers were characterised by GPC, IR and NMR.

GPC was used to determine the molar masses and the purity of the copolymers. Typical chromatograms of a copolymer are presented in figure 4.12. The chromatograms are obtained as UV response (upper peak) and RI response (lower peak). The dual detectors on the GPC system were used to obtain a ratio of UV and RI responses (only styrene units in the copolymer contribute to the UV response), and any change in the ratio of these responses can be judged by the addition of units which are transparent to UV. The copolymer chromatograms are single peaked (RI & UV), and show no impurity peaks at high elution volume (retention volume) due to unreacted monomers and solvent. The molar masses of the copolymers were determined as polystyrene equivalents and were obtained with a polystyrene standards calibration curve (see section 3.6.2.2). The number average molar mass for the precursor copolymer (SHD) is given in table 4.3.

The IR spectrum of a pure copolymer (SHD) is presented in figure 4.13. The broad peak at 3300-3600 cm<sup>-1</sup> due to hydroxyl groups is prominent and was observed in all copolymer spectra. A strong band due to carbonyl ester appeared at 1730 cm<sup>-1</sup>. Two bands in the finger print region characteristic of monosubstituted benzene ring were observed at 750-650 cm<sup>-1</sup>. These important bands indicated that the copolymer consisted of Sty and HEMA units.

The NMR spectrum of a copolymer (SHD) is shown in figure 4.14. The important chemical shifts due to Sty and HEMA units were used for qualitative and quantitative analysis. The five aromatic protons in Sty resonate at  $\delta$ =6.5 ppm. The-(CH<sub>2</sub>)-protons in styrene and HEMA units resonate at  $\delta$ =1.2 ppm. Four -(CH<sub>2</sub>)- protons adjacent to an ester group, -COO(CH<sub>2</sub> CH<sub>2</sub>)- in a HEMA unit appeared as a broad chemical shift at  $\delta$ =3.1-4.1 ppm. These significant chemical shifts again suggested a copolymer of Sty and HEMA units. The composition of the copolymer was calculated by comparing integration heights due to five aromatic protons in Sty which resonate at  $\delta$ =6.5 ppm with the total integration heights of the rest of the protons in the spectrum. If the integrated height due to Sty aromatic protons is H<sub>A</sub> then the moles of Sty units in the copolymer will be proportional to H<sub>A</sub>/5. The moles of HEMA units







Figure 4.13 IR spectrum of Sty-HEMA copolymer (SHD).





can be calculated by determining the integration height per proton for a HEMA unit. The moles of HEMA units will be proportional to the total integration heights  $H_T$  minus the integration due to Sty protons and dividing by total protons in a HEMA unit. If  $m_1$  represents moles of Sty units and  $m_2$  moles of HEMA units then the copolymer composition as a molar ratio will be given by equation (4.4).



The mole fractions of Sty and HEMA determined for copolymers is given in table 4.2, where these values are compared with the monomer feed values. It appears that the HEMA content in the copolymers are not very far from the feed.

## 4.2.2 Poly(Sty-HEMA)-g-PMMA graft copolymer.

The Sty-HEMA copolymer backbone (SHD) containing 11.5 mole % HEMA was grafted with acid chloride terminated PMMA prepolymers of molar mass in the range of 1500-4400 g mol<sup>-1</sup> (table 4.3). The copolymer with HEMA content 11.5 mole % was chosen since this copolymer had the lowest concentration of hydroxyl groups per chain and will have least intermolecular hydrogen bonding. The reacting acid chloride end groups on the prepolymer will be less hindered by this effect and will have accessibility to hydroxyl groups. The grafting of PMMA onto Sty-HEMA copolymer was used as a model experiment. The solubility of these polymers in common organic solvents is reasonably good making this system easier to investigate. The synthesised graft copolymers were characterised by GPC, IR and NMR.

## 4.2.2.1 Gel permeation chromatography (GPC).

GPC was used for the comparison of chromatograms of precursor, Sty-HEMA copolymers and grafted products and for the determination of molar masses of the Sty-HEMA copolymer and graft copolymers (in order to establish the change in molar masses). GPC was performed at room temperature with THF as eluent using dual RI and UV detectors attached to the GPC system. The UV response of the UV detector is



## Figure 4.15 <u>Comparison of chromatograms of a poly(Sty-HEMA)-g-PMMA</u> (SH20) with Sty-HEMA copolymer (SHD).

only due to the Sty units while the HEMA and MMA units are transparent to UV. The sensitivity settings of RI and UV detectors and chart recorder speed remained fixed for all experiments (see section 3.6.2.2). Comparison of typical chromatograms of precursor copolymer (SHD) and graft copolymer (SH20) is given in figure 4.15. The upper traces represent a UV response and the lower traces represent a RI response in terms of concentration of copolymers respectively. The shift of chromatograms towards low elution volume (retention volume) of a graft copolymer compared to Sty-HEMA copolymer indicates a change in the molar mass of the graft copolymer. The reduction in peak heights of UV and RI responses in the graft copolymer compared to the precursor Sty-HEMA copolymer can also be observed and can be used qualitatively to judge graft copolymer formation. Thus, the decrease in the UV peak height is expected from the incorporation of non-UV absorbing methacrylate units onto a backbone consisting mainly of styrene units which are UV absorbing. Several workers (162,163) have used GPC with a chromatograph equipped with UV and RI detectors in series for the qualitative confirmation that graft copolymer is formed. It is observed for the chromatograms in figure 4.15 that the peak height ratio defined as a UV/RI ratio decreases by graft copolymer formation, and so values of this ratio can provide a guide to the extent of product grafting. The ratio of the peak heights of UV and RI responses of the Sty-HEMA copolymer backbone was compared with the graft copolymers. The results of these peak ratios for the graft copolymers and Sty-HEMA copolymer are given in table 4.3. It can be seen that this ratio decreases in the graft copolymer and this decrease is greater as the number of grafts per chain (determined from GPC molar masses) increases.

The molar masses of the graft copolymers presented in table 4.3 are polystyrene equivalents obtained from a calibration curve based on linear polystyrene standards (see section 3.6.2.2). Graft copolymers have a branched structure, and as a result their hydrodynamic volume will be smaller than for a linear polymer with the same molar mass which will affect their GPC elution behaviour. GPC separates on the basis of hydrodynamic volume and the molar masses of the graft copolymer obtained could be lower than the actual values. Drott and Mendelson (164) have compared the calibration curves of several branched polyethylene samples with linear polyethylene samples and obtained a

 

 Table 4.3
 Comparison of molar masses and UV/RI peak ratios of precursor Sty-HEMA copolymer (SHD) and poly(Sty-HEMA)

 -g-PMMA graft copolymers obtained by GPC.

Sample	Mn×	Mn×	UV/RI	Mn ×	UV/RI	Number
· · ·	10 <sup>-3</sup>	10-3	ratio	10-3	ratio	of
	(PMMA)	⁺ (Sty-	(Sty-	(graft	(Graft	grafts
•	end	HEMA)	HEMA)	copoly.)	copoly)	per chain
	group	GPC		GPC	·	
SH15	1.5	8.2	2.05	40	1.5	17
SH20	2.0	8.2	2.05	37	1.7	14
· · · ·					e e en	n an an Array
SH30	3.0	8.2	2.05	29	1.8	7
SH44	4.4	8.2	2.05	33	1.8	5
	· .					

similar calibration curve for both types of samples. They concluded that the branching effect becomes significant only at higher molar masses (above  $10^4$  g mol<sup>-1</sup>). The graft copolymers prepared here are within the range of these molar masses and it is quite possible that in a GPC column the branching effect is less significant for these copolymers. Therefore, the molar masses obtained are likely to be close to the actual values.

The molar masses of the precursor Sty-HEMA copolymer and the product graft copolymers are given in table 4.3. The graft copolymers show a change in molar masses which supports the qualitative changes in terms of chromatograms. These molar masses were used to determine the number of grafts per chain and are shown in table 4.3. It can be seen that a short chain prepolymer is more effective in grafting compared to a longer chain as can be observed by the change in the number of grafts in the series.

## 4.2.2.2 Infra-red spectroscopy (IR).

Infra-red spectroscopy was used for the qualitative analysis of graft copolymers. IR spectrum of graft copolymer SH20 is given in figure 4.16. The graft copolymer shows a band at 1730 cm<sup>-1</sup> due to carbonyl esters present in the HEMA and MMA units. The two bands of a monosubstituted benzene ring appeared at 750-650 cm<sup>-1</sup>. The C-H stretching due to HEMA and MMA units appeared at the same region 2960-2850 cm<sup>-1</sup> and are difficult to differentiate. However, the disappearance of the significant broad band at 3300-3600 cm<sup>-1</sup> due to O-H groups strongly indicates the replacement of these groups by PMMA side chains.

## 4.2.2.3 <u>Nuclear magnetic resonance spectroscopy (NMR).</u>

<sup>1</sup>H NMR was used for qualitative and quantitative analyses of the graft copolymers. The NMR spectrum of a graft copolymer (SH20) is presented in figure 4.17. It shows significant chemical shifts due to the Sty-HEMA copolymer and the PMMA side chains. The chemical shift due to five aromatic protons in Sty units appeared at  $\delta$ =6.5 ppm. The methyl ester -COOCH<sub>3</sub> protons resonate at  $\delta$ =3.5 ppm, -(CH<sub>2</sub>)-protons in Sty units and HEMA units resonate at  $\delta$ =1.5 ppm, while -(CH<sub>2</sub>)-



Figure 4.16 IR spectrum of poly(Sty-HEMA)-g-PMMA (SH20).



Figure 4.17 <sup>1</sup><u>H NMR spectrum of poly(Sty-HEMA)-g-PMMA (SH20)</u>,

## Table 4.4 Composition of poly(Sty-HEMA)-g-PMMA graft copolymers by <sup>1</sup>H NMR.

Sample	mole fraction (Sty)	mole fraction (HEMA)	mole fraction (MMA)
SH15	0.735	0.10	0.165
SH20	0.77	0.105	0.125
SH30	0.835	0.11	0.055
SH44	0.835	0.115	0.05

protons in MMA units appeared at a lower value of  $\delta$ =1.2 ppm. The other significant chemical shift of -CH<sub>3</sub> protons in MMA was observed at  $\delta$ =1.1 ppm value. These important chemical shifts of the copolymers together with the changes in molar mass by GPC suggest a graft copolymer structure of Sty-HEMA backbone and PMMA side chains.

The composition of the graft copolymer was determined by comparing the integrated height of five aromatic protons in Sty with the integration heights of the total protons present in the spectrum, and hence moles of MMA units in the graft copolymer were determined. If H<sub>A</sub> represent the integration of five aromatic protons then the moles of Sty units (m<sub>1</sub>) will be represented by H<sub>A</sub>/5. The moles of MMA units (m<sub>2</sub>) will be total integration heights (H<sub>T</sub>) minus the integration of the Sty protons divided by total protons in the MMA unit and can be represented by equation (4.5),



The graft copolymer compositions determined are shown in table 4.4 It appears that the mole fraction of MMA decreases in the series from SH15 to SH44, which correlates with the number of grafts per chain (table 4.3). This incorporation of MMA indicates the extent of grafting of a short chain and a long chain PMMA prepolymer onto a Sty-HEMA copolymer.

## 4.2.2.4 <u>Evidence of grafting reaction.</u>

Graft copolymers were synthesised by the coupling reaction between acid chloride terminated prepolymer and hydroxyl containing copolymer backbone. The characterisation techniques GPC, IR, and NMR suggested the structural features of the graft copolymer as Sty-HEMA copolymer backbone and PMMA side chains. However, it is possible to produce somewhat different grafted structures in copolymer products if -COOCH<sub>3</sub> groups in the reacting prepolymer undergo a transesterification reaction with hydroxyl groups on the copolymer backbone. It has been presumed that carboxyl terminated prepolymer



## Figure 4.18 Comparison of chromatograms of Sty-HEMA copolymer (SHD, solid lines) and a reaction product (BLA, broken lines) of butanethiol terminated PMMA with Sty-HEMA copolymer.

Table 4.5GPC results of molar masses and UV/RI peak ratios of<br/>product obtained as a result of reaction of acid chloride<br/>terminated PMMA and butanethiol terminate PMMA,<br/>with Sty-HEMA copolymer backbone (SHD).

Sample	Mn×	Mn×	UV/RI	Mn×	UV/RI
	10 <del>-</del> 3	10-3	ratio	10 <del>-</del> 3	ratio
	(PMMA)	(Sty-	(Sty-	(product)	(product)
	end	HEMA)	HEMA)		
	group			GPC	
		GPC			
SH15	1.5	8.2	2.05	40	1.5
grafted					
product					
			~	-	
BLA	1.5	8.2	2.05	9	2.00
ungrafted		· · · · · ·			

converted to acid chloride, by reacting with oxalyl chloride, is far more reactive than ester groups and in the presence of these acid chloride groups such side reactions by transesterification are minimum. However, these transesterification reactions are catalysed by acidic media and it could be possible for the HCl, eliminated during the coupling reaction of acid chloride terminated prepolymer and hydroxyl groups on the backbone, to catalyse such side reactions. In order to study the possibility of any such side reaction a prepolymer having such ester groups but no carboxyl acid end groups was synthesised by polymerising MMA in the presence of initiator (AIBN) and the chain transfer agent butanethiol (see section 3.3.2). This prepolymer of molar mass 1500 g mol<sup>-1</sup> was reacted with Sty-HEMA copolymer backbone (SHD), having hydroxyl groups, under the same reaction conditions in the presence of an organic acid catalyst, p-toluene sulphonic acid (see section 3.3.2). The resultant product was analysed by GPC to study any changes in the chromatographic peaks and the UV/RI ratio response. The chromatograms of the resultant product and the backbone copolymer are compared in figure 4.18. It can be seen that there is no change in the UV and RI peaks and hence no change in the molar mass has occurred. The results of molar mass and the UV/RI ratio are presented in table 4.5. It appeared that the resultant product neither showed any change in molar mass nor change in the UV/RI ratio. These results suggested that the change in the molar masses of the Sty-HEMA backbone are not due to any such side reactions but in fact due to coupling reactions between acid chloride terminated PMMA and hydroxyl groups on the copolymer backbone.

## 4.3. <u>Characterisation of ethylene-vinyl acetate copolymers.</u>

Before modifying ethylene-vinyl acetate (EVA) copolymers to ethylenevinyl alcohol (EVOH) copolymers, a basic characterisation parameter of EVA copolymer was the percentage vinyl acetate (VA) incorporated. An accurate knowledge of VA content expressed as percentage by weight or by mole was essential to distinguish different EVA copolymer samples. To determine percentage of VA incorporated several methods have been examined, including chemical decomposition (165), NMR (165), pyrolysis (166) and infra-red spectroscopy (167). According to Vander Linden (167), IR spectroscopy is

the most convenient and applicable of these methods. In order to obtain quantitative IR data about the VA content, a calibration curve should be available. Usually this can be obtained by determining the absorption ratio of a band characteristic to the acetoxy groups and one typical to the ethylene sequence from a EVA, IR spectrum. A typical IR spectrum of EVA copolymer is presented in figure 4.19. The important IR bands which can be used for the quantitative analysis of EVA copolymer are given in table 4.6. For EVA copolymer samples pressed to a thin film, Mayor and Sodonka (168) used the 610/720 cm<sup>-1</sup> absorption ratio and found a reproducibility of 5 weight (wt) % VA for the 0-35 wt % VA range. Siryuk and Bulgakova (169) obtained a better reproducibility, 2.6 wt % VA by using the 1743/1465 cm<sup>-1</sup> absorption ratio. Koopman et al (170) proposed several possibilities for such a calibration curve, for example 3400/2678 cm<sup>-1</sup>, 1020/2678 cm<sup>-1</sup> and 610/2678 cm<sup>-1</sup> absorption ratios. In all these methods a calibration curve of absorption ratio for a band characteristic of the acetoxy group in VA, and one for ethylene sequences versus VA content was established. This requires standard EVA samples with known VA content. Janca and co-workers (171) used a method to determine the VA content in poly(vinyl chloride-vinyl acetate) copolymers. This method is simple and requires only a poly(vinyl acetate) (PVA) calibration curve of carbonyl absorption at 1743 cm<sup>-1</sup> versus concentration of a PVA solution in THF. This method was adopted to determine the VA content in the EVA copolymer samples. A calibration curve of carbonyl absorption at 1743 cm<sup>-1</sup> versus concentration of PVA solutions in toluene was established. Solutions of EVA copolymer samples of known concentration were prepared in toluene. The carbonyl absorption of these solutions were determined by FTIR. From the PVA calibration curve the concentrations of VA content in EVA samples were calculated. The details of the method are given in experimental section 3.6.3. A wide range of EVA copolymer samples were investigated to asses the reliability of the calibration method. The EVA copolymer samples presented in table 4.7 were analysed by this method and are compared with the suppliers composition.

## Table 4.6 Important IR bands for quantitative analysis of

ethylene-vinyl acetate copolymers.

Band characterisation Wave number υ Cm<sup>-1</sup> C=O stretching 3460 -CH<sub>2</sub>- stretching. 2678 )c=0 1743 stretching (ester). -CH<sub>2</sub>- bending. 1465 C=O<sub>stretching</sub> 1250 (acetate ester). -COOR bending. 1020  $--CH_2 - n \ge 4$ 720 rocking. 610 -COOR wagging.

# Table 4.7 Ethylene-vinyl acetate copolymer samples used for thedetermination of VA content by PVA calibration curve.

		A second s
Sample code.	VA content	VA content
- <b>1</b>	by	(determined
	(supplier)	by PVA
	VA % w/w	calibration
		curve.)
н 		VA % w/w.
D50ARS	41	40
28-20JD	26	26
538/539	18	20
JR6309	16	20
28-150	41	45
18-150	21	25
		and the second

## 4.3.1 <u>Hydrolysis of ethylene-vinyl acetate copolymers.</u>

The hydrolysis of EVA copolymers to EVOH copolymers was straightforward, except for several important precautions. First, EVA pellets had to be entirely dissolved in the solvent. Second, separation of the newly formed EVOH copolymer and solvent was difficult, which was overcome by pouring the reaction mixture into an excess of nonsolvent (methanol). The complete removal of potassium acetate was also important which was accomplished by washing copolymer thoroughly with distilled water. The hydrolysed EVOH copolymers were qualitatively characterised by FTIR as shown in figure 4.20. In the IR spectrum of EVA copolymer (figure 4.19) the strong absorption at 1743 cm<sup>-1</sup> of the carbonyl ester represents VA units and absorption at 1465 cm<sup>-1</sup> indicates ethylene (-CH<sub>2</sub>-)n units. The IR spectrum of EVOH in figure 4.20 indicates a strong band at 1465 cm<sup>-1</sup> due to (-CH<sub>2</sub>-)n stretching in ethylene units which becomes more prominent after hydrolysis. A broad band due to hydroxyl groups in vinyl alcohol units appeared at 3350-3500 cm<sup>-1</sup>. The complete disappearance of band at 1743 cm<sup>-1</sup> due to carbonyl ester suggests the complete hydrolysis of EVA copolymer to EVOH copolymer.

In the partial hydrolysis of EVA copolymer, a sample of EVA (28-150) with a VA content of 21 mole % was chosen, to prepare a terpolymer of ethylene-vinyl acetate-vinyl alcohol with a vinyl alcohol content approximately similar to the hydrolysed EVA copolymer sample (18-150 with a VA content of 9.8 mole %). This was considered to be of interest in order to study the reactivity of hydroxyl groups on the copolymer backbone, in the presence of acetate groups, with the reacting acid chloride terminated prepolymers (see section 4.6). To achieve the desired degree of hydrolysis the moles of KOH used was equal to the moles of VA required for hydrolysis. The composition of the partially hydrolysed product was obtained by determining the VA. content in the terpolymer (as described in section 4.3). By knowing the VA content in a terpolymer and the precursor (EVA) copolymer, the vinyl alcohol content was calculated, which gave the composition of the terpolymer in terms of ethylene, vinyl acetate and vinyl alcohol units.



Figure 4.19 IR spectrum of ethylene vinyl acetate copolymer (EVA) (18-150).



Figure 4.20 IR spectrum of ethylene vinyl alcohol copolymer (EVOH) (18-150).

## 4.4 Poly(ethylene-vinyl alcohol) graft copolymers.

Two types of ethylene-vinyl alcohol copolymer with vinyl alcohol contents of 9.8 mole % and 21 mole % and a terpolymer of ethylene-vinyl-acetate-vinyl alcohol with a vinyl alcohol content of 8.0 mole % were used as backbones. Three different types of carboxyl terminated prepolymers with molar masses in the range 1400 to 4400 g mol<sup>-1</sup> were grafted onto backbone copolymers. Samples of the backbone copolymers and prepolymers were synthesised and characterised separately before grafting.

## 4.4.1 <u>Poly(ethylene-vinyl alcohol)-g-PMMA graft copolymers.</u>

PMMA samples having molar masses ranging from 1400 to 4400 g mol<sup>-1</sup> were grafted either onto a EVOH copolymer backbone with a VOH contents 9.8 mole % and 21 mole % or onto a terpolymer of ethylene-vinyl acetate-vinyl alcohol with a VOH 8.0 mole %. Table 4.8 indicates the types of PMMA prepolymers and EVOH copolymers and their concentration used for the synthesis of graft copolymers. The grafting of PMMA onto EVOH copolymers and terpolymer was a simple coupling reaction in which two polymers with reactive functional groups were allowed to react in a high boiling solvent (xylene at 140 °C). The pure graft copolymers were isolated, purified as described in section 3.4.3, and characterised by GPC, NMR and IR.

## 4.4.1.1 <u>Gel permeation chromatography (GPC).</u>

GPC was used to establish the change in the molar masses of graft copolymer products with respect to the precursor samples. EVA precursors can be characterised by high temperature GPC (about 140  $^{\circ}$ C) with o-dichlorobenzene as solvent as described in section 3.6.2.3.

Comparisons of chromatograms of EVA copolymer and graft copolymers samples are given in figures 4.21-4.25. The EVA copolymer sample used for comparison in figures 4.21 & 4.22 was sample (18-150) (see table 4.7) from which an EVOH copolymer of a VOH content 9.8 mole % was produced. GPC chromatograms of EVA sample (18-150) and EVOH sample (18-150) are presented in figure 4.26, while the EVA

# Table 4.8 Poly(ethylene-vinyl alcohol)-g-PMMA samples synthesised, \_prepolymers, precursor and their concentration used for the \_grafting reactions.

Sample	Mn×10 <sup>-3</sup> (PMMA) prepolymer	VOH content mole % in (EVOH) precursor	concentration mol dm <sup>-3</sup> 10 <sup>-2</sup> (Prepolymer)	concentration mol dm <sup>-3</sup> 10 <sup>-4</sup> (EVOH)
E10D	1.4	9.8	2.9	8.3
E14D	2.9	9.8	2.9	8.3
E11D	4.4	9.8	2.9	8.3
E12D	1.4	9.8	5.2	10
E15D	2.9	9.8	5.2	10
E13D	4.4	9.8	5.2	. 10
E16D	1.4	8.0	2.0	6.6
E17D	2.9	8.0	2.0	6.6
E18D	4.4	8.0	2.0	6.6

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copolymer sample used for comparison in figures 4.24 & 4.25 was (28-150) (see table 4.7) from which an EVOH copolymer of VOH content 21 mole % and a terpolymer of VOH content 8.0 mole % were produced. The chromatograms of EVA sample (28-150) and EVOH sample (28-150) are given in figure 4.27. Similarly, GPC chromatograms of EVA sample (28-150) and partially hydrolysed terpolymer are presented in figure 4.28. The chromatograms are plotted in terms of the concentration of polymer determined with an IR detector at fixed wavelength (3.42 microns) represented as my versus retention volume. All the comparisons in each figure were performed at the same experimental conditions of the GPC system (section 3.6.2.3). For this comparison EVA was preferred to EVOH, because ester based segments in the precursor and product samples are both in a good solvent environment in hot o-dichlorobenzene and so both copolymer types should exhibit size exclusion separation behaviour with little or no adsorption onto polystyrene gel in a GPC column. EVOH is a much more polar polymer and its retention may be dependent on interaction effects involving pendant hydroxyl groups with the column gel. It has been established that the separation of small molecules by GPC can be perturbed by interaction mechanisms involving polar groups such as -OH (153). It is possible that polymers bearing -OH groups in some solvents might separate by both size exclusion and adsorption mechanisms. Consequently, it appeared unsatisfactory to use GPC of EVOH samples to establish molar masses changes for grafted products. It was preferred for the comparison to use GPC data of precursor EVA samples to establish that samples of EVA in o-dichlorobenzene or trichlorobenzene separate in GPC at high temperature by size exclusion with minimum adsorption problems, since the universal calibration principle in GPC has been shown to operate for EVA (172). It is therefore assumed that the grafted product will also separate in GPC by size exclusion with o-dichlorobenzene at 140 °C.

Figure 4.21 shows the comparison of an EVA sample (18-150) with a VA content 9.8 mole % with a poly(ethylene-vinyl alcohol)-g-PMMA sample (E10D). In figure 4.22 chromatograms of a series of graft copolymers prepared from PMMA of molar masses ranging from 1400 to 4400 g mol<sup>-1</sup> and an EVA sample with a VA content of 9.8 mol % are shown. In these chromatograms the clear shift of the main peaks toward low retention volume indicate high molar mass of products









<u>Comparison of GPC chromatograms of a series of</u> poly(ethylene-vinyl alcohol)-g-PMMA, E10D, E14D and E11D with EVA precursor sample (18-150).





<u>Comparison of chromatograms of a impure poly(ethylenevinyl alcohol)-g-PMMA sample (E10C) with a pure graft</u> <u>copolymer sample (E10D)</u>.



RET VOL (m1)







Śh.

<u>Comparison of GPC chromatograms of samples E16D and E18D with precursor EVA (28-150).</u>



Figure 4.26

A comparison of GPC chromatograms of ethylene-vinyl acetate copolymer (EVA) (18-150) and ethylene-vinyl alcohol copolymer (EVOH) (18-150).









compared with the precursor EVA samples and suggests successful grafting reactions. The broad peak in samples E14D and E11D compared to sample E10D might be associated with inter-molecular interaction of unreacted -OH groups present in the graft copolymer backbone. The chromatograms also indicate the purity of graft copolymers, as the chromatograms show a single peak with no peak at high retention volume due to remaining traces of unreacted low molar mass PMMA. The chromatograms of typical pure and impure graft copolymers are presented in figure 4.23. The peak at high retention volume (at 14.3 ml), adjacent to the marker peak in the chromatogram of impure graft copolymer product is due to unreacted PMMA, while the chromatograms of pure graft copolymer do not show any traces of unreacted PMMA at this retention value. A comparison of chromatograms of EVA samples having VA content 21 mole % and the graft copolymer E12D with a PMMA side chain of 1400 g mol<sup>-1</sup> and E15D with a PMMA side chain of 4400 g mol<sup>-1</sup> are shown in figure 4.24. The shift in the main peaks toward low retention volume again indicates the change in the molar masses of graft copolymers compared to the EVA precursor. Figure 4.25 includes a comparison of a series of prepolymers with molar masses 1400, 2900 and 4400 g mol<sup>-1</sup> grafted onto the terpolymer backbone. These chromatograms indicate the shift of the main GPC peaks toward low retention volumes because of increases in molar masses compared to the precursor EVA.

The fact that the shift in peaks in the GPC chromatograms are from grafting reactions of PMMA onto a backbone copolymer was supported by a series of reactions in which a molar ratio of 1:3 was used for end groups in a prepolymer to the hydroxyl groups present in the precursor. PMMA samples of molar masses ranging from 2000 g mol<sup>-1</sup> to 5000 g mol<sup>-1</sup> were reacted with EVOH copolymer sample (18-150) with a VOH content of 9.8 mole %. The reactions were performed under the same experimental conditions. Products were purified and analysed by GPC. The comparison of chromatograms of these products with EVOH sample 18-150 for the reaction) in figures 4.29-4.32 indicate smaller shifts in the peaks of the products with respect to the EVA copolymer.





<u>Comparison of GPC chromatograms of a poly(ethylene-vinyl</u> alcohol)-g-PMMA graft copolymer (E3D). obtained as a result of low grafting reaction from a EVOH sample (18-150) with a VOH content of 9.8 mole% and PMMA molar mass 2000 g mol<sup>-1</sup>, where E3A (EVA). E3B (EVOH). E3C (impure product and E3D (pure product).





<u>Comparison of GPC chromatograms of a poly(ethylene-vinyl</u> <u>alcohol)-g-PMMA graft copolymer (E4D), obtained as a result</u> <u>of low grafting reaction from a EVOH sample (18-150) with a</u> <u>VOH content of 9.8 mole% and PMMA molar mass 3000 g</u> <u>mol<sup>-1</sup>, where E4A (EVA), E4B (EVOH), E4D (product) and</u> <u>E4E (prepolymer).</u>





<u>Comparison of GPC chromatograms of a poly(ethylene-vinyl alcohol)-g-PMMA graft copolymer (E5D), obtained as a result of low grafting reaction from a EVOH sample (18-150) with a VOH content of 9.8 mole% and PMMA molar mass 4000 g mol<sup>-1</sup>, where E5A (EVA), E5B (EVOH), E5D ( product) and E5E (prepolymer).</u>



Figure 4.32

Comparison of GPC chromatograms of a poly(ethylene-vinyl alcohol)-g-PMMA graft copolymer (E6D), obtained as a result of low grafting reaction from a EVOH sample (18-150) with a VOH content of 9.8 mole% and PMMA molar mass 5000 g mol<sup>-1</sup>, where E6A (EVA), E6B (EVOH), E6D (product) and E6E (prepolymer).

## 4.4.1.2 <u>Nuclear magnetic resonance spectroscopy (NMR).</u>

The <sup>1</sup>H NMR spectrum of a purified graft copolymer (E10D), is shown in figure 4.33. The chemical shifts due to various protons are assigned in table 4.9. The pure graft copolymer was dissolved in deuturated chloroform and tetramethylsilane (TMS) was added as an internal reference for NMR (see section 3.6.4). The EVA and EVOH copolymers were not soluble in chloroform. However, literature (173,174), NMR spectra of these copolymers indicates two important chemical shifts due to methylene  $-(CH_2)_n$ - protons and a methine -(CH)- proton which provide important structural information. All methylene -(CH2)protons in ethylene, vinyl acetate and vinyl alcohol resonate at  $\delta = 1.2$ ppm value (173,174) due to a similar structural environment. The methine -(CH)- protons in EVA and EVOH are reported (173), to  $\delta$  = 4.8 ppm. The ester -OCOCH3 protons in EVA resonate at copolymers resonate at  $\delta = 2.0$  ppm value. From the NMR spectrum of a graft copolymer (E10D), shown in figure 4.33, two important chemical shifts at  $\delta = 1.2$  ppm due to methylene -(CH<sub>2</sub>)- protons and at  $\delta = 4.8$ ppm due to a methine -(CH)- proton indicate the presence of a backbone in the graft copolymer consisting of polyethylene. The chemical shift due to various PMMA side chain protons in the graft For example, the methyl ester copolymer are also prominent. -COOCH3 protons at  $\delta$  = 3.8 ppm, the methylene -CH2-S- protons of the PMMA end group at  $\delta = 3.1$  ppm and methyl -CH3 protons at  $\delta = 1.0$ ppm can clearly be seen in the NMR spectrum of the graft copolymer. The presence of these important chemical shifts due to copolymer backbone and PMMA side chain suggest the structural features of the synthesised graft copolymers as a polyethylene backbone and PMMA side chain.

The composition of graft copolymers were determined by NMR. Composition was obtained in terms of moles of MMA units per gram of graft copolymer. Moles of MMA units per gram of graft copolymer was preferred in order to compare the moles of MMA obtained from IR. The chemical shift due to backbone polyethylene -(CH<sub>2</sub>)<sub>n</sub>- protons resonating at  $\delta = 1.2$  ppm and is completely separates from the rest of the spectrum. Similarly, the chemical shift due to methyl ester -COOCH<sub>3</sub> protons resonating at  $\delta = 3.4$  ppm and is completely separate



Figure 4.33 <sup>1</sup>H <u>NMR spectrum of poly(ethylene-vinyl alcohol)-g-PMMA</u> (E10D)

# Table 4.9 Assignment of important chemical shifts in <sup>1</sup>H NMRof poly(ethylene-vinyl alcohol)-g-PMMA (E10D).

Chemical shift	Assignment.	Label.	
δppm			
		·	
1.25	- ( CH <sub>2</sub> ) <sub>n</sub> -	а	
4.80	-CH-	b	
3.1	-CH2-S-	C	
3.8	-COOCH3	d	
1.0	-CH3	e	
1.9	-CH2-	f	



from the rest of spectrum. The integrated trace heights due to these protons can easily be measured separately. Let the integrated height of the three methyl ester protons peak be  $H_M$  thus, moles of MMA units will be  $H_M/3$ . Let the integrated height due to -(CH<sub>2</sub>)- protons peak be  $H_E$  so moles of -(CH<sub>2</sub>)- units will be  $H_E/2$ . This integrated height is contributed by four -(CH<sub>2</sub>)- protons in ethylene units and two -(CH<sub>2</sub>)protons in vinyl alcohol units. The moles of VOH in the precursor EVOH copolymers are known which are 9.8 mole % in EVOH sample (18-150), 21 mole % in EVOH sample (28-150) and 8.0 mole % in a terpolymer and from which moles of ethylene units in the precursor copolymers can be determined. Knowing the moles of ethylene units and VOH units in the precursor copolymer and the total integration height due to six -(CH<sub>2</sub>)- protons of ethylene units and VOH units in the graft copolymer, the moles of these units in the graft copolymer are given by equations (4.6 & 4.7),

Moles of ethylene units in graft copolymer,

 $= \frac{A}{2A+B} \times \frac{H_E}{2} \cdots \cdots \cdots \cdots \cdots (4.6)$ 

Moles of vinyl alcohol units in graft copolymer,

 $= \frac{B}{2A+B} \times \frac{H_E}{2} \cdots \cdots \cdots \cdots \cdots (4.7)$ 

where A and B are moles of ethylene and VOH units in the precursor copolymer backbone.

Thus, moles of MMA per gram of graft copolymer will be moles of MMA from the integration height  $H_M/3$  (X) divided by the weight (grams) of graft copolymer (Y) and is given by equation (4.8),

where 28, 44, and 100 are the molar masses of the ethylene, vinyl alcohol and methyl methacrylate units respectively.
Similarly, the graft copolymers prepared from the precursor terpolymer contain ethylene, vinyl alcohol and vinyl acetate units. The integrated height of -(CH<sub>2</sub>)- will also be contributed by -(CH<sub>2</sub>)- in the acetate units. The moles of MMA per gram of graft copolymer prepared from a terpolymer backbone will be given by equation(4.9),

X	н <sub>м</sub> /3		. (4.9)
Y	$\frac{28A}{2A+B+C} \times \frac{H_E}{2} + \frac{44B}{2A+B+C} \times \frac{H_E}{2} + \frac{86C}{2A+B+C} \times \frac{H_E}{2} + 100\frac{H_N}{3}$	<u>/1</u>	

where 86 is molar mass of vinyl acetate and C moles of vinyl acetate units in the precursor terpolymer.

The results presented in table 4.10 are in terms of moles of MMA units per gram of graft copolymer and are compared with the theoretical moles of MMA units. Theoretical moles of MMA units per gram of graft copolymer were determined by calculating moles of MMA units in the graft copolymer and dividing by the weight of graft copolymer. If all the O-H groups in the EVOH copolymer are replaced by PMMA side chains, then moles of PMMA in the graft copolymer and moles of VOH in EVOH copolymer will be the same and from this moles of MMA units can be determine by multiplying with the number of monomer repeat units.

It appears that moles of MMA obtained by NMR are close to the theoretical values and indicate the incorporation of MMA units in the graft copolymer, which confirm quantitatively the presence of MMA units as result of grafting reactions of PMMA prepolymer onto EVOH copolymer backbone. The increase in the values in a series, for example E10D to E11D, where graft copolymers are prepared from the same EVOH copolymer precursor but PMMA prepolymers of different molar masses (ranging from 1400 to 4400 g mol<sup>-1</sup>) show an increase in moles of MMA which is due to increase in the chain length of the prepolymers.

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		of modies of b			<b>TA TEA</b>
Table. 4.	to <u>Comparison</u>	of moles of A	MMA deter	<u>minea by NM</u>	<u>K, IK and</u>

1		<u> </u>			ſ
	Sample.	Moles of	Moles of	Moles of	
		MMA	MMA per	MMA per	
		per gram of	gram of graft	gram of graft	
		graft	copolymer	copolymer	
		copolymer	(NMR)	(IR)	
		(theoretical)	10-3	10-3	
		10-3			
	· · ·				
	E10D	8.5	7.62	7.53	
	E14D	8.9	8.4	7.6	
and and a second se	E11D	9.23	8.7	8.3	and the second
	E12D	8.7	8.5	8.3	
	E15D	8.93	8.45	8.6	
	F13D	9 56	9.0	84	
	E15D			0.1	
	E16D	7.40	7.0	-	
	T-1 (77)	0.5	0.0		
	E17D	8.5	8.0	- -	
• .	E18D	9.0	8.5	-	
	·				

## 4.4.1.3 Infra-red spectroscopy (IR).

The IR spectrum of a pure graft copolymer (E10D) and EVOH copolymer (18-150), are compared in Figures 4.34 & 4.35. As described earlier (section 4.3), the IR spectrum of an EVOH copolymer provides two important structural features, the polyethylene  $-(CH_2)_n$ - absorption band at 1465  $\text{cm}^{-1}$  and a broad band at 3300-3500  $\text{cm}^{-1}$ due to hydroxyl groups. The IR spectrum of a graft copolymer shows the disappearance of band at 3300-3500 cm<sup>-1</sup>due to hydroxyl groups, which indicates the replacement of -OH groups by PMMA side chains. The band due to  $-(CH_2)_n$  - methylene groups appears at 1465 cm<sup>-1</sup>. However, it is not as strong as compared to a EVOH copolymer, which is explained by the presence of PMMA side chains. The important ester -COOCH3 absorption at 1732  $cm^{-1}$  due to PMMA can clearly be seen in the IR spectrum of the graft copolymer (figure 4.35). The presence of important bands due to the backbone and side chain in graft copolymers again suggest the same structural features as derived from NMR, that is, a graft copolymer as a polyethylene backbone and PMMA side chains.

The composition of the graft copolymers were determined by IR in terms of moles of MMA units per gram of graft copolymer. The MMA units in graft copolymers have prominent carbonyl absorbance at 1732 cm<sup>-1</sup>. From a suitable calibration curve of carbonyl absorbance versus moles of MMA in a gram of graft copolymer, the moles of MMA present in a sample can be calculated. For such a calibration curve butanethiol terminated PMMA was used in order to avoid the interaction of carboxyl, carbonyl absorbance with the ester carbonyl absorbance. The detailed method is described in section 3.6.3. The results obtained are presented in table 4.10. Results for samples E16D, E17D and E18D are not given as these graft copolymers were prepared from a terpolymer backbone in which the MMA units and VA units contribute to carbonyl absorbance which makes it difficult to determine MMA concentration. The moles of MMA units obtained by IR are compared with the theoretical value and with the result obtained by NMR. These results indicate the values obtained by IR and NMR are in good agreement with each other and suggest the validity of the methods. The moles of MMA by NMR and IR in conjunction with the



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Figure 4.34 IR spectrum of precursor ethylene-vinyl alcohol (EVOH) copolymer (18-150).





IR spectrum of a poly(ethylene-vinyl alcohol)-g-PMMA graft copolymer (E10D).

increase in the molar mass of the precursor suggests the success of grafting reactions.

## 4.4.2 <u>Poly(ethylene-vinyl alcohol)-g-PPHETMA graft copolymers.</u>

Various samples of poly(ethylene-vinyl alcohol)-g-PPHETMA were synthesised with carboxyl terminated PPHETMA prepolymers and ethylene-vinyl alcohol copolymer backbones. The PPHETMA prepolymers with molar masses ranging from 1800 to 4000 g mol<sup>-1</sup> and EVOH copolymer backbones of VOH content 9.8 mole % and 21 mole % and a terpolymer ethylene-vinyl alcohol-vinyl acetate with a VOH content of 8 mole % were used. Precursor samples and their concentration used for the synthesis of graft copolymers are given in table 4.11. The pure graft copolymers were isolated, purified as described in section 3.4.3 and characterised by GPC, NMR and IR.

## 4.4.2.1 <u>Gel permeation chromatography (GPC).</u>

In order to establish the change in the molar mass of the graft copolymers compared to precursor EVA copolymers, samples of graft copolymers and EVA copolymers were characterised by high temperature GPC (140  $^{\circ}$ C) with o-dichlorobenzene as a solvent. The samples were studied by the procedure as described in section 3.6.2.3.

Comparison of chromatograms of EVA copolymer samples and graft copolymers are given in figures 4.36-4.39. The EVA copolymer sample used for comparison in figures 4.36 and 4.37 was sample (18-150) from which an EVOH copolymer with a VOH content of 9.8 mole % was produced. While EVA copolymer sample used for comparison in figures 4.38 and 4.39 was (28-150) (see table 4.7) from which an EVOH copolymer with a VOH content of 21 mole % and a terpolymer with a VOH content of 8.0 mole % were produced. The chromatograms are plotted in terms of IR detector response representing polymer concentration versus retention volume. All comparisons in each figure were performed at the same experimental conditions of the GPC system (section 3.6.2.3). For this comparison EVA was preferred to EVOH, because of the reason discussed in section 4.4.1.1. Figure 4.36 shows the comparison of chromatograms of a graft copolymer F1D and a EVA precursor. The shift of the main peak towards low retention 

 Table 4.11 Poly(ethylene-vinyl alcohol)-g-PPHETMA samples synthesised,

 prepolymers, precursor and their concentration used for

 grafting reactions.

Sample	Mn × 10 <sup>-3</sup> (PPHETMA) prepolymer	VOH content mok % in (EVOH) precursor	concentration mol dm <sup>-3</sup> 10 <sup>-2</sup> (Prepolymer)	concentration mol dm <sup>-3</sup> 10 <sup>-4</sup> (EVOH)
F1D	1.8	9.8	2.9	8.3
F4D	3.0	9.8	2.9	8.3
F7D	4.0	9.8	<sup>,</sup> 2.9	8.3
F2D	1.8	21	5.2	10
F5D	3.0	21	5.2	. 10
F8D	4.0	21	5.2	10
F3AD	1.8	8.0	2.0	6.6
F6D	3.0	8.0	2.0	6.6
F9D	4.0	8.0	2.0	6.6





Comparison of chromatograms of EVA precursor (18-150) and poly(ethylene-vinyl alcohol)-g-PPHETMA (F1D)



## Figure 4.37

<u>Comparison of chromatograms of EVA precursor (18-150)</u> with a series of poly(ethylene-vinyl alcohol)-g-PPHETMA samples, F1D,F4D and F7D.









volume suggests a change in the molar mass of a graft copolymer. Changes in molar mass of graft copolymers compared to precursor EVA copolymer can be clearly seen in figure 4.37, where a series of graft copolymers prepared from the prepolymer samples of molar masses of 1800, 3000 and 4000 g mol<sup>-1</sup> and precursor EVA copolymer with a VA content of 9.8 mole % are compared. Figure 4.38 indicates the same trend, where graft copolymers (F5D & F8D) prepared from the prepolymers of molar masses 3000 and 4000 g mol<sup>-1</sup> and precursor EVA copolymer with a VA content of 21 mole % are compared. Shift of the main peak (figure 4.38) in sample F8D towards low retention volume is greater as compared to sample F5D suggesting a higher molar mass for the sample. Similarly, figure 4.39 shows a change in the molar mass of graft copolymers (F3AD, F6D & F9D) compared to the EVA precursor. In this series graft copolymers were prepared from the prepolymer samples of molar masses 1800, 300 and 4000 g mol<sup>-1</sup> and a terpolymer backbone with a VOH content of 8.0 mol %. These shift of peaks of graft copolymers toward low retention volumes compared to the precursor copolymers suggested successful grafting reactions.

## 4.4.2.2 Nuclear magnetic resonance spectroscopy (NMR).

<sup>1</sup>H NMR spectroscopy was used for the characterisation and composition determination of the graft copolymers. The characterisation of the graft copolymer was performed by compiling the important chemical shifts due to the polyethylene backbone and PPHETMA side chain. An NMR spectrum of a pure graft copolymer  $(F_1D)$  is presented in figure 4.40. The assignments of various important chemical shifts are given in table 4.12. The chemical shifts due to polyethylene -(CH<sub>2</sub>)- protons (a) resonating at  $\delta$ = 1.25 ppm and the methine -(CH)- proton (b) resonating at  $\delta$ = 4.85 ppm can clearly be seen in the spectrum. The PPHETMA side chain generates a significant chemical shift due to five aromatic protons (h) resonating at  $\delta$ = 7.2 ppm (175) which can be seen in the NMR spectrum of the graft copolymer. The chemical shift due to methylene -COO-(CH<sub>2</sub>)-CH<sub>2</sub>-Ph protons (g) adjacent to an aromatic ring resonate at  $\delta = 3.0$  ppm and methylene protons (f) adjacent to an ester group resonate at a higher value of  $\delta =$ 4.2 ppm. The other chemical shifts due to  $\alpha$ -methyl protons (d) resonating at  $\delta = 0.9$  ppm and methylene -CH<sub>2</sub>-S- protons (c) resonating at  $\delta$ =3.1 ppm were also detected. All these chemical shifts suggest the

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Figure 4.40

<sup>1</sup>H <u>NMR spectrum of a poly(ethylene-vinyl alcohol)</u>-g-<u>PPHETMA graft copolymer sample (F1D)</u>,

# Table. 4.12 Assignment of chemical shifts in <sup>1</sup>H NMR spectrum of poly(ethylene-vinyl alcohol)-g-PPHETMA.

Chemical	Assignment	Label
shift		
δppm		

1.2	- (-CH <sub>2</sub> -) <sub>n</sub>	a
5.0	-ÇH-	b
3.1	-CH2-S-	c
0.9	CH <sub>3</sub> -	d
1.8	-(-CH <sub>2</sub> -C-)-	е
4.2	-COOCH2-	f
3.0	COO-CH2-(CH2)-Ph	g
7.2	Ph-	h



structural features of a graft copolymer with a polyethylene backbone and PPHETMA side chains.

The composition of the graft copolymers were determined by calculating the moles of PHETMA units per gram of graft copolymer. The methylene -(CH<sub>2</sub>)<sub>n</sub>- protons of the backbone and the five aromatic protons in the side chain resonate separately from the rest of the spectrum. The integrated heights at these chemical shifts can be easily measured separately. If the integrated height of phenyl protons is H<sub>ph</sub>, then the moles of PHETMA will be H<sub>ph</sub>/5. As discussed earlier in section 4.4.1.2, the moles of ethylene units and vinyl alcohol units are given by equations (4.6 & 4.7).

Thus, moles of PHETMA per gram of graft copolymer will be moles of PHETMA from integration height  $H_{Ph}/5$  (X) divided by weight (grams) of graft copolymer (Y) and is given by equation (4.10),

$$\frac{X}{Y} = \frac{\frac{H_{Ph}}{5}}{\frac{28A}{2A+B} \times \frac{H_E}{2} + \frac{44B}{2A+B} \times \frac{H_E}{2} + 190\frac{H_{Ph}}{5}} \cdots \cdots (4.10)$$

where 28, 44, and 190 are the molar masses of the ethylene, vinyl alcohol and PHETMA units respectively. A and B are the moles of ethylene and vinyl alcohol units in the precursor EVOH copolymer.

Similarly, moles of PHETMA per gram of graft copolymer prepared from a terpolymer backbone will be given by equation (4.11).

$$\frac{X}{Y} = \frac{\frac{H_{Ph}}{5}}{\frac{28A}{2A+B+C} \times \frac{H_E}{2} + \frac{44B}{2A+B+C} \times \frac{H_E}{2} + \frac{86C}{2A+B+C} \times \frac{H_E}{2} + 190\frac{H_{Ph}}{5}} \cdots (4.11)$$

where 86 is molar mass and C is moles of vinyl acetate units in the precursor terpolymer.

The results obtained are given in table 4.13 and are compared with the theoretical values (see section 4.4.1.2), demonstrating that composition

 Table 4.13 Comparison of moles of PHETMA determined by NMR, IR and

 theoretical values in poly(ethylene-vinyl alcohol)-g-PPHETMA.

Sample.	Moles of	Moles of	Moles of
	PHETMA per	PHETMA per	PHETMA per
	gram of graft	gram of graft	gram of graft
	copolymer	copolymer	copolymer
	(theoretical)	(NMR)	(IR)
	10-3	10-3	10-3
F1D	4.40	3.0	2.75
F4D	4.70	3.8	3.0
F7D	4.84	4.1	3.0
F2D	4.74	3.2	3.4
F5D	4.90	3.9	3.0
F8D	5.0	4.0	3.2
F3AD	4.14	3.8	
F6D	4.53	4.0	-
F9D	4.69	4.0	-

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data obtained by NMR are close to the theoretical values suggesting successful grafting reactions.

## 4.4.2.3 Infra-red spectroscopy (IR).

IR was used for qualitative and quantitative analyses of graft copolymers. An IR spectrum of graft copolymer (F<sub>1D</sub>) is given in figure 4.41. The important band due to -(CH<sub>2</sub>)- of the polyethylene backbone at 1465 cm<sup>-1</sup> is prominent. The band due to carbonyl ester of the PPHETMA side chain appears at 1732 cm<sup>-1</sup>. The appearance of these two significant bands of the backbone and the side chain and the disappearance of broad band at 3300-3500 cm<sup>-1</sup> due to O-H groups suggest the structural features of a graft copolymer with a polyethylene backbone and PPHETMA side chains.

The composition of the graft copolymers was determined by IR as described in section 3.6.3. Results for samples F3AD, F6D and F9D were not obtained, since these graft copolymers were prepared from a terpolymer backbone containing VA which makes it difficult to differentiate carbonyl absorbance in the product due to PHETMA units and VA units. However, results obtained for other graft copolymers are presented in table 4.13, where good agreement is observed for moles of PHETMA per gram of graft copolymer obtained by IR and NMR. It is therefore reasonable to suggest that these results in conjunction with the changes in molar mass indicated by GPC demonstrate that grafting reactions have been successful.

## 4.4.3 <u>Poly(ethylene-vinyl alcohol)-g-PBA graft copolymers.</u>

Three types of carboxyl terminated PBA prepolymers with molar masses in the range of 1900-4000 g mol<sup>-1</sup> were grafted onto the EVOH copolymer backbone with a VOH content of 9.8 mole % and a terpolymer backbone of ethylene-vinyl alcohol-vinyl acetate with a VOH content of 8.0 mole % (table 4.14). The isolation and purification of the graft copolymers are described in section 3.6.2.3. The pure graft copolymers were characterised by GPC, NMR and IR.

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Figure 4.41 IR spectrum of a poly(ethylene-vinyl alcohol)-g-PPHETMA sample (F1D).

## Table 4.14 Poly(ethylene-vinyl alcohol)-g-PBA samples, synthesised prepolymers, precursor and their concentrations used for the grafting reactions.

Sample	Mn × 10-3	VOH	concentration	concentration
	(PBA)	content	mol dm <sup>-3</sup>	mol dm <sup>-3</sup>
	prepolymer	mol %	10-2	10-4
		in	(Prepolymer)	(EVOH)
		(EVOH)		
		precursor		
G1AD	1.9	9.8	2.9	8.3
G4AD	3.0	9.8	2.9	8.3
G7AD	4.0	9.8	2.9	8.3
G2D	1.9	8.0	2.0	6.6
G6BD	3.0	8.0	2.0	6.6
G9BD	4.0	8.0	2.0	6.6

### 4.4.3.1 <u>Gel permeation chromatography (GPC).</u>

The pure poly (ethylene-vinyl alcohol)-g-PBA, graft copolymers were characterised by high temperature (140 °C) GPC with odichlorobenzene as solvent, in order to study changes in molar mass of graft copolymers compared with precursor EVA copolymer samples. Chromatography characterisation of samples was performed under the same experimental conditions as described in section 3.6.2.3. The resultant chromatograms of the graft copolymers and the precursor EVA copolymer sample are compared in figures 4.42-4.44. In figure 4.42 & 4.43 EVA copolymer sample (18-150) from which EVOH sample (18-150) with a VOH content of 9.8 mole % was produced and in figure 4.44 EVA copolymer sample (28-150) from which a terplymer with a VOH content of 8.0 mole% was produced are compared. EVA copolymer was preferred over EVOH copolymer for such comparisons because of the reasons discussed in section 4.4.1.1. Figures 4.42 & 4.43 show the comparison of a series graft copolymers (G1AD,G4AD and G7AD ) prepared from the prepolymer of molar masses 1900, 3000 and 4000 g mol<sup>-1</sup> and a copolymer backbone with a VOH content of 9.8 mole %. The clear shift of main peaks in these chromatograms toward low retention volumes indicates an increase in the molar mass of the graft copolymers. Similar changes in molar mass of the graft copolymers can be observed in figure 4.44 for graft copolymers (G2D and G9BD) prepared from the prepolymers with molar masses 1900 and 4000 g mol<sup>-1</sup>and a terpolymer backbone with a VOH content of 8 mol %. The clear shifts in the main peaks in these chromatograms suggest grafting reactions.

## 4.4.3.2 Nuclear magnetic resonance spectroscopy (NMR).

The characterisation and the composition of the graft copolymers were performed by <sup>1</sup>H NMR. The characterisation was performed by comparing the important chemical shifts (table 4.15) of the PBA prepolymers and the polyethylene backbone in the NMR spectrum of the graft copolymer. A typical NMR spectrum of a pure graft copolymer (G1AD) is presented in figure 4.45. The chemical shifts of the polyethylene backbone due to -(CH<sub>2</sub>)<sub>n</sub>- protons (a) resonating at  $\delta = 1.2$ ppm and a methine proton(I) resonating at  $\delta = 4.8$  ppm were detected at



Figure 4.42 <u>Comparison of chromatograms of a poly(ethylene-vinyl</u> alcohol)-g-PBA sample (G1AD) with EVA precursor (18-150).







Figure 4.44 <u>Comparison of chromatograms of a series of poly(ethylene-</u> <u>vinyl alcohol)-g-PBA samples (G2D) and (G9BD) with EVA</u> <u>precursor (28-150)</u>.

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the same positions. The chemical shifts of the PBA side chain due to methylene protons (e) adjacent to an ester group resonating at  $\delta$ =4.0 ppm. The methylene protons (f) resonate at  $\delta$ =1.6 ppm and protons (g) resonating at  $\delta$ =1.4 ppm are displayed in figure 4.45. The other chemical shifts of the PBA side chain at  $\delta$  = 3.2 ppm due to -CH<sub>2</sub>-S- protons (b) of the carboxyl end group and methine -(CH)- protons (c) at  $\delta$  =2.3 ppm were also detected in the NMR spectrum of the graft copolymer. These significant chemical shifts because of the polyethylene backbone and PBA side chain again suggest successful grafting reactions.

The composition of the graft copolymer by NMR was determined by comparing the integrated heights of the prominent chemical shift in the backbone and the side chain. The polyethylene methylene  $-(CH_2)_n$ -protons on the backbone (as described earlier in section 4.4.12 and 4.4.2.2) and methylene  $-COO-CH_2$ - protons of the PBA side chain resonate separately and so the integrated heights due to these protons can easily be measured. The moles of BA per gram of graft copolymer (as described in section 4.4.1.2 )will be moles of BA from the integration height H<sub>BA</sub>/2 (X) divided by the grams of graft copolymer (Y) and is given by equation(4.12).

$$\frac{X}{Y} = \frac{\frac{H_{BA}}{2}}{\frac{28A}{2A+B} \times \frac{H_{E}}{2}} + \frac{\frac{44B}{2A+B} \times \frac{H_{E}}{2}}{\frac{44B}{2} + \frac{128}{2}} + \frac{128}{2}$$

where 28, 44 and 128 are the molar masses of ethylene vinyl alcohol and BA units respectively.

Similarly, the moles of BA per gram of graft copolymer prepared from a terpolymer backbone will be given by equation (4.13).

$$\frac{X}{Y} = \frac{H_{BA}/2}{\frac{28A}{2A+B+C} \times \frac{H_E}{2} + \frac{44B}{2A+B+C} \times \frac{H_E}{2} \times \frac{86C}{2A+B+C} \times \frac{H_E}{2} + 128\frac{H_{BA}}{2} \dots (4.13)}$$

where 86 is the molar mass of the vinyl acetate unit.

The results obtained are given in table 4.16 and are compared with the theoretical values (see section 4.4.1.2). The reasonable agreement amongst these values suggest the same conclusion as obtained for the



Figure 4.45

<sup>1</sup>H <u>NMR spectrum of a poly(ethylene-vinyl alcohol)-g-PB/</u> sample (G1AD).

Table. 4.15	Assignment of chemical shifts in <u>HNMR spectrum</u>
	of poly(ethylene-vinyl alcohol)-g-PBA (G1AD).

Chemical shift	Assignment	Label
δppm		
1.25	- (-CH <sub>2</sub> -) <sub>n</sub>	a
3.2	-CH2-S-	b
2.3	-CH-	c
1.9	-CH2-	d
4.0	-COOCH2	е
1.6	COOCH2-(CH2)-	f
1.4	-CH2-(CH2)-CH3	g
0.9	-CH3	h

4.9



I



Table 4.16Comparison of moles of BA determined by NMR and IRwith theoretical values in poly(ethylene-vinyl alcohol)-g-PBA

Sample	Moles of BA (theoretical) 10 <sup>-3</sup>	Moles of BA (NMR) 10 <sup>-3</sup>	Moles of BA (IR) 10 <sup>-3</sup>
G1AD	6.61	6.4	6.0
G4AD	7.0	6.7	6.2
G7AD	7.19	6.6	6.3
G2D	6.22	5.5	-
G6BD	6.7	6.0	-
G9BD	7.0	6.5	-

Poly(ethylene-vinyl alcohol )-g-PMMA graft copolymers and poly(ethylene-vinyl alcohol)-g-PPHETMA graft copolymers, that is grafting of PBA onto the polyethylene backbone had occurred.

### 4.4.3.3 <u>Infra-red spectroscopy (IR)</u>

IR was used for the qualitative and quantitative analyses of the graft copolymers. An IR spectrum of a graft copolymer (G1AD) is presented in figure 4.46. This spectrum shows significant bands due to the polyethylene backbone and PBA side chain. The band due to polyethylene -(CH2)<sub>n</sub>- appears at 1465 cm<sup>-1</sup>. The band at 1732 cm<sup>-1</sup> due to carbonyl ester indicates the presence of a PBA side chain. The appearance of important bands of the backbone and the side chain and the disappearance of the strong O-H band at 3300-3500 cm<sup>-1</sup> suggests successful grafting reactions.

The composition of the graft copolymer was determined by IR to give the moles of BA present per gram of the graft copolymer. The method is described in section 3.6.3. The results obtained are presented in table 4.16 and are compared with the theoretical and NMR values. The results for samples G2D, G6BD and G9BD are not given , since these samples were prepared from a terpolymer backbone which also contains VA units and carbonyl absorbance in the graft copolymer is because of both VA and BA units which makes it difficult to determine the concentration of BA. However, moles of BA determined by NMR are compared with theoretical values which are close to these values. The IR and NMR values in G1AD, G4AD and G7AD are in good agreement with each other.

## 4.5 Molar masses of the graft copolymers from GPC.

IR chromatograms obtained by GPC were analysed to determine molar masses of the precursor EVA, EVOH and graft copolymer (see section 3.6.2.3). The results of molar masses obtained are presented in tables 4.17-4.19, which indicate significant changes in the molar masses of the graft copolymers from the EVA copolymer precursors. The changes in the molar masses of poly(ethylene-vinyl alcohol)-g-PMMA (table 4.17) prepared from the EVA copolymer of VA content 9.8 mole % (E10D-E11D) and a terpolymer with VA content 8.0 mole % (E16D-E18D) could



Figure 4.46 IR spectrum of a poly(ethylene-vinyl alcohol)g-PBA sample (G1AD).

be compared. Changes in molar masses are less in the products prepared from a terpolymer which may show the intermolecular hydrogen bonding effect of O-H groups. Similarly, this effect can be seen in the poly(ethylene-vinyl alcohol)-g-PBA (table 4.19) (G1AD-G7AD & G2D- G9BD). It appears that changes in the molar masses of the graft copolymers are greater in the PMMA system as compared to PPHETMA and PBA indicating the grafting level of the three carboxyl terminated prepolymers to the O-H backbone copolymers. This could be due to the polarity of PMMA compared to PPHETMA and PBA which disrupts the intermolecular hydrogen bonding between O-H groups and provides a much greater chance for the acid chloride group at the end of a PMMA chain to undergo a coupling reaction.

The molar masses presented in tables 4.17-4.19 are polystyrene equivalents and were obtained with a polystyrene calibration curve (section 3.6.2.3). Since the graft product has a branched structure , calibration with polystyrene standards will not provide absolute molar masses (164). However, it is possible that the level of branches and level of methacrylate incorporation will not necessarily be the same over the whole range of chain sizes, so the product could have branching and composition distributions as well as a molar mass distribution.

In this circumstance it will be extremely difficult to provide an accurate GPC calibration curve. Therefore, a polystyrene calibration was used to provide a relative comparison of molar masses of EVA precursors and the graft copolymers.

## 4.6 Number of grafts per chain.

The molar masses obtained by GPC for the poly(ethylene-vinyl alcohol)-g-PMMA, poly(ethylene-vinyl alcohol)-g-PPHETMA and poly(ethylene-vinyl alcohol)-g-PBA graft copolymers were used to determine the number of grafts per chain. The values obtained by GPC were compared with the IR, NMR. and the theoretical values (table 4.20-4.22). The theoretical number of grafts was obtained by calculating the number of hydroxyl groups per chain in the EVOH copolymer backbone and assuming:

number of grafts per chain = number of hydroxyl groups per chain.

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 Table 4.17 Comparison of number average molar masses of precursors and

 products in poly(ethylene-vinyl alcohol)-g-PMMA.

Sample	Mn × 10 <sup>-3</sup> (PMMA)	Mn × 10 <sup>-3</sup> (EVA)	Mn × 10 <sup>-3</sup> (EVOH)	Mn×10 <sup>-3</sup> (graft
	end group	GPC	GPC	copolymers)
	analysis			GPC
E10D	1.4	18	12	54
E14D	2.9	18	12	84
E11D	4.4	18	12	95
E12D	1.4	17	10	48
E15D	2.9	<b>17</b>	10	· · · 140 ·
E13D	4.4	17	10	174
E16D	1.4	17	15	50
E17D	2.9	17	15	69
E18D	4.4	17	15	48

N.B. i) Samples E10D,E14D & E11D, EVOH precursor of VOH content 9.8 mole %
ii) Samples E12D,E15D & E13D, EVOH precursor of VOH content 21 mole %
iii) Samples E16D, E17D & E18D, a terpolymer precursor of VOH content 8.0 mole %.

 

 Table. 4.18 Comparison of number average molar masses of precursors and products in poly(ethylene-vinyl alcohol)-g- PPHETMA.

Sample	Mn × 10 <sup>-3</sup> (PPHETMA) end group analysis	Mn×10 <sup>-3</sup> (EVA) GPC	Mn × 10 <sup>-3</sup> (EVOH) GPC	Mn × 10 <sup>-3</sup> (graft copolymer) GPC
F1D	1.8	18	12	55
F4D	3.0	18	12	42
F7D	4.0	18	12	44
F2D	1.8	17	10	82
F5D	3.0	17	10	65
F8D	4.0	17	10	51
F3AD	1.8	17	15	51
F6D	3.0	17	15	45
F9D	4.0	17	15	52

N.B. i) Samples F1D,F4D & F7D, EVOH precursor of VOH content 9.8 mole %.

ii) Samples F2D,F5D & F8D, EVOH precursor of VOH content 21 mole %.

iii) Samples F3AD, F6D & F9D , a terpolymer precursor of VOH content 8.0 mole %

Table 4.19 Comparison of number average molar masses of precursorsand products by GPC in poly(ethylene-vinyl alcohol)-g-PBA.

Sample	$Mn \times 10^{-3}$	$Mn \times 10^{-3}$	$Mn \times 10^{-3}$	$Mn \times 10^{-3}$
ompro	(PBA)	(EVA)	(EVOH)	(graft
	end group	GPC	GPC	copolymer)
	analysis		· 1	GPC
G1AD	1.9	18	12	61
G4AD	3.0	18	12	75
G7AD	4.0	18	12	81
G2D	1.9	17	15	34
G6BD	3.0	17	15	30
G9BD	4.0	17	15	41

N.B. i) Samples G1AD,G4AD & G7AD, EVOH precursor of VOH content 9.8 mole %. ii) Samples G2D, G6BD & G9BD, a terpolymer precursor of VOH content 8.0 mole %. This assumption is based on all the hydroxyl groups on the EVOH copolymer precursor reacting with acid chloride terminated prepolymer so that the number of prepolymer branches and the hydroxyl groups per chain would be the same. The numbers of grafts by IR and NMR are based on the moles of prepolymer units determined by these techniques (see section 4.4) together with the known molar masses of graft copolymers and prepolymer chains.

The results obtained are presented in tables 4.20-4.22, where theoretical numbers of grafts are compared with the values obtained by GPC, IR and NMR. It appears that in all three graft copolymer systems the experimental values are close to the theoretical values, indicating that the hydroxyl groups on the precursor backbone are replaced by the prepolymer side chains. Moreover, the number of grafts obtained by the three experimental methods IR, NMR and GPC are close indicating the reliability of the values obtained by these methods. The results presented in table 4.20 were obtained for poly(ethylene-vinyl alcohol)g-PMMA graft copolymers, results for samples E16D, E17D and E18D by IR are not shown as described in section 4.4.1.3 these graft copolymers were prepared from a terpolymer backbone and resultant product has carbonyl groups containing VA and MMA units which makes it difficult to determine moles of MMA from a carbonyl calibration curve. It appears that in the series E10D to E11D the number of grafts decreases as the molar mass of the prepolymer increases (figure 4.47). The same trend can be seen in series E16D to E18. However, in this series the numbers of grafts are less compared to the E10 to E11D series of corresponding prepolymer (figure 4.47). This might be due to the hydrogen bonding effect of O-H groups which increases with the presence of VA groups on the precursor backbone. As graft copolymers E16 to E18D were prepared from a terpolymer backbone, ethylene-vinyl acetate-vinyl alcohol, while E10 to E11D graft copolymers were prepared from ethylene-vinyl alcohol copolymer backbones.

The results presented in table 4.21 were obtained for the poly(ethylenevinyl alcohol)-g-PPHETMA graft copolymers. Samples in the series F1D to F7D indicate the effect of prepolymer chain length on the number of grafts. The number of grafts decreases as the prepolymer chain length increases (figure 4.48). The same conclusion can be drawn from the other two series F2D to F8D and F3AD to F9D.

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## Table 4.20 Number of grafts per chain obtained in poly(ethylene-vinyl alcohol)-g-PMMA graft copolymer by different methods.

Sample	Number of	Number of	Number of	Number of
	grafts per	grafts per	grafts per	grafts per
· · · ·	chain.	chain	chain	chain
	(theoretical)	(GPC)	(IR)	(NMR)
E10D	34	25	29	29
E14D	34	22	22	24
E11D	34	17	18	18
E12D	52	22	28	28
E15D	52	42	41	40
E13D	52	35	33	35
E16D	30	23	<b>I</b> .	25
E17D	30	18	-	19
E18D	30	7	-	10

N.B. i) E10D,E14D & E11D, EVOH precursor with a VOH content 9.8 mole %.
ii) E12D,E15D & E13D,EVOH precursor with a VOH content 21 mole %.
iii) E16D,E17D & E18D, a terpolymer precursor with a VOH content of 8 mole %.

 

 Table 4.21 Number of grafts per chain obtained in poly(ethylenevinyl alcohol)-g-PPHETMA graft copolymers.

Sample	Number of	Number of	Number of	Number of
	grafts per	grafts per	grafts per	grafts per
	chain	chain	chain	chain
	(theoretical)	(GPC)	(IR)	(NMR)
F1D	34	20	15	17
F4D	34	8	9	10
F7D	34	6	7	9
F2D	52	36	29	27
F5D	52	16	13	16
F8D	52	8	7	10
F3AD	30	18	· -	20
F6D	30	9	-	11
F9D	30	8	-	10

N.B. i) F1D,F4D & F7D, EVOH precursor with a VOH content of 9.8 mole %
ii) F2D,F5D & F8D, EVOH precursor with a VOH content of 21 mole %.
iii) F3AD,F6D & F9D, a terpolymer precursor with a VOH content 8 mole %.

 Table 4.22 Number of grafts obtained in poly(ethylene-vinyl alcohol)-g-PBA by different methods.

Sample	Number of grafts per			
	chain	chain	chain	chain
	(Theoretical)	(GPC)	(IR)	(NMR)
G1AD	34	22	24	26
G4AD	34	19	19	21
G7AD	34	16	16	17
G2D	30	9		13
G6D	30	5	-	8
G9BD	30	6	-	8

N.B. i) G1AD,G4AD & G7AD, EVOH precursor with a VOH content 9.8 mole %. ii) G2D,G6D & G9BD, a terpolymer precursor with a VOH content 8 mole %. Table 4.22 shows the number of grafts in the poly(ethylene-vinyl alcohol)-g-PBA graft copolymer systems. The decrease in the number of grafts with the increase in molar mass of prepolymer can be seen in the G1AD to G7AD series G2D to G9BD (figure 4.49).

Results of number of grafts obtained for the three graft copolymer systems showed that the number of grafts are greater in short chain prepolymers. Noryuki and co-workers (176) studied the reactivity of functional groups at the ends of polymer chains. Their results showed that the chain length influenced the reactivity of functional groups at the ends of polymer chains. Functional groups at the ends of long chain polymers are less reactive than the functional groups at the ends of short chains. This trend for prepolymer chains was found in all three graft copolymer systems except one sample E12D a poly(ethylenevinyl alcohol)-g-PMMA. It appears that in poly(ethylene-vinyl alcohol)-g-PMMA the number of grafts is higher than in the other two graft copolymer systems which supports the conclusion obtained in section 4.5, that is, PMMA being more polar disrupts the hydrogen bonding of O-H groups. Therefore, the acid chloride groups on PMMA chain ends have easy access to hydroxyl groups for coupling reactions which results in a higher level of grafting. It can also be observed that the number of grafts in samples (E16D, E17D and E18D) prepared from a terpolymer backbone with a VOH content of 8.0 mole % and number of grafts in samples (E10D, E14D and E11D) prepared from a copolymer backbone with a VOH content of 9.8 mole % are less. This could be due to a hydrogen bonding effect which is more pronounced due to the presence of additional VA groups in the terpolymer. Similar effects can be seen in the series G1AD to G7AD and G2D to G9BD (table 4.22).

## 4.7 Evidence of grafting reaction.

Examples of the synthesis of graft copolymers by the coupling reaction of terminal functional groups with antagonist functional groups are not very common in the literature. Redford (177) has used a similar reaction for the synthesis of diblock polymers, in which the two polymers with reactive terminal functional groups were coupled in a common solvent. The grafting onto method involves various difficulties (see section 2.1.3), such as incompatibility of two polymer chains in a common solvent due to different chemical nature, lower



Figure 4.47 Plots of number of grafts versus molar mass of prepolymer in poly(ethylene-vinyl alcohol)-g-PMMA.

Prepolymer molar mass

N.B i) E10D,E11D & E14D, EVOH precursor with a VOH content of 9.8 mole % ii) E12D,E15D & E13D, EVOH precursor with a VOH content of 21 mole % iii) E16D,E17D & E18D, a terpolymer precursor with a VOH content of 8.0 mole %.



Figure 4.48 Plots of number of grafts versus prepolymer molar mass in poly(ethylene-vinyl alcohol)-g-PPHETMA.

Prepolymer molar mass

N.B i) F1D,F4D & F7D, EVOH precursor with a VOH content of 9.8 mole%. ii) F2D,F5D & F8D, EVOH precursor with a VOH content of 21 mole% iii) F3AD,F6D & F9D, a terpolymer precursor with a VOH content of 8.0 mole%.


# Figure 4.49 Plots of number of grafts versus prepolymer molar mass in poly(ethylene-vinyl alcohol)-g-PBA

Prepolymer molar mass

N.B i) G1AD,G4AD & G7AD, EVOH precursor with a VOH content of 9.8 mole %. ii) G2D,G6D & G9BD, a terpolymer with a VOH content of 8.0 mole %. reactivity of functional groups in a long chain polymer and inaccessibility of functional groups to each other due to different behaviours in solvent. A further difficulty may arise from specific types of side reactions. A possible side reaction in these grafting reactions could occur from transesterification. Since the carboxyl terminated prepolymers have -COOCH3 ester groups in PMMA, -COOCH2CH2Ph ester groups in PPHETMA and -COO-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub> ester groups in PBA, it may be possible for a backbone polymer chain having -OH groups to interact with a prepolymer chain having ester groups in a common solvent at high temperature (xylene b.p. 140 °C) to undergo transesterification reactions and to produce graft copolymers of different structures. Since carboxyl terminated prepolymers were converted to acid chloride terminated prepolymers, in the presence of ester groups and acid chloride, there will be a competition among these groups to react with hydroxyl groups, but since acid chloride groups are more reactive than esters the possibilities of such side reactions to occur should be minimised. However, such transesterification reactions are catalysed by acidic media. It could be possible that acid chloride terminated prepolymer after several coupling reactions eliminates HCl to catalyse such side reactions. In order to study the possibility of any transesterification reaction and to establish that the change in molar mass of the products are because of coupling reactions between acid chloride functional groups at the ends of prepolymer chains and the hydroxyl groups on the backbone, a series of reactions were performed. For this purpose prepolymers of PMMA, PPHETMA and PBA with no carboxyl acid end groups were prepared. These were chosen because prepolymers with no carboxyl functional groups only have ester groups and if these prepolymers were allowed to react with a backbone having hydroxyl groups in acidic media, then only transesterification reactions are possible. The prepolymers PMMA, PPHETMA and PBA with no carboxyl end groups and of molar mass 1500 g mol<sup>-1</sup> were synthesised using butanethiol chain transfer agent and AIBN initiator (see section 3.4.3). These low molar mass prepolymers were reacted with EVOH copolymer backbones with a VOH content of 9.8 mole % and a VOH content of 21 mole % for PMMA and PPHETMA and a EVOH copolymer backbone of VOH content 9.8 mole % for PBA using p-toluene sulphonic acid catalyst in xylene under similar conditions for the grafting reactions (see section



Figure 4.50

<u>Comparison of chromatograms of PMMA product (BL1)</u> with EVA copolymer precursor (18-150).



Figure 4.51

<u>Comparison of chromatograms of PMMA product (BL3)</u> with EVA\_copolymer precursor (28-150). 3.4.3). The products isolated as a result of these reactions were analysed by GPC under similar experimental conditions.

The GPC chromatograms of the products obtained from these experiments are presented in figures 4.50-4.54. In these figures a chromatogram of each product is compared with an EVA copolymer precursor. The GPC experiment conditions used for comparisons in each figure were similar. (see section 3.6.2.3). In figure 4.50 chromatograms of product (BL1) obtained as a result of reaction between PMMA prepolymer and EVOH copolymer precursor with a VOH content of 9.8 mole % are compared with the EVA copolymer precursor. In figure 4.51 a chromatogram of product (BL3) obtained by the reaction of PMMA prepolymer and EVOH copolymer with a VOH content of 21 mol % is compared with EVA copolymer precursor. In these figures no shift in the retention volume peaks toward lower values indicates no change in the molar masses of the products and suggests no transesterification reactions. Similarly, in figures 4.52 and 4.53 the products (BL2&BL4) obtained as a result of reaction between PPHETMA prepolymers with EVOH copolymer precursors with a VOH content of 9.8 mole % and of 21 mole % are compared with their respective EVA copolymer precursors. These chromatograms also indicate no shift in the retention volume peaks towards lower values. The product (BL5) in figure 4.54 which is a result of reaction between PBA prepolymer and EVOH copolymer precursor with a VOH content of 9.8 mol % is compared with EVA copolymer precursor. A similar observation can be seen in this comparison, that is, no shift in the retention volume peak towards a lower value. The molar masses determined by GPC of these products are given in table 4.23. When molar masses of the products are compared with precursor EVA copolymer, no changes were observed, which again supports the same conclusion as obtained by the comparison of chromatograms, that is, no transesterification reaction occurs. From the GPC results in terms of chromatograms and molar masses it is clear that in the GPC results of the poly(ethylene-vinyl alcohol)-g-PMMA, poly(ethylene-vinyl alcohol)-g-PPHETMA and poly(ethylene-vinyl alcohol)-g-PBA graft copolymers ( in sections 4.4.1, 4.4.2 and 4.4.3 respectively) the shift of retention volume peaks toward lower values and change in molar masses compared to precursors are due to coupling reactions of acid



Figure 4.52 <u>Comparison of chromatograms of PPHETMA product (BL2)</u> with EVA copolymer precursor (18-150).



Figure 4.53 <u>Comparison of chromatograms of PPHETMA product (BL4)</u> with EVA copolymer precursor (28-150).



Figure 4.54 Comparison of chromatograms of PBA product (BL5) with EVA\_copolymer precursor (18-150).

Table 4.23Molar masses obtained by GPC of the products resulting from<br/>reactions of butanethiol terminated prepolymers and EVOH<br/>copolymer backbones compared with the precursors.

Sample	Prepolyme <b>r</b>	Mn × 10 <sup>-3</sup> (EVA) GPC	Mn × 10 <sup>-3</sup> (EVOH) GPC	Mn × 10 <sup>-3</sup> (reaction product) GPC	VOH content mole % (EVOH precursor)
BL1	PMMA	18	12	15	9.8
BL2	PPHETMA	18	12	12	9.8
BL5	PBA	18	12	22	9.8
BL3	PMMA	17	10	9	21
BL4	PPHETMA	17	10	5	21

N.B.

i) BL1, BL2 & BL5, EVOH precursor with a VOH content of 9.8 mole %.
ii) BL3 & BL4, EVOH precursor with a VOH content of 21 mole %

chloride terminated prepolymers and hydroxyl groups on the precursor backbone and are not due to transesterification reactions.

### 4.8 <u>Differential scanning calorimetry (DSC)</u>.

Differential scanning calorimetry (DSC) analysis of graft copolymers was performed in order to study changes in the morphology of the EVOH copolymer samples after the introduction of amorphous prepolymer side chains. To study this effect DSC analysis of the precursor copolymers will be discussed first, and then the changes in thermal behaviour of these copolymers as a result of grafting reactions will be considered. Prior to DSC analysis all samples were subjected to the same thermal conditions to have a similar thermal history. Samples were dried in a vacuum oven at 60 °C for 24 hours and cooled to room temperature. Samples were scanned in three experiment modes (see section 4.8.2). The samples were first heated up to 130 <sup>0</sup>C at the rate of 10 <sup>0</sup>C per minute above the melting point of precursor EVOH annealed for 30 minutes then cooled down to 0 <sup>0</sup>C at the rate of 10 <sup>0</sup>C where the temperature was held constant for 10 minutes and reheated again to 130 <sup>0</sup>C at the same rate. Thermograms are presented for an initial heating experiment (endothermic) followed by a cooling experiment (exothermic).

### 4.8.1 <u>Ethylene-vinyl acetate and ethylene-vinyl alcohol copolymers.</u>

The DSC thermograms of EVA sample (18-150) with a VA content of 9.8 mole % is shown in figure 4.55 and EVA sample (28-150) with a VA content of 21 mole % in figure 4.56. The endothermic peak (73  $^{0}$ C) (bottom trace) in sample (18-150) is larger compared to sample (28-150) (51  $^{0}$ C), while the exothermic peaks (top trace) are reasonably sharp and prominent compared to the endothermic peaks. It appears that sample (18-150) is larger (28-150). The sample with low vinyl acetate content (9.8 mole %) shows that in exothermic mode the ethylene units were crystallised giving a large peak compared to the sample with high VA content, indicating that the increase in VA content prohibits ethylene units to rearrange and to crystallise. Salyer and co-workers (178) observed the same phenomenon for EVA copolymer samples. They reported that with an increase in the VA content in EVA copolymer, crystallinity



decreased gradually until zero crystallinity was reached at approximately 25 mole % VA content. At that point randomly spaced branched comonomer units interrupt crystallinity because on average there are four carbons on each side of the branches so for such short sequences crystallisation is not possible. Since the EVA copolymer sample (28-150) has 21 mole % VA content this effect is pronounced and it would be difficult for the ethylene units to generate highly crystalline regions. The heat of fusion for EVA copolymer sample (18-150) (10 mg) was found to be 34.51 J/g and Tm 73 <sup>0</sup>C while for EVA copolymer sample (28-150) (10 mg),the value of the heat of fusion was 10.86 J/g and Tm 51 <sup>0</sup>C which also indicated the highly crystalline regions in a sample with low VA content.

The DSC traces of EVOH copolymers from hydrolysed EVA copolymer samples are presented in figures 4.57& 4.58. Both samples gave prominent endothermic (bottom traces) and exothermic (top traces) peaks, which indicate that the replacement of acetate groups by hydroxyl groups enhanced the crystallisation of the copolymer. This increase in the crystallinity as shown by the heat of fusion (table 4.24) is due to intermolecular hydrogen bonding caused by hydroxyl groups and since these groups are smaller in size compared to acetate groups they can fit into a crystal lattice of polyethylene. Bunn (179) has indicated that the hydroxyl groups can enter into a polyethylene crystal lattice. The increase in the heat of fusion and crystalline melting point (Tm) of EVOH copolymer samples compared to EVA copolymer samples (table 4.24) also indicated the increased in crystallinity in EVOH copolymer. The EVOH copolymer sample (18-150) hydrolysed from EVA sample (18-150) with a VA content of 9.8 mole % showed Tm at 113 <sup>0</sup>C and heat of fusion (10 mg sample) of 134 J/g, while EVOH copolymer sample (28-150) hydrolysed from EVA copolymer sample (28-150) showed Tm at 107 <sup>0</sup>C and heat of fusion (10 mg sample) of 22 J/g which indicated that an increase in O-H content in EVOH copolymer decreased the crystallinity. The multiple peaks in the EVOH (18-150) (figure 4.57) trace have also been observed by other workers (180,181). Buga (182) suggested that the minor endothermic peak prior to the main transition is due to partial melting and recrystallisation of crystallites as the temperature in the DSC cell is increased.



#### 4.8.2 <u>Poly(ethylene-vinyl alcohol) graft copolymers.</u>

The DSC traces of graft copolymers poly(ethylene-vinyl alcohol)-g-PMMA, poly(ethylene-vinyl alcohol)-g-PPHETMA and poly(ethylenevinyl alcohol)-g-PBA are presented in figures 4.59-4.69. The thermograms presented in figure 4.59 are for poly(ethylene-vinyl alcohol)-g-PMMA graft copolymer E10D prepared from a EVOH with a VOH content of 9.8 mole %. Thermograms in figure 4.60 are for a graft copolymer (E12D) prepared from a EVOH precursor with a vinyl alcohol content of 21 mole % and in figure 4.61 for a graft copolymer (E16D) synthesised from a terpolymer precursor with vinyl alcohol content of 8.0 mole %. The endothermic (bottom) and exothermic (top) traces of all samples show no peaks suggesting that these graft copolymers are mainly amorphous, which indicated that the replacement of hydroxyl groups by the PMMA prepolymers as result of grafting reactions has disturbed the regular arrangement of the ethylene units. Since EVOH precursor copolymers are crystalline, the introduction of any uncrystallisable side chain will hinder the ethylene units to rearrange into a definite crystalline lattice. Results of DSC analysis of the poly(ethylene-vinyl alcohol)-g-PMMA samples prepared clearly show that graft copolymers did not show any melting peak and suggest that these samples are mainly amorphous as summarised in table 4.24. The disappearance of endothermic and exothermic peaks in the graft copolymers are due to PMMA side chains which was supported by studying graft copolymer samples with very low grafts (see section 4.4.1.1). The resultant traces for these lowly grafted products are presented in figures 4.62-4.64. These thermograms clearly show endothermic (bottom) and exothermic (top) peaks indicating some crystallinity in these samples. Data for heat of fusion of these samples are presented in table 4.25 and are compared with values for the precursor EVOH copolymer samples. The values clearly indicate a decrease in the crystallinity of graft copolymers as these values of heat of fusion are low compared to EVOH copolymer precursors.

The DSC thermograms of poly(ethylene-vinyl alcohol)-g-PPHETMA graft copolymers are shown in figures 4.65-4.67. The traces in figure 4.65 indicate the endothermic and exothermic modes of a graft copolymer (F1D) prepared from a EVOH copolymer precursor with a VOH content





Figure 4.62

DSC traces of poly(ethylene-vinyl alcohol)-g-PMMA sample (E4D), with low number of grafts.

Table 4.24	<b>Comparison</b>	of `Tm` a	<u>and heat</u>	of fusion	<u>of precursor</u>	<u>EVA and</u>
	EVOH sam	<u>ples with</u>	poly(eth	<u>ylene-vin</u>	<u>yl alcohol)-g</u>	-PMMA.

	Tm		Tm	Heat	DSC	Number
sample		Heat		of	results	of grafts
	(EVA)	of	(EVOH)	fusion		per chain
	<sup>0</sup> C	fusion	٥C	(EVOH)	(graft	(GPC)
	-	(EVA)	с. А.	J/g	copoly).	
		J/g				
E10D	73	34.51	113	134	no peak	25
E14D	73	34.51	113	134	no peak	22
E11D	73	34.51	113	134	no peak	17
E12D	51	10.86	107	22	no peak	22
E13D	51	10.86	107	. 22	no peak	42
E15D	51	10.86	107	22	no peak	35
E16D	51	10.86	107	22	no peak	23
E17D	51	10.86	107	22	no peak	18
E18D	51	10.86	107	22	no peak	7

N.B. i) E10D,E14D & E11D, precursors EVA (18-150) and EVOH (18-150).

ii) E12D,E13D & E15D, precursors EVA (28-150) and EVOH (28-150).

iii) E16D,E17D & E18D, precursors EVA (28-150) and partially hydrolysed EVA (28-150).









DSC traces of poly(ethylene-vinyl alcohol)-g-PMMA sample (E6D), with low number of grafts.

Table 4.25Comparison of `Tm` and heat of fusion of precursor EVA and<br/>EVOH copolymer samples with low grafted products.

Sample	Tm	Heat of	Tm	Heat of	Tm	Heat of	Number
	(EVA)	fusion		fusion	(graft	fusion	of grafts
		(EVA)	(EVOH)	(EVOH)	copoly)	(graft	per
	°C	J/g	°C	J/g	°C	copoly) J/g	chain.
E4D	73	34.51	113	134	98	29	8
E5D	73	34.51	113	134	102	40	3
E6D	73	34.51	113	134	96	38	• 4

N.B.

E4D,E5D & E6D, precursors EVA (18-150) and EVOH (18-150).

of 9.8 mole % and figure 4.66 shows a graft copolymer (F2D) from a EVOH copolymer precursor with a VOH content of 21 mole %. These thermograms do not show any peak. However, sample F3AD (figure 4.67) shows a small peak at 48  $^{0}$ C and heat of fusion 5.25 J/g which is low compared to the precursor (22 J/g). This suggests that graft copolymers are mainly amorphous and the same conclusion can be obtained, that is, after grafting reactions PPHETMA prepolymers disturbed the crystallinity of the polyethylene units in the precursor EVOH copolymer. Results of DSC analysis of poly(ethylene-vinyl)-g-PPHETMA samples prepared are presented in table 4.26 and are compared with EVOH copolymer precursors, which shows the changes in the thermal behaviour of EVOH precursor copolymer after the grafting of PPHETMA prepolymer side chains. Since these graft copolymers did not show any melting peak, while precursor EVOH copolymers show prominent melting peak and heat of fusion, it is suggested that PPHETMA prepolymer has disturbed the regular arrangement of polyethylene units in the precursor EVOH copolymers.

DSC traces of poly(ethylene-vinyl alcohol)-g-PBA are presented in figures 4.68-4.69. In each figure traces of a graft copolymer from the same EVOH copolymer precursors are shown. The endothermic and exothermic traces of the sample G1AD in figure 4.68 prepared from the EVOH precursor with a VOH content of 9.8 mole % show small endothermic and exothermic peaks. The heat of fusion 5.53 J/g is very low compared to the precursor which is 134 J/g indicating very low crystallinity in the sample. Thermograms presented in figure 4.69 of a graft copolymer sample (G2D) prepared from a terpolymer with a VOH content of 8.0 mole % indicated no melting peak suggesting amorphous behaviour of the samples. Results of DSC analysis of poly(ethylene-vinyl alcohol)-g-PBA are given in table 4.27 and are compared with the precursor EVOH copolymer. The graft copolymer products do not show any melting peaks indicating an amorphous behaviour and suggesting the grafting of PBA prepolymers onto EVOH copolymer backbone.

DSC analysis of the graft copolymers prepared showed no crystallinity in the samples, which supports the replacement of the hydroxyl groups on the precursor backbones with prepolymer side chains. Okui (183) studied the effect of uncrystallised units, if introduced randomly onto a



Figure 4.65 DSC traces of poly(ethylene-vinyl alcohol)-g-PPHETMA\_ sample (F1D).



Sample	Tm (EVA)	Heat of fusion (EVA)	Tm (EVOH)	Heat of fusion (EVOH)	DSC result (graft	Number of grafts per chain
	٥C	J/g		J/g	copoly)	(GPC).
F1D	73	34	113	134	no peak	· 22
F4D	73	34	113	134	no peak	8
F7D	73	34	113	134	no peak	6
F2D	י <b>5</b> 1	10	107	22	no peak	36
F5D	51	10	107	22	no peak	13
F8D	51	10	107	22	no peak	7
F3AD	51	10	107	22	small	18
					peak	
F6D	51	· 10	107	22	no peak	9
F9D	51	10	107	22	no peak	. 8

 Table 4.26 Comparison of DSC results of EVA and EVOH precursors

 with poly(ethylene-vinyl alcohol)-g-PPHETMA samples.

## N.B.

i) F1D,F4D & F7D, precursors EVA (18-150) and EVOH (18-150). ii) F2D,F5D & F8D, precursors EVA (28-150) and EVOH (28-150).

iii) F3AD,F6D & F9D, precursors EVA (28-150) and partially hysrolysed EVA (28-150).

 Table 4.27 Comparison of DSC results of EVA and EVOH precursors

 with poly(ethylene-vinyl alcohol )-g-PBA samples.

Sample	Tm	Heat of	Tm	Heat of	DSC	Number
	(EVA)	fusion	(EVOH)	fusion	results	of grafts
	∘റ	(EVA)	°C	(EVOH)	(graft	per chain
-		J/g		J/g	copoly.)	(GPC).
G1AD	73	34	113	134	small	22
					peak	
G4AD	73	34	113	134	no peak	19
G7AD	73	34	113	134	no peak	16
G2D	51	10	107	22	no peak	13
G6BD	51	10	107	22	no peak	8
G9BD	51	10	107	22	no peak	9

N.B.

i) G1AD,G4AD & G7AD, precursor EVA (18-150) and EVOH (18-150)

ii) G2D,G6BD & G9BD, precursor EVA (28-150) and partially hydrolysed EVA(28-150).



(G2D).

•

•

crystallisable chain. He observed that such units might prohibit chain folding crystallisation but will participate in intermolecular crystallisation, which will give rise to a fringe micelle type structure. (figure 4.70). He suggested that the transition from the chain folding crystallisation to intermolecular crystallisation is considered to occur at a comparatively low composition of the uncrystallisable component and below this critical composition the chains are expected to fold back in a manner such that the uncrystallisable units are excluded from the crystalline lattice and will concentrate with the fold resulting in loose loops (figure 4.70). It could be possible that the prepolymer side chain as a result of such intermolecular crystallisation allows ethylene units to arrange in loose loops or a fringe micelle crystallisation. In order to study this possibility the graft copolymers were studied in three thermal modes as described earlier in section 4.8. Typical resultant traces for such experiments are presented in figures 4.71 & 4.72 for sample E10D. It appeared from these endothermic and exothermic traces that no such recrystallisation has occurred, which suggested that these graft copolymers have long side chains which inhibit the polyethylene units to recrystallise. Cole and Holmes (184) studied the effect of length of side chains on the intermolecular crystallinity and observed that intermolecular crystallinity destroying power is in the order as follows,

### methyl branch < ethyl branch < propyl branch.

Prepolymers are long chain polymers with monomer units in the range of 14-44 in poly(ethylene-vinyl alcohol)-g-PMMA, 10-21 monomer units in poly(ethylene-vinyl alcohol)-g-PPHETMA and 14-31 monomer units in poly(ethylene-vinyl alcohol)-g-PBA graft copolymers. Thus, it would be extremely difficult for the ethylene units to have such order to establish crystallinity.

### 4.9 <u>Wide angle x-ray scattering (WAXS).</u>

Crystallinity of polyethylene decreases drastically as comonomer units are introduced in the chain via copolymerisation, and if the comonomer level is sufficiently high the copolymer in fact becomes totally amorphous. In EVA copolymers the increase in the vinyl acetate content decreases the crystallinity of polyethylene (178). When EVA



# a- Chain fold-lamella with loose loop.



# BRANCH

b-Chain fold-lamella fringe micelle structure.

Figure 4.70

Schematic representation of conformational change of crystallisation of polymer chains (reproduced from Ref. 186)



Figure 4.72

DSC traces of poly(ethylene-vinyl alcohol)-g-PMMA sample (E10D), second heating mode.

copolymer was hydrolysed to EVOH copolymer, an increase in the heat of fusion indicated an increase in crystallinity of polyethylene (section 4.8.1), which is caused by intermolecular hydrogen bonding and a decrease in the size of comonomer unit from VA to VOH which can enter into the crystalline lattice of polyethylene and facilitate ethylene units to establish crystallinity. This rearrangement of ethylene units is disturbed drastically, when the hydroxyl groups are replaced by some other larger groups or side chains as a result of grafting reactions. In order to study the effect of prepolymer side chains on the crystallinity of sequences of ethylene units to establish a change in the morphology of EVOH precursors as a result of grafting reactions, powder samples of graft copolymers of poly(ethylene-vinyl alcohol)-g-PMMA and cast films from chloroform for poly(ethylene-vinyl alcohol)-g-PPHETMA and poly(ethylene-vinyl alcohol)-g-PBA were analysed with a wide angle x-ray diffractometer. (see section 3.6.6).

The x-ray diffraction patterns of EVA copolymer sample (18-150) with a VA content of 9.8 mole % and EVA copolymer sample (28-150) with a VA content of 21 mole % are presented in figures 4.73 & 4.74. For both samples a sharp diffraction peak appears at  $21.6^{0}$  (2 $\theta$ ). However, the sample with a high VA content exhibits a less intense diffraction peak indicating that the copolymer is almost amorphous. The x-ray diffraction patterns of EVOH copolymer sample (18-150) with a VOH content of 9.8 mole % and EVOH copolymer (28-150) with a VOH content of 21 mole % are given in figures 4.75 & 4.76. It is clear from the diffraction patterns of these two samples that a higher VOH content produces lower crystallinity compared to a sample with low VOH content

An x-ray diffraction pattern of a poly(ethylene-vinyl alcohol)-g-PMMA sample (E10D) is given in figure 4.77. It shows that the sample was mainly amorphous as no intense peak appeared, which suggested that the PMMA had replaced the hydroxyl groups on the EVOH copolymer chains and caused a disturbance in the regular arrangement of ethylene sequences. The amorphous behaviour of the graft copolymer observed from this analysis is supported by DSC results, that is , no melting peak due to crystalline regions. When a graft copolymer sample (E4D) with a low number of grafts (see section 4.6) was analysed, the diffraction pattern showed a sharp diffraction peak at  $21.6^0$  (20) (figure 4.78)



Figure 4.73 X-ray diffraction pattern of a EVA copolymer sample (18-150) with a VA content of 9.8 mole %.



Figure 4.74 X-ray diffraction pattern of a EVA copolymer sample (28-150) with a VA content of 21 mole %.





Figure 4.77 X-ray diffraction pattern of a poly(ethylene-vinyl alcohol)-g-PMMA sample (E10D).







Figure 4.79 X-ray diffraction pattern of a poly(ethylene-vinyl alcohol)-g-<u>PPHETMA sample (F1D).</u>



# Figure 4.80

X-ray diffraction pattern of a poly(ethylene-vinyl alcohol)-g-PBA sample (G1AD).

indicating the presence of crystalline regions in the sample. The x-ray diffraction pattern of a typical poly(ethylene-vinyl alcohol)-g-PPHETMA sample (F1D) is presented in figure 4.79. A broad diffraction pattern shows that this sample is mainly amorphous. The x-ray diffraction pattern of a typical poly(ethylene-vinyl alcohol)-g-PBA sample(G1AD) is given in figure 4.80. A broad diffraction pattern again indicates the amorphous behaviour of this sample.

The x-ray diffraction patterns of these graft copolymers indicated that when the hydroxyl groups in the EVOH copolymers were replaced by the prepolymer side chains the presence of long side chains prepolymer inhibited the rearrangement of ethylene sequences into a crystalline lattice. The results obtained by DSC (section 4.8) showed no endothermic and exothermic peaks due to crystalline regions in the graft copolymers, while precursor EVA and EVOH copolymers showed prominent endothermic and exothermic peaks indicating crystallinity in the samples. On the basis of these results it is reasonable to conclude that the resultant graft copolymers were obtained by the grafting of acid chloride prepolymers onto EVOH copolymer backbones which have changed the morphology of a crystalline copolymer into an amorphous sample.

### 4.10 Dynamic mechanical thermal analysis (DMTA).

Since the three graft copolymers systems poly(ethylene-vinyl alcohol)g-PMMA, poly(ethylene-vinyl alcohol)-g-PPHETMA and poly(ethylene-vinyl alcohol)-g-PBA were prepared from EVOH copolymer backbones and PMMA, PPHETMA and PBA prepolymers, the backbones and the prepolymers having different chemical structures should have different dynamic mechanical behaviours. In order to study these effects it would be reasonable first to study the DMTA behaviour of the backbone copolymers and prepolymers. From these data it would be possible to find out how the DMTA behaviour of the graft copolymers are related to those of their component copolymers and prepolymers, that is whether they are additive or somewhat of an average, or whether it is possible to distinguish resultants in a completely new set of properties.



Figure 4.81

DMTA traces of EVA copolymer samples EVA (18-150) with a VA content of 9.8 mole % and EVA (28-150) with a VA content of 21 mole %.

#### 4.10.1 DMTA analysis of ethylene-vinyl acetate copolymers.

The DMTA traces of the EVA sample (18-150) with a VA content of 9.8 mole % and the EVA sample (28-150) with a VA content of 21 mole % are presented in figure 4.81, which are plotted in terms of modulus (E) and tan  $\delta$  versus temperature. The EVA (18-150) showed a single broad tan  $\delta$  peak at 92 °C. The drop in modulus (E) to a low value at (-10 °C) indicates that the tan  $\delta$  peak is actually due to the melting of the crystalline regions of the copolymer over a wide range of temperature. The EVA sample (28-150) showed two transitions, one at low temperature (-9 °C) and the other a broad tan  $\delta$  peak at 77 °C. The lower transition could be due to the rotational motion of acetoxy and alkyl branches (185). The higher transition is because of the melting of the crystalline regions in the copolymer and this temperature is lower than for the EVA sample with low vinyl acetate content (92 °C). From DSC studies (section 4.8.1) and x-ray studies (section 4.9) it appears that EVA copolymer with a low VA content are more crystalline and the depression of melting temperature in sample (28-150) is due to a higher VA content of 21 mole %.

#### 4.10.2 DMTA analysis of prepolymers.

The DMTA curves of the carboxyl terminated PMMA prepolymers with molar masses in the range of 1400-4400 g mol<sup>-1</sup> are shown in figure 4.82. The low molar mass PMMA sample (6HA) showed a broad tan  $\delta$  peak due to softening of glassy polymer. The PMMA sample (6Ka) with molar mass 3000 g mol<sup>-1</sup> and sample (5B) of molar mass 4400 g mol<sup>-1</sup> showed prominent transitions at 110 °C and at 124 °C respectively. which suggested that an increase in the Tg of the PMMA prepolymers was due to increased molar mass.

The DMTA analysis results of carboxyl terminated PPHETMA prepolymers are shown in figure 4.83. The low molar mass (1800 g mol<sup>-1</sup>) sample (PhET 4B) showed a broad transition at 37 °C, while sample (PhEt5A) of molar mass 3000 g mol<sup>-1</sup> and sample (PhEt8) of molar mass 4000 g mol<sup>-1</sup> indicated broad transitions at a similar temperature (80 °C). It appears that the effect of molar mass on Tg of sample (PhEt5A) and sample (PhEt8) is not as prominent as for PMMA samples (6Ka)



Figure 4.82 DMTA traces of PMMA prepolymers. 6HA (molar mass 1400 g mol<sup>-1</sup>), 6KA (molar mass 2900 g mol<sup>-1</sup>) and 5B (molar mass 4400 g mol<sup>-1</sup>).



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DMTA traces of PPHETMA prepolymers. PhEt 4B (molar. mass 1800g mol<sup>-1</sup>), PhEt 5A (molar mass 3000 g mol<sup>-1</sup>) and PhEt 8 (molar mass 4000 g mol<sup>-1</sup>).



Figure 4.84

### DMTA traces of PBA prepolymers. BA5 (molar mass 1900 g mol<sup>-1</sup>)and <u>BA7 (molar mass 4000 g mol<sup>-1</sup>)</u>



VERSION VE.00

# Figure 4.85

DMTA traces of a PBA prepolymer. BA6 (molar mass 3000 g mol<sup>-1</sup>).


Figure 4.86 Plots of Tg values and molar mass of prepolymers PMMA, PPHETMA and PBA.



and (5B). This could be due to the difference in molar masses in these samples not being as much as in PMMA.

The PBA samples with molar masses in the range of 1900-4000 g mol<sup>-1</sup> showed prominent tan  $\delta$  peaks at low temperature (figure 4.84 & 4.85); sample (BA5) with molar mass 1900 g mol<sup>-1</sup> at -37 °C, sample (BA6) with molar mass 3000 g mol<sup>-1</sup> at -30 °C and sample (BA7) with molar mass 4000 g mol<sup>-1</sup> at -29 °C respectively. The difference in Tg with respect to molar mass is not as significant when compared to PMMA this again could be due to the difference in molar mass being not as great as in PMMA prepolymer. However, the low temperature transition appears in PBA because of increase in the length of side groups which have caused an increase in free volume due to poorer chain packing.

In the three prepolymer systems studied PMMA showed higher Tg values compared to PPHETMA and PBA. Hoff and co-workers (186) studied the effect of ester side chain from methyl to n-butyl, on the softening process of several polymers and concluded that, on increasing the length of ester side chain the main softening process moved to a lower temperature due to reduction of interchain cohesive forces, caused by main chain separation. PMMA has -COOCH<sub>3</sub> side groups while PPHETMA with -COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> side groups will have less cohesive forces and larger chain separation compared to PMMA which will result in lower Tg values. Plots of Tg values of prepolymers versus molar masses are given in figure 4.86, which show that an increase in molar mass increases the Tg, and this increase is more significant in PMMA compared with PPHETMA and PBA prepolymers.

#### 4.10.3 DMTA analysis of graft copolymers.

DMTA analyses of the poly(ethylene-vinyl alcohol)-g-PMMA graft copolymers are given in figures 4.87-4.89. The results presented in figure 4.87 indicate a series of graft copolymers prepared from a EVOH precursor with a VOH content of 9.8 mole %. All samples gave reasonably sharp tan  $\delta$  peaks. The sample E10D prepared from low molar mass (1400 g mol<sup>-1</sup>) prepolymer indicated a Tg at 76.5 °C while sample E14D with a side chain molar mass 3000 g mol<sup>-1</sup> indicated a Tg



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Figure 4.88

DMTA traces of a series of poly(ethylene-vinyl alcohol)-g-PMMA samples E12D, E15D and E13D from the same EVOH precursor (28-150) with a VOH content of 21 mole %.



Figure 4.90 Comparison of Tg values of poly(ethylene-vinyl alcohol)-g-PMMA with Tg values and molar mass of prepolymers.

Molar mass of prepolymer

N.B i) E10D,E11D & E14D, EVOH precursor with a VOH content of 9.8 mole%. ii) E12D,E15D & E13D, EVOH precursor with a VOH content of 21 mole%. iii) E16D,E17D & E18, a terpolymer precursor with a VOH content of 8.0 mole%.









Figure 4.91

DMTA traces of a series of poly(ethylene-vinyl alcohol)-g-PPHETMA samples F1D, F4D and F7D from the same precursor EVOH (18-150) with a VOH content of 9.8 mole %.

Table 4.28Comparison of DMTA results of precursor EVA and<br/>prepolymers with poly(ethylene-vinyl alcohol)-g-PMMA.

Sample	Tg (PMMA)	Tm or Tg	Tg (Graft	Wt fraction (PMMA)	Wt fraction (polyethylene)
		(EVA)	copoly)	per gram of	per gram of
м -	°C		°C	graft copoly.	graft
		°C			copolymer.
E10D	77	92	75	0.76	0.24
E14D	110	92	100	0.84	0.16
E11D	124	92	110	0.87	0.13
E12D	77	77.6 & -9.5	84	0.85	0.15
E15D	110	77.6 & -9.5	95	0.84	0.16
E13D	124	77.6 & -9.5	105	0.90	0.10
E16D	<b>77</b>	77.6 & -9.5	73	0.75	0.25
E17D	110	77.6 & -9.5	101	0.85	0.15
E18D	124	77.6 & -9.5	110	0.90	0.10

at 100 °C, and E11D with side chain molar mass 4400 g mol<sup>-1</sup> indicated a Tg 110 °C. These Tg values are close to the respective carboxyl terminated prepolymers (table 4.28) indicating that the prepolymers retained their transitions in the graft copolymers. Figure 4.88 shows the DMTA results of a series of graft copolymers synthesised from the EVOH precursor with a VOH content of 21 mole %. The tan  $\delta$  peaks appeared at 84.3 °C for sample E12D, at 95.4 °C for E15D and at 105 °C for E13D. The prepolymers used for these samples were in the molar mass range of 1400-4400 g mol<sup>-1</sup>. These sharp tan  $\delta$  peaks together with results from DSC (section 4.8.2) and x-ray diffraction patterns (section 4.9) indicated that the graft copolymers are mainly amorphous. It can be noticed that these tan  $\delta$  peaks are close to the precursor prepolymers. The DMTA traces of the graft copolymers prepared from a terpolymer backbone with a VOH content of 8.0 mole % are shown in figure 4.89. In this series E16D to E18D the tan  $\delta$  peaks at 73, 101 and 110 °C were sharp for samples with molar masses of prepolymers in the range of 1400-4400 g mol<sup>-1</sup>. The plots of Tg values of prepolymers and graft copolymers versus molar mass of prepolymers are given in figure 4.90. It appears that the Tg values of graft copolymers in series E10D, E14D and E11D are lower than their respective prepolymers. A similar trend can be seen in E15D and E13D. E12D has a higher Tg than its respective prepolymer. This increase in Tg in sample E12D, which has a lower number of grafts compared to E15D and E13D (see section 4.6) and higher unreacted hydroxyl groups. The unreacted hydroxyl groups caused hydrogen bonding which might stiffen the prepolymer chains and raise the Tg. Samples in the series E16D, E17D and E18D also showed decreased in the Tg values compared to their corresponding prepolymers.

The DMTA analysis of the poly(ethylene-vinyl alcohol)-g-PPHETMA graft copolymers are presented in figures 4.91-4.94 and table (4.29). The results shown in figure 4.91 are the DMTA traces of the graft copolymer prepared from the EVOH backbone with a VOH content of 9.8 mole %. The sample F1D with prepolymer molar mass 1800 g mol<sup>-1</sup> showed a Tg peak at 37 °C, F4D with prepolymer molar mass 3000 g mol<sup>-1</sup> at 51.5 °C and F7D with molar mass 4000 g mol<sup>-1</sup> at 68.1 °C. These Tg values are close to the peaks for corresponding prepolymers indicating that the graft copolymers showed a transition mainly due to side chains and no transition due to the backbones was observed. Similarly, figure 4.92

101

Table 4.29 Comparison of DMTA results of precursor EVA and prepolymer with poly(ethylene-vinyl alcohol)-g-PPHETMA.

Sample	Тg (РРНЕТМА) ℃	Tm or Tg (EVA) ℃	Tg (Graft copoly) °C	Wt fraction (PPHETMA) per gram of graft copoly.	Wt fraction (polyethylene) per gram of graft copoly.
F1D	33	92	37	0.57	0.43
F4D	60	92	51	0.72	0.28
F7D	60	92	59	0.77	0.23
F2D	33	77.6 & -9.5	33	0.60	0.40
F5D	33	77.6 & -9.5	47	0.74	0.26
F8D	60	77.6 & -9.5	56	0.76	0.24
F3AD	33	77.6 & -9.5	42	0.72	0.28
F6D	60	77.6 & -9.5	50	0.76	0.24
F9D	60	77.6 & -9.5	53	0.79	0.21







#### Figure 4.93

DMTA traces of a series of poly(ethylene-vinyl alcohol)-g-PPHETMA samples F3AD and F6D from the same precursor a terpolymer with a VOH content of 8.0 mole %.



Figure 4.94

DMTA traces of a poly(ethylene-vinyl alcohol)-g-PPHETMA sample F9D from a terpolymer precursor with a VOH content of 80 mole %.





Molar mass of prepolymer

N.B i) F1D,F4D & F7D, EVOH precursor with a VOH content of 9.8 mole%.
ii) F2D,F5D & F8D, EVOH precursor with a VOH content of 21 mole %
iii) F3AD,F6D & F9D, a terpolymer precursor with a VOH content of VOH 8.0 mole%.

represents the DMTA traces of the graft copolymer prepared from the EVOH precursor with a VOH content of 21 mole % and prepolymers of molar masses in the range of 1800-4000 g mol<sup>-1</sup>. The Tg values of the samples F2D, F5D and F8D are again close to their corresponding prepolymers giving the same observation, that is graft copolymers only showed transitions due to the side chain. Figures 4.93 & 4.94 indicate the DMTA traces of the series of graft copolymers prepared from a terpolymer with a VOH content of 8.0 mole %. All samples showed a prominent Tg value at or near to that of their prepolymers . Plots of Tg values and molar mass are given in figure 4.95. It can be seen that the Tg values of graft copolymers are close to the Tg values of their corresponding prepolymers.

The DMTA analysis results of the poly(ethylene-vinyl alcohol)-g-PBA graft copolymers are given in figures 4.96-4.98 and table (4.30). The graft copolymers prepared from EVOH precursor with a VOH content of 9.8 mole % are shown in figures 4.96-4.97. It appears that Tg values of the graft copolymer samples G1AD, G4AD and G7AD have values close to those of the corresponding prepolymers. These DMTA traces do not show any transitions due to precursor backbones; the only transitions obtained are similar to the prepolymers as indicated by the other graft copolymers. The DMTA results in figure 4.98 represent the graft copolymers G2D, G6D and G9BD prepared from a terpolymer precursor with a VOH content of 8.0 mole % and molar masses in the range of 1900 to 4000 g mole<sup>-1</sup>. These samples also indicated sharp tan  $\delta$  peaks. The plots of Tg values of graft copolymers versus molar mass of the prepolymers (figure 4.99) showed a similar trend as observed for the other two graft copolymers systems, that is Tg values of graft copolymers are close to their prepolymers.

The DMTA results of the synthesised graft copolymers discussed above showed single transitions and these transition are close to their corresponding prepolymer precursors. These graft copolymers have a polyethylene backbone which is non-polar and PMMA, PPHETMA and PBA grafts which are more polar. The backbone and side chain components are of a different chemical nature and they are insoluble in each other which might enhance microphase separation in the graft copolymer. However, DMTA analysis did not indicate such microphase separation as only single Tg values were obtained. These two

 Table 4.30 Comparison of DMTA results of precursor EVA and

 prepolymer with poly(ethylene-vinyl alcohol)-g-PBA.

Sample	Tg (PBA) <sup>0</sup> C	Tm or Tg (EVA) <sup>0</sup> C	Tg (Graft copolymer) <sup>0</sup> C	Wt fraction (PBA) per gram of graft copoly.	Wt fraction (Polyethylene) per gram of graft copoly.
G1AD	-37	92	-25	0.81	0.19
G4AD	-30	92	-22	0.85	0.15
G7AD	-29	92	-24	0.84	0.16
G2D	-37	77 & -9.5	-27	0.76	0.24
G6D	-37	77 & -9.5	-27	0.83	0.17
G9BD	-27	77 & -9.5	-20	0.89	0.11





DMTA traces of a series of poly(ethylene-vinyl alcohol)-g-PBA samples G1AD and G4AD from the same precursor EVOH (18-150) with a VOH content of 9.8 mole %.



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Figure 4.98

DMTA traces of a series of poly(ethylene-vinyl alcohol)-g-PBA samples G2D, G6D and G9BD from the same precursor a terpolymer with a VOH content of 8.0 mole %.

20

Temperature (\*C)

. 15

-.10

r.05

60

40

## Figure 4.99 Comparison of Tg values of poly(ethylene-vinyl alcohol)-g-PBA with Tg values and molar mass of PBA.



Molar mass of prepolymers

N.B. i) G1AD,G4AD & G7AD, EVOH precursor with a VOH content of 9.8 mole%. ii) G2D,G6D & G9BD, a terpolymer precursor with a VOH content 8.0 mole%. incompatible components are joined by a chemical bond which may hinder the formation of separate phases exhibiting individual DMTA behaviours. Kargin (147) investigated in detail the glass transition behaviour of such a graft copolymer, having incompatible components (see section 2.2.2.1) and concluded that microphase separation should occur in such graft copolymers but it does not appear due to the chemical linking between two sequences of polymers. This separation can be observed by plasticising one of the sequences in the graft copolymer, and individual glass transition behaviour can then be seen (147). The significant transition observed in all graft copolymers was dominated by the transition of prepolymers. It could be due to the fact that the graft copolymers have high weight fractions of prepolymer and the overall contribution by the polyethylene backbone in the graft copolymer is low. Therefore the only transition appearing is due to the prepolymer. The weight fractions of prepolymers were determined from the moles of prepolymer units per gram of graft copolymer obtained by NMR (see tables 4.10, 4.13 and 4.16). The results of weight fractions of prepolymers obtained by NMR per gram of graft copolymers are given in tables 4.28, 4.29 and 4.30. It can be observed that the graft copolymers have high proportions of prepolymers which showed the main transitions on DMTA.

The DSC analysis (section 4.8.1) of the graft copolymers and the x-ray diffraction patterns (section 4.9) of these samples indicated their amorphous behaviour. A single sharp tan  $\delta$  peak for graft copolymers obtained by DMTA is due to the softening of amorphous regions in the graft copolymers. On the basis of these results it is reasonable to conclude that the crystalline nature of the EVOH copolymers is greatly effected by non-crystalline prepolymer side chains after grafting reactions.

#### 4.11 <u>Blends of graft copolymers and poly(vinyl chloride)(PVC).</u>

Grafting is a method of modifying polymer properties. Similarly, blending is also a way to modify the properties of a polymer. It was considered worthwhile to examine changes in properties of a graft copolymer resulting from blending when these copolymers are blended with another polymer. Poly(vinyl chloride) (PVC) is widely used in polymer blends with various polymers. For example, PVC forms a

miscible blend in all proportions with copolymers of butadiene and acrylonitrile (187,188) and homopolymer of PMMA (189). PVC was chosen to blend with the graft copolymer since both components are soluble in THF at room temperature and it is easier to have a solution blend of these samples. Poly(ethylene-vinyl alcohol)-g-PMMA samples were blended with PVC in different proportions. The method of blending is described in section 3.5. DMTA was used to check the miscibility of these blends. Samples for DMTA analysis were prepared according to the following procedure. A solution of a blend in THF was left in a crystallisation dish in a fume cupboard for several hours to evaporate off the THF. The blend film was then dried in a vacuum oven at 60 <sup>0</sup>C for 24 hours in order to removed THF. Then, samples were pressed as an impregnate filter paper on a hydraulic press at 120  $^{0}$ C above the softening point of PVC and graft copolymer for five minutes for further removal of THF. The filter paper samples were cooled to room temperature and were analysed in the temperature range of -50  $^{0}$ C to 130  $^{0}$ C at a heating rate of 5  $^{0}$ C per minute and frequency 1 Hz (for detailed procedure see section 3.6.7). Results are presented in figures 4.100-4.108. In each figure the DMTA traces of the resultant blends are compared with the component graft copolymer and PVC. In figures 4.100, 4.101 and 4.102 DMTA traces of a graft copolymer (E10D) blended with PVC in the proportions of 70/30, 50/50 and 30/70 w/w are compared with the component graft copolymer (E10D) and PVC. It appears that the blend samples have a single Tg which is lower than its components . It was thought that the Tg values of the blends which were below those of components could be due to remaining traces of THF which generated a plasticising action to the PVC during sample preparation such that the time given to the samples for drying was not adequate. Similar observations can be obtained from figures 4.103, 4.104 and 4.105 where DMTA traces of graft copolymer (E12D) blends with PVC in the proportions of 70/30, 50/50 and 30/70 w/ w are compared with the components graft copolymer (E12D) and PVC. In figures 4.106, 4.107 and 4.108 DMTA traces of graft copolymer (E16D) blended with PVC in proportions of 70/30, 50/50 and 30/70 w/w are compared with its components. Again lower Tg values of the blend samples indicated the plasticising effect of THF. The results of Tg values of all blends are given in table 4.31, where these values are compared with the blend components. The Tg values of blends are

Table 4.31Results of `Tg` values of poly(ethylene-vinyl alcohol)-g-PMMA blended with PVC and compared with the Tg valuesof components.

Sample	Tg	Tg	Tg	Tg
	(PMMA) <sup>0</sup> C	(PVC) <sup>0</sup> C	(Graft copoly) <sup>0</sup> C	(Blend) <sup>0</sup> C
E10D: PVC 70:30	77	95	75	67
E10D:PVC 50:50	77	95	75	71
E10D:PVC 30:70	77	95	75	77
E14D:PVC 70:30	110	95	100	57
E14D:PVC 50:50	110	95	100	59
E14D:PVC 30:70	110	95	100	62
E11D:PVC 70:30	124	95	110	63
E11D:PVC 50:50	124	95	110	61
E11D:PVC 30:70	124	95	110	59
E12D:PVC 70:30	77	95	84	49
E12D:PVC 50:50	77	95	84	60
E12D:PVC 30:70	77	95	84	59
E15D:PVC 70:30	110	95	95	60
E15D:PVC 50:50	110	95	95	58
E15D:PVC 30:70	110	95	95	61
E13D:PVC 70:30	124	95	105	68
E13D:PVC 50:50	124	95	105	67
E13D:PVC 30:70	124	95	105	69
E16D:PVC 70:30	77	95	77	54
E16D:PVC 50:50	77	95	77	59
E16D:PVC 30:70	77	95	77	72
E18D:PVC 70:30	124	95	110	68
E18D:PVC 50:50	124	95	110	75
E18D:PVC 30:70	124	95	110	77



#### (E10D)and PVC.

with components. poly(ethylene-vinyl alcohol)-g-PMMA



VERSION: V5.00

### Figure 4.103

DMTA traces of a blend of E12D:PVC (70:30w/w) compared with components, poly(ethylene-vinyl alcohol)-g-PMMA E12D) and PVC.



Figure 4.105

DMTA traces of a blend of E12D:PVC (30:70w/w) compared with components, poly(ethylene-vinyl alcohol)-g-PMMA (E12D) and PVC.



VERSION: V5.00



DMTA traces of a blend of E16D:PVC (50:50w/w) compared with components, poly(ethylene-vinyl\_alcohol)-g-PMMA\_ (E16D) and PVC.



. .

Figure 4.108

DMTA traces of a blend of E16D:PVC (30:70w/w) compared with components, poly(ethylene-vinyl alcohol)-g-PMMA (E16D) and PVC.

lower than the graft copolymers. The lower Tg values of the blends might be due to plasticising effect caused by residual THF in the PVC in the blend during the sample preparation for DMTA analysis. This plasticising action might occur during the drying process when samples were pressed between filter papers on a hydraulic press. To study this effect a series of filter paper samples of graft copolymer (E10D) blends with PVC were dried in a vacuum oven at (100  $^{0}$ C) above the glass transition temperature of PVC for 24 hours and cooled to room temperature. The results of DMTA traces are given in figures 4.109-4.114 and table 4.32. In figures 4.109, 4.110 and 4.111 DMTA trace before drying at 100 <sup>0</sup>C for 24 hours of graft copolymer (E10D) blends with PVC in proportions of 70/30, 50/50 and 30/70 w/w are shown, while in figures 4.112, 4.113 and 4.114 DMTA traces of the same sample after drying at 100  $^{0}$ C for 24 hours are given. From the single Tg it appears that the graft copolymers have some miscibility with PVC. A miscible polymer blend exhibits a single Tg value between the two unmixed components, whose exact position depends on the blend composition. Several equations have been proposed to describe the composition dependence of Tg for miscible polymer blends (190-192). The Fox equation is widely used and is given in equation (4.14).

$$\frac{1}{Tg} = \frac{W_A}{Tg_A} + \frac{W_B}{Tg_B} \cdots \cdots (4.14)$$

where Tg<sub>A</sub> and Tg<sub>B</sub> are the glass transition temperatures of the component polymers A and B,  $W_A$  and  $W_B$  are the weight fraction of the components polymer A and B respectively. The Tg values calculated from the Fox equation and the experimental values are given in table 4.32. These results indicated that after drying samples at 100  $^{0}$ C for 24 hours, above the glass transition temperature of PVC, the Tg values of blends shift markedly to higher values and are close to the theoretical values calculated by the Fox equation. It can be concluded that these graft copolymers have some miscibility with PVC.

#### 4.12 Solution viscosity of graft copolymers.

The solution properties of graft copolymers are very much influenced by the interactions between chemically unlike sequences. Graft copolymers may have highly branched structures so a large number of possible contacts between unlike chain segments may be achieved. In











DMTA traces of a blend of poly(ethylene-vinyl alcohol)-g-PMMA (E10D) and PVC (50:50 w/w) before drying at 100 °C for 24 hours.



Figure 4.111

DMTA traces of a blend of poly(ethylene-vinyl alcohol)-g-PMMA (E10D) and PVC (30:70 w/w) before drying at 100 °C for 24 hours.



for 24 hours.





# Table 4.32Comparison of Tg values of graft copolymer blended<br/>with PVC, samples before drying at 100 °C and after<br/>drying at 100 °C for 24 hours.

Sample	Tg (Before drying sample at 100 <sup>0</sup> C for 24 hours) <sup>0</sup> C	Tg (After drying sample at 100 <sup>0</sup> C for 24 hours) . <sup>0</sup> C	Tg (Fox equation) <sup>0</sup> C
E10D:PVC 70/30	67	77	79
E10D:PVC 50/50	71	86	83
E10D:PVC 30/70	77	89	87

poly(ethylene-vinyl alcohol)-g-PMMA graft copolymers the two sequences of polymer chains have different chemical natures and are linked by chemical bonds. In solution these two sequences of chains will behave differently depending on the nature of the solvent. For example, a solvent good for one sequence will solvate it, while the other sequence which is less solvated will be protected by the solvated chain because of chemical linkage between them. In such a situation the volume occupied by the graft copolymer chain will be entirely different to a non-segregated conformation and as a net result the viscosity of the graft copolymer will be effected. To observe this effect, intrinsic viscosity can provide useful information in a simple way. Intrinsic viscosity is a measure of the contribution of individual polymer molecules to solution viscosity. It is related to the volume the polymer chains occupy in solution and to their shape and size. The intrinsic viscosity [¶] is defined by (135), (193-195),

where  $\eta_{SP}$  and  $\eta_{rel}$  are the specific and relative viscosities which are related by  $\eta_{SP} = \eta_{rel} -1$ . The dependence of solution viscosity on polymer concentration is represented empirically by the following equations.

$$\frac{\eta_{SP}}{C} = [\eta] + k' [\eta]^2 C \dots (4.16)$$
$$\frac{(\ln \eta_{rel})}{C} = [\eta] - k' [\eta]^2 C \dots (4.17)$$

where k and k are known as the Huggins and Kraemer constants respectively. The constants are related by k+k = 0.5, and their values depend on the polymer-solvent system. Since k is greater than k, equation (4.17) is the preferred method of extrapolating to zero concentration to find [ $\eta$ ]. Often, equations (4.16) and (4.17) are extrapolated on the same graph to the same intercept to determine the intrinsic viscosity.

The intrinsic viscosities of the graft copolymers E10D, E14D and E11D, E16D, E17D and E18D in toluene at 25  $^{0}$ C and E12D, E15D and E13D in THF at the same temperature were determined. Intrinsic viscosities

 
 Table 4.33
 Results of intrinsic viscosities of poly(ethylene-vinyl alcohol)
 -g-PMMA and slope constant k.

Sample	Intrinsic viscosity [η] at 25 <sup>0</sup> C	Slope constant k	solvent
E10D	0.49	0.77	Toluene
E14D	0.56	0.60	Toluene
E11D	0.65	0.65	Toluene
E12D	0.68	0.69	THF
E15D	0.60	0.63	THF
E13D	0.69	0.63	THF
E16D	0.52	0.52	Toluene
E17D	0.55	0.63	Toluene
E18D	0.58	0.58	Toluene

# Figure 4.115 $\frac{Plots of}{C} \frac{\ln \eta_{rel}}{C} \text{ and } \frac{\eta_{SP}}{C} \frac{\text{versus concentration of}}{poly(ethylene-vinyl alcohol)-g-PMMA (E10D)}.$



Concentration % W/V

•

were obtained by using equations (4.16) & (4.17) and extrapolating, on the same graph, to determine an intercept which gave a value of intrinsic viscosity. A typical graph for sample E10D is presented in figure (4.115).

The results of intrinsic viscosities obtained are given in table (4.33). It appears from the intrinsic viscosities that the increase in the molar mass of the graft copolymer (for molar masses see section 4.5) has increased the intrinsic viscosity. The relationship between intrinsic viscosity and molar mass is given by equation (4.18) (197).

where K and <sup>a</sup> are Mark-Houwink constants and M molar mass. The value of K = $(5 \times 10^{-4})$  and of <sup>a</sup> = (0.7) for polyethylene in odichlorobenzene at 138 <sup>o</sup>C are reported (197). With these values in equation (4.18) for a typical EVA copolymer of molar mass 18000 g mole<sup>-1</sup> the intrinsic viscosity value of 0.47 was obtained. This is the lower limit and the results of intrinsic viscosities of graft copolymers obtained were higher than this limit, which suggested an increase in the molar mass of precursor EVA after the grafting reaction.

In the series E12D to E13D the sample E15D has lower intrinsic viscosity than E12D and E13D. Since these graft copolymers were prepared from the EVOH precursor with a VOH content of 21 mole %, it is quite possible that the interaction between polymer chains caused aggregation which effects the intrinsic viscosities of these graft copolymers. The interaction between two different polymer chains in dilute solution may be judged by the hydrodynamic interaction constant (k) obtained by dividing the slope of the plot of  $\eta_{SP}/C$  against concentration by  $[\eta]^2$  (196). In a sufficiently poor solvent, preference of polymer-polymer, rather then polymer-solvent, contacts may be strong enough to cause the formation of aggregates of polymer molecules, which effect the value of intrinsic viscosity and usually has a marked effect on the slope constant k. The values of k exceeds 0.5 in the case of aggregation and it increases to higher values as the degree of aggregation increases. The values of k determined for the graft copolymers are given in table (4.33). It can be seen that these values are above the lower limit (0.5) reported (196) for aggregation, which

indicates that these copolymers can show aggregation behaviour in dilute solution with tetrahydrofuran and toluene.

### CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

#### 5.1 <u>Conclusions</u>

Synthesis of graft copolymers by a non-ionic grafting onto process can be achieved by the use of a free-radical method to synthesise a prepolymer chain with a terminal functional group and a backbone with reactive functional groups distributed randomly along the chain. The backbone polymer or copolymer having functional groups along the chain can be prepared either by copolymerisation of functional monomers or by the chemical modification of a polymer or copolymer to a backbone with desired functional groups.

Synthesis of graft copolymers by this method can be performed by a coupling reaction between reactive functional groups on a backbone and at the end of a prepolymer chain. In such coupling reactions compatibility of two reacting polymers in a common solvent plays an important role. If the reacting polymers are less compatible, then the access of reacting functional groups to each other will be less which results in low grafting.

A functional group at the end of a long polymer chain is less accessible than a functional group at the end of a short polymer chain. An increase in the functional groups on a polymer backbone results in intermolecular hydrogen bonding and polymer coils are less expanded which inhibit the reacting functional group at the end of a prepolymer chain for a possible coupling reaction.

Characterisation of precursor prepolymer and backbone prior to reacting provides a guide to the isolation and characterisation of the newly formed grafted product. Moreover, knowing the structure of the precursors the success of a grafting reaction can be predicted.

GPC can be used to establish the success of a grafting reaction by comparing the retention volumes of the precursor and the grafted product. The change in the retention volume of a peak toward lower values, due to changes in the molar mass of the precursor, was confirmed by the molar masses obtained from a polystyrene calibration curve. However, the chemical nature of the precursor and the graft copolymers must be considered very carefully for such a comparison as the copolymers might exhibit interactions in GPC columns which can lead to some errors.

Compositions of graft copolymers determined by IR and NMR were in good agreement and comparison with theoretical values supported the grafting of prepolymer onto a precursor backbone. The number of grafts per chain obtained by IR and NMR were close to values obtained by GPC. Comparison of these with theoretical values indicated the validity of the methods.

The grafting of an amorphous prepolymer onto a crystalline copolymer backbone can qualitatively be judged by DSC and wide angle x-ray analysis. DSC traces of precursor EVA and EVOH copolymer showed a prominent `Tm` and the heat of fusion indicated the crystalline behaviour of the copolymers. Graft copolymers do not show any melting peak indicating amorphous behaviour, which suggested grafting of an amorphous prepolymer onto EVOH copolymer backbones.

The x-ray diffraction patterns of the EVOH copolymer showed a peak due to crystalline regions. X-ray diffraction patterns of graft copolymer did not show any peak, which supported the results obtained by DSC and suggested the grafting of amorphous prepolymer onto a crystalline copolymer backbone.

Dynamic mechanical behaviour of the graft copolymer showed a single tan  $\delta$  peak similar to the prepolymer side chain. This domination of a prepolymer transition in a graft copolymer by DMTA was due to the high proportion of the prepolymers in the product indicating a high level of grafting. The composition of the graft copolymer from NMR showed the high proportion of the prepolymer in the graft copolymer and explained the main transition due to prepolymers in graft copolymer by DMTA.

Blends of poly(ethylene-vinyl alcohol)-g-PMMA graft copolymers with PVC in three different proportions 70/30, 50/50 and 30/70 w/w were analysed by DMTA. Results showed a single Tg for the blends lower than that of the components. The lowering of the Tg of the blends was
due to the plasticising action by THF to the PVC of the blends , indicating that the time given for the removal of THF from the blend sample was not adequate. When samples were dried for a longer period and then were analysed by DMTA , blends showed a single Tg which was close to the average of the components indicating that the graft copolymers and PVC have some miscibility.

Plots of solution viscosity data according to Huggin's equation of poly(ethylene-vinyl alcohol)-g-PMMA graft copolymers in THF and toluene at 25  $^{0}$ C gave the values of slope constant 'k' greater than 0.5 which indicated that graft copolymers aggregate in solution.

## 5.2. <u>Recommendations</u>

The compatibility of prepolymers and a precursor backbone was encountered in the synthesis of graft copolymers. It would be interesting to synthesise a graft of PBA and copolymer EVOH with a VOH content of 21 mole %, since PBA is less polar and EVOH has high VOH content which increases the polarity of the copolymer.

The number of grafts per chain obtained by experiments and comparison with the theoretical values revealed that all the hydroxyl groups were not replaced by the acid chloride terminated prepolymers. In order to increase the number of grafts per chain the molar ratio of the acid chloride terminated prepolymers to the hydroxyl groups can be increased to study any change in the number of grafts per chain. It would be interesting to study the effect of certain reactions parameters on the grafting reaction. Time, temperature or use of catalyst for example, molecular sieves (198) or pyridine (199) which scavenge HCl during the condensation reaction between acid chloride and hydroxyl group can affect the grafting of acid chloride terminated prepolymer onto hydroxyl containing backbone.

The solution viscosity measurement of poly(ethylene-vinyl)-g-PMMA in toluene and THF at 25 <sup>0</sup>C showed that these graft copolymers aggregate in toluene and THF. The solution properties of the other two graft copolymer systems poly(ethylene-vinyl alcohol)-g-PPHETMA and poly(ethylene-vinyl alcohol)-g-PBA can be studied and the comparison of solution properties of these three systems could be interesting. The backbone and the side chains in the graft copolymer are of different chemical nature and may show interesting behaviour in selective solvents. Small angle x-ray scattering can provide useful information on the micelle behaviour of the graft copolymers. The hydrodynamic properties of the graft copolymers can be studied by light scattering and in combination with solution properties the behaviour of two polymer sequences in graft copolymers can be predicted

The graft copolymers prepared have polyethylene (non-polar) backbone and prepolymer (polar) side chains. DMTA analysis of the graft copolymers showed a single Tg similar to the prepolymers. The appearance of a single Tg showed that graft copolymer has a single phase, but due to the different nature of the backbone and the side chain these graft copolymers should tend to separate in bulk. In order to study the phase separation behaviour in these graft copolymers electron microscopy can be use to study the existence of any domains due to backbone and side chains.

Miscibility of poly(ethylene-vinyl alcohol)-g-PMMA was investigated with PVC. The difference in the Tg values of the graft copolymer systems polyethylene(vinyl-alcohol)-g-PPHETMA and poly(ethylenevinyl alcohol)-g-PBA and PVC are much greater than poly(ethylenevinyl alcohol)-g-PMMA. It would be easier to judged the miscibility of these graft copolymers with PVC. Blends of PVC and poly(ethylenevinyl alcohol)-g-PPHETMA and poly(ethylene-vinyl alcohol)-g-PBA graft copolymer would show interesting results.

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