CHAPTER – 2

SYNTHESIS AND CHARACTERIZATION OF INTERFACIAL AGENTS

CONTENTS

2.1 Fundamentals of compatibilization

2.1.1 Definition of compatibilization

In the most scientific literature the term 'Compatibility' is often used in a thermodynamic sense to be synonymous with miscibility. However, in the technological literature it is used to characterize the relative ease of fabrication or the properties of two polymers in a blend[1,2]. Components that resist gross phase separation and /or give desirable blend properties are frequently said to have a degree of 'Compatibility' even though in a thermodynamic sense they are not miscible. Confusion results from this dual usage but both practices are widespread.

Compatibility is frequently defined as miscibility on a molecular scale. This undoubtedly has the merit of clarity, but has the disadvantage of confining the definition to encompass only those blends showing true thermodynamic miscibility. But it excludes a large number of blends both academically studied and commercialized, which many workers would consider compatible.

Another way of defining compatible blends is polymer mixtures, which do not exhibit gross symptoms of phase separation. This widens the scope considerably and it is certainly true that most compatibilized blends contain very finely dispersed phases. But the definition still excludes some blends, which have been modified to facilitate the generation of a preferred, but not necessarily fine morphology and hence preferred physical properties.

A third definition is simply to consider blends as compatible when they possess a (preferably commercially) desirable set of properties. This leaves unanswered the question of how this is achieved and therefore allows the material developers free rein to exploit any avenue, which will lead to a technologically useful product.

So, from the above discussion, we can now define the term 'Compatibilization' as any physical or chemical action which will give a stabilization to the polymer blend morphology[1].

2.1.2 Compatibilization mechanisms

In most cases, melt mixing of two polymers results in blends which are weak and brittle. This is because the incorporation of a dispersed phase in a matrix leads to the presence of stress concentrations and weak interfaces, arising from poor mechanical coupling between phases. Compatibilization is mostly achieved by addition of a third component, or by in situ chemical reaction leading to modification of the polymer interfaces in two phase blends and thereby tailoring the phase structure and hence properties.

The factors contributing to end-use properties during manufacture of a blend by melt compounding and subsequent processing to produce a finished article, are illustrated in Fig. 2.1[3].

The mechanical properties of a blend or alloy will be determined not only by the properties of its components, but also by the phase morphology and the interface adhesion. Both are important from the viewpoint of stress transfer within the blend in its end-use application. The phase morphology will normally be determined by the processing history to which the blend has been subjected. Factors such as the process (mixer type, rate of mixing and temperature history), the rheology of the blend components and the interfacial tension between phases in the melt are important. The phase morphology is unlikely to be in thermodynamic equilibrium, but generally will have been stabilized against de-mixing by quenching below the glass transition temperature of one or both phases, or through the occurrence of crystallinity in one or both phases, or occasionally by crosslinking.

In short compatibilization in principle affects the final blend properties in complex ways. The main three effects are

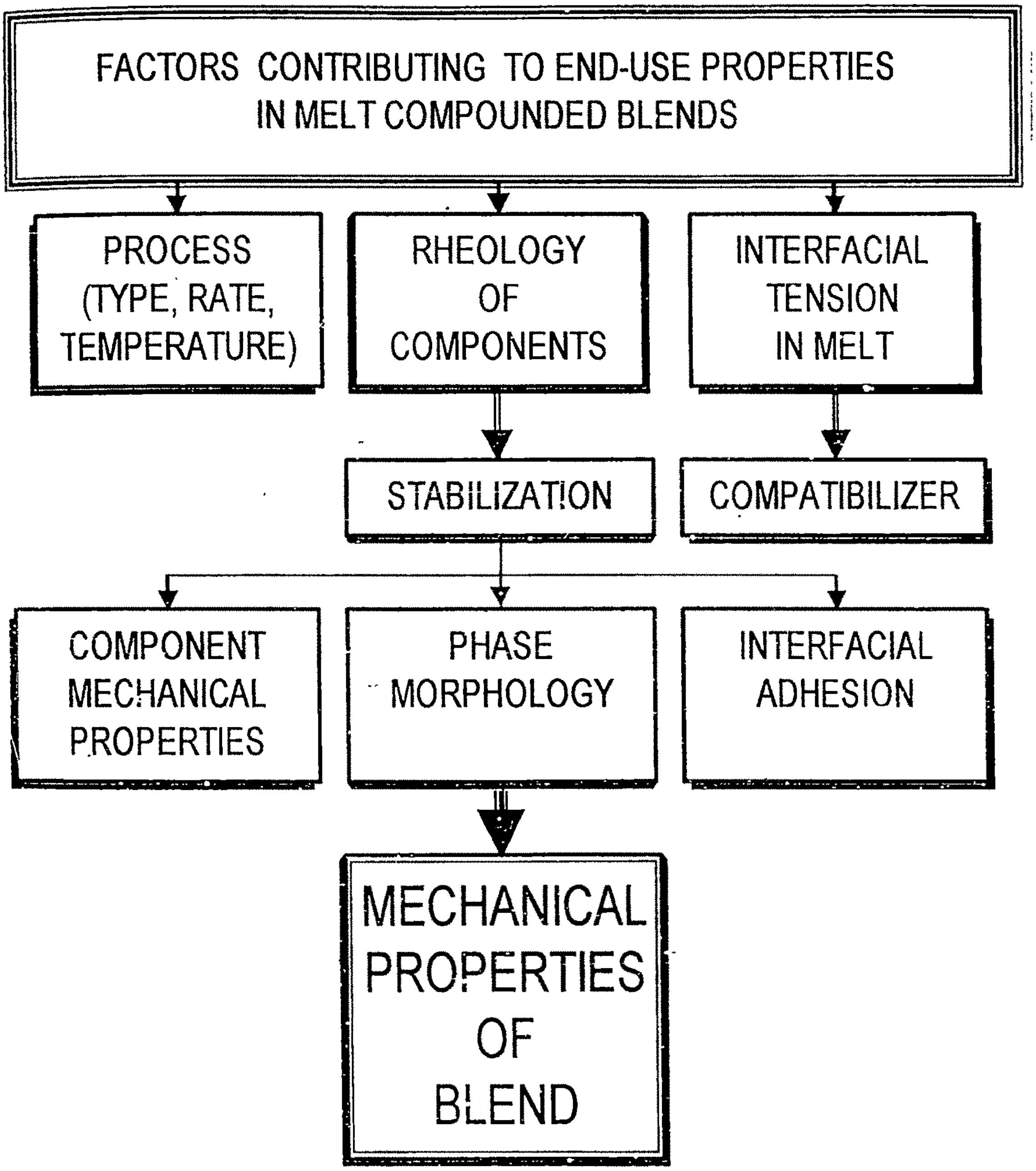


Figure 2.1: Factors influencing the end-use properties of melt compounded blends

- reduction in the interfacial tension in the melt, causing an emulsifying effect and leading to an extremely fine dispersion of one phase in another,
- increase in the adhesion at phase boundary, giving improved stress transfer and
- stabilization of the dispersed phase against growth during annealing, through the modification of the phase-boundary interface.

In practice it is likely that all these effects will be seen to some extent with the addition of a particular compatibilizer and it may also affect the rheology of blends.

2.1.3 Methods of compatibilization

The compatibility of polymeric blends may be enhanced by various methods. Cocrystallization and cocrosslinking can often result in stable phase morphologies that are resistant to coalescence. Strong interactions such as acid-base or ion-dipole, hydrogen bonding and transition metal complexation have also been shown to enhance thermodynamic miscibility. More commonly, compatibility is promoted through copolymers (e.g. block, graft) with segments capable of specific interactions and / or chemical reactions with the blend components. The copolymer compatibilizer often contains segments that are chemically similar to those in the blend components (non-reactive compatibilizer). These block or graft polymers can be added separately or formed in situ by blending suitably functionalized polymers. Compatibility can also be enhanced through the addition of specific low molecular weight compound promoting copolymer formation and / or crosslinking. Adhesion may be augmented through interpenetration and entanglement.

There are several techniques of compatibilizing immiscible blends, including compatibilization through the introduction of nonreactive graft or block copolymers, nonbonding specific interactions through low molecular weight coupling agent and through reactive polymers[1,3,5].

2.1.3.a Addition of copolymers

The addition of suitable block, graft, or random copolymers represents the most extensively researched approach to compatibilization of polymer blends[5-7]. These copolymers may be conveniently classified as nonreactive and reactive. Nonreactive copolymers have segments that are capable of specific interactions with each of the blend components. Their miscibility is often dictated by their closely matched solubility parameters. In reactive copolymers, segments are capable of forming stronger covalent or ionic bonds with at least one of the blend components. The Table 2.1 lists some polymer blends compatibilized by nonreactive and reactive compatibilizers.

2.1.3.b Utilization of nonbonding specific interactions

Nonbonding specific interactions between the blend components, such as hydrogen bonding, ion-dipole, dipole-dipole, donor-acceptor, and π-electron interactions can enhance the compatibility of polymer blends[4,5]. The importance of specific interactions in enhancing compatibility has been reported in the literature by a number of researchers. Some of the interactions are given in Table 2.1.

These specific interactions however are generally weak and high concentration to provide one interacting group per repeating unit is often required for effective compatibilization.

2.1.3.c Addition of low molecular weight coupling agents

The addition of low MW compounds in a polymer blends may promote compatibility through formation of copolymers (random, block, or graft) or through the combined effect of copolymer formation and crosslinking. Low MW compounds are usually added at relatively low concentrations (typically 0.1 - 3 wt %). This may thus offer economic advantages over polymeric compatibilizers that are usually effective at higher concentrations.

Blends containing crosslinkable constituents may be compatibilized through addition of suitable curatives. It is generally believed that compatibilizing copolymers are also formed in situ. It is possible to crosslink one or both phases. Phase separation in these systems is inhibited by the presence of an intercrosslinked morphology with good interface bonding. Some examples are given in Table 2.1.

2.1.3.d Reactive compatibilization

A comparatively new method of producing compatible blends is by reactive blending. The graft or block copolymer compatibilizer can be formed in situ through covalent or ionic bonding of suitably functionalized polymers during the melt blending. In this kind of compatibilization, one polymer phase generally contains reactive groups in the chains, whereas the other has no inherent functionality. The reactive groups can be incorporated into the second phase by adding to it a functionalized polymer that is miscible with it. In some cases, both phases may have to be functionalized. This method is different from other compatibilizing routes where the blend components are either chosen or modified so that reaction can occur during melt blending, with no addition of a separate compatibilizer. The in situ-formed copolymer compatibilizer has segments that are chemically identical to those in the respective unreactive homopolymers and are thought to be located preferentially at the interface.

Reactive compatibilization can be achieved by following ways :

- In situ formation of graft or block copolymer by chemical reactions between reactive groups on polymer component, or by addition of a free radical initiator during blending.
- Formation of a block copolymer by an interchange reaction in the backbone of the components, which is most likely in condensation polymers.

Table 2.1: compatibilization of polymer bends through various methods[5]

Sr. No.	Major component	Minor component	Compatibilizer
A. NON-REACTIVE COMPOYMERS			
1.	PE or PS	PS or PE	PS/PE graft copolymer, SEBS, SB, SEP
2.	PE or PP	PP or PE	EPM, EPDM
3.	PET	HDPE	SEBS
B. REACTIVE COMPOYMERS			
1.	ABS	PA6/PA66	SAN/MA Copolymer
2.	PE	PA6 or PA66	Carboxyl functional PEs
3.	PP or PE	PET	PP-g-AA, Carboxyl functional PEs
4.	PA66	EPM	SMA or EPM-g-MA
C. NON-BONDING SPECIFIC INTERACTIONS			
	Specific Interactions		Examples
1.	Hydrogen bonding		Poly(vinyl acetate), Polyacrylates, with PVC
2.	Ion-dipole interaction		PS-ionomer/poly (alkylene oxide)
3.	Dipole-dipole interaction		Poly(vinyl acetate) or polyacrylates with PVDF
D. LOW MOLECULAR WEIGHT COMPOUNDS			
	Polymer Blends		Low MW Compounds
1.	PET / PA66		p-Tolunesulfonic acid
2.	PA6 / PA66		Tripheyl phosphite
3.	PE / PP		Peroxide

- Mechanical scission and recombination of component polymers to form graft or block copolymers, which is generally induced by high shear levels during processing.
- Promotion of reaction by catalysts.

In situ reactive compatibilization has already been implemented in a number of commercial products and in many instances appears to be an effective method of compatibilization and toughening for polymer blends. A few examples for each type of reactive groups are given in Table 2.2

2.2 Copolymerization

Polymeric substances containing two or more chemically different repeating units are termed as copolymers. Simultaneous polymerisation of two or more monomers or one polymer and one monomer or two polymers in the given reaction mixture, to produce copolymers is termed as copolymerisation. Copolymerisation is the most general and powerful method of achieving desirable changes in polymer properties and is widely used in the production of various commercial polymeric materials. Copolymerisation influences the symmetry of the polymer chain and modulates both intermolecular and interamolecular forces and hence alters the properties such as melting point, glass transition temperature, crystallinity, stability, elasticity, permeability and chemical reactivity. There is practically unlimited scope for variation in polymer structure and polymer properties through copolymerisation.

2.2.1 Classification of copolymers

Classification of copolymers based on the morphology and arrangement of the monomeric units in the copolymer is as follows,

(i) **Random copolymers :** In which the distribution of two repeating units in the polymer is in a statistically random fashion along a linear chain.

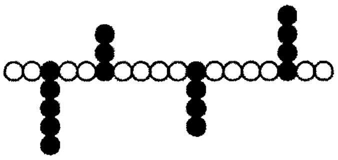
Table 2.2: Polymer blends compatibilized through reactive compatibilization

Sr. No.	Type of functionality	Reactive groups	Blends	Reaction type	Properties improved
1.	Maleic anhydride	Grafted MA	PA6/EPR	Imidation	Impact Crystallization
		Grafted MA	PA66/EPR	Ester interchange	Morphology
		Copolymerized MA	PA6/SMA	Imidation	HDT
		Grafted MA	PE/NR	Ring opening	Tensile
2.	Carboxylic acid	Carboxylic Acid (grafted)	PET / PP	Esterification	Morphology
		Carboxylic Acid (copolymerized)	PS / NBR	Ring opening	Impact
		Carboxylic Acid (copolymerized)	PA 6 / PE	Amidation	Permeability
		Carboxylic Acid (copolymerized)	PS / AC	Ionic bonding	Thermal
3.	Carboxylic acid deriv.	Grafted Acrylate	PA 6 /PE	Aminolysis	Impact
		Backbone	PET/ EPDM	Concerted Addition	Impact
		Maleate Backbone ester	PC/ Phenoxy	Trans esterification	Tensile
		Backbone ester	PET / PC	Ester interchange	Compatibility
4	Primary and s- Amine	Terminal Amine	PA 6 / SAN	Ring opening	Impact
		Terminal Amine	PA 6 /ABS	Imidation	Tensile
5	Hydroxyl and Epoxide groups	Terminal Hydroxyl	PBT / EPR	Esterification	Impact Tensile
		Grafted Epoxide	PE / NR	Rig opening	Tensile

(ii) **Alternating copolymers :** In which the two repeating units are distributed alternately throughout the polymer chain.

(iii) **Block copolymers :** In which a sequence or block of one unit is followed by a block of other unit and so on.

(iv) **Graft copolymers :** In which long or short chains of one type of monomer units are attached to a polymer back-bone consisting of another repeat unit. This copolymer has different configurational features from other copolymers. The back-bone and side chains may be homopolymer or copolymeric units.



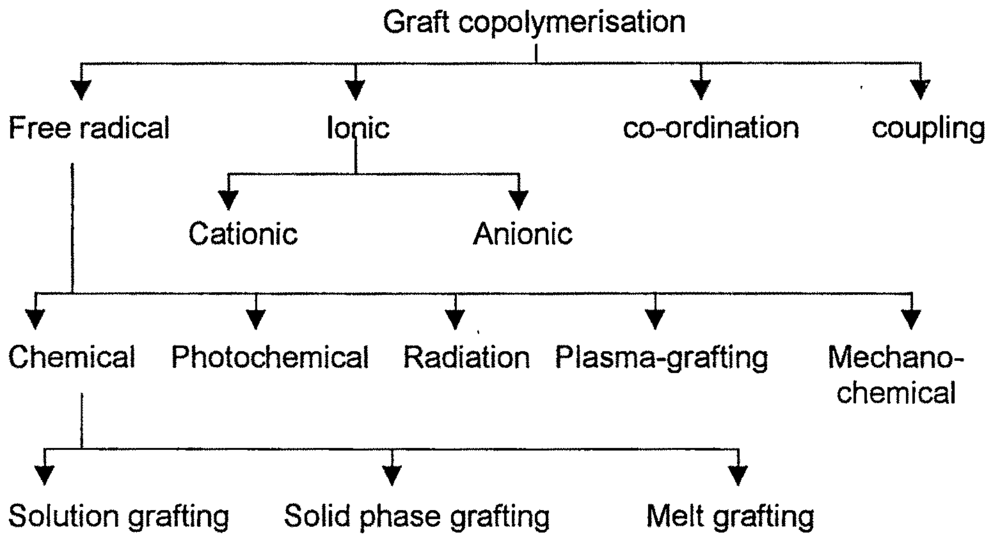
This class of copolymers has been further used as compatibilizer in iPP/ABS blends studied here and hence is discussed in detail below.

2.2.2 Graft copolymers

Graft copolymerisation is a well known method for modification of chemical and physical properties of polymeric materials[8,9] and is of a particular interest for achieving desired properties without altering the core structure of substrate. Usually main chain and branch chains are thermodynamically incompatible. Macrophase separated graft copolymers can exhibit many of the unique thermal and mechanical properties observed in block copolymers, including thermoplastic elasticity. There is similarity in processing and fabrication of graft copolymers and many other polymeric materials. The graft copolymers have a greater sensitivity towards processing and fabrication due to their multicomponent nature. Grafting improves adhesion, tensile strength, abrasion resistance and dyeing and dye retention capacity of the copolymer. Grafting also improves compatibility and thermal as well as photochemical stability[10-12]. The history of graft modification of polypropylene goes back to the late 1950s when Natta, et.al.,[13] successfully used hydroperoxidic derivatives of crystalline and amorphous poly-α-olefins as initiators. In general, the tertiary hydrogen atoms in polypropylene offer following two distinct possible modes for free radical grafting.

- Oxidation to hydroperoxide or other functional groups and subsequent decomposition to free radicals with or without a catalyst, and
- Chain transfer initiation.

2.2.3 Methods of graft copolymerisation

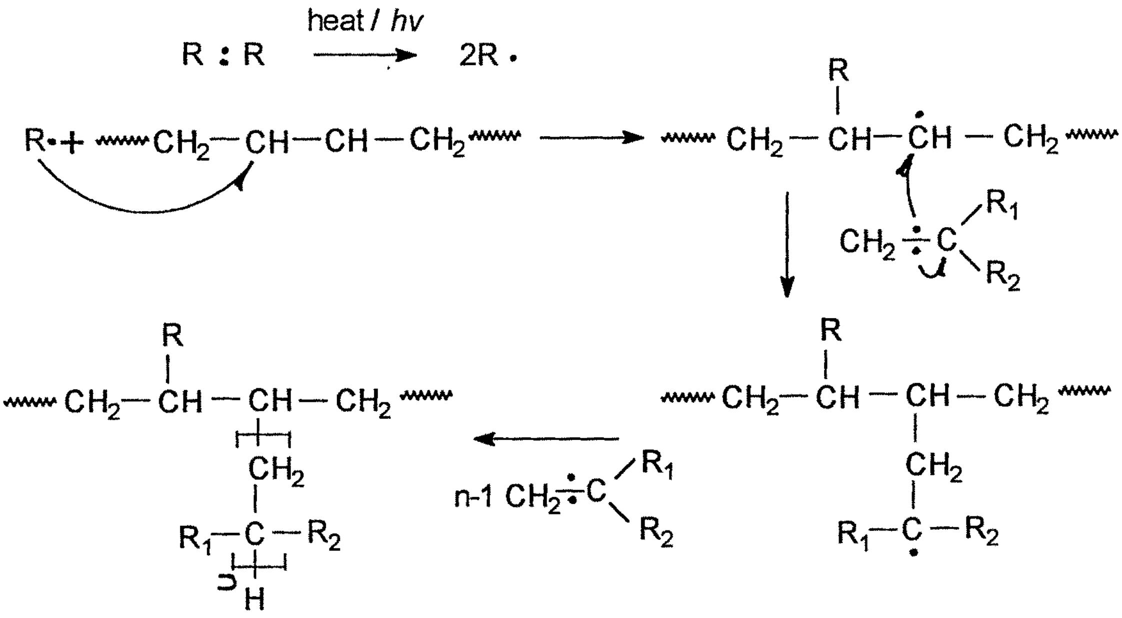


2.2.3.a Free radical polymerization

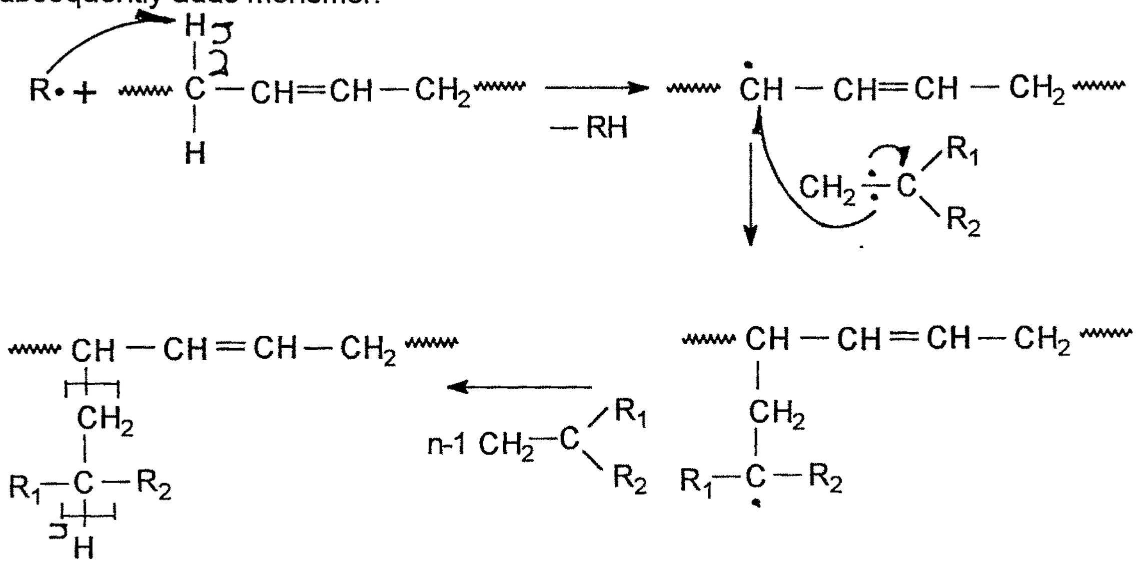
The free radical polymerisation is the oldest and most widely used procedure for the synthesis of graft copolymers. There are five major methods for grafting a monomer onto polymer back-bone.

(i) Chemical method

Graft copolymerisation through chemical initiation takes place by decomposition of the added initiator such as benzoyl peroxide, lauryl peroxide, dicumyleperoxide[13-15] which abstracts hydrogen atom from the polymer chain to yield a free radical site for the grafting of monomer unit. This is also called as a chain transfer reaction. The radical, generated from decomposition of initiator may attack in-chain double bond, and lead to further addition of monomer to form the graft copolymer.



Or it may abstract an allylic hydrogen forming an allylic radical which subsequently adds monomer.



The efficiency of an initiator is an important factor in graft copolymerisation. The nature of the monomer also plays an important role and success of chain transfer method to produce graft copolymers depends upon the relative reactivity ratios of monomers.

(ii) Photo-chemical method[16,17]

There are two modes of photo chemical grafting

- The chromophoric groups in the polymer absorb electromagnic radiation in the visible or UV region. This results in bond breaking and subsequently in free radical generation which in turn may lead to initiate the grafting.
- If the polymer is non-absorbing, indirect photolysis is initiated by using photosensitizer which absorbs the light and transfers this light energy to the polymer molecule present in the system, thus activating the molecule to give rise to free radical sites for the reaction.

(iii) High energy Radiation induced grafting

In this method graft copolymerization starts at radical sites generated along the polymer backbone due to high energy radiation[18,19] e.g. gamma rays. The main disadvantages of this technique are crosslinking, homopolymerization and degradation of the polymer backbone during grafting. In pre-irradiation technique, free radicals are trapped when the polymer is irradiated in the absence of air and afterwards monomer is introduced into the system to graft onto polymer backbone. Sundardi[20], investigated the graft copolymerization of vinylpyrolidone and acrylic acid by the trapped radical initiation technique.

(iv) Plasma grafting

The grafting at polymers by glow discharge is know as plasma grafting. In this method the polymer in the form of either fiber or film is exposed to glow discharge, which produces free radicals on the backbone, which initiate graft copolymerization. A low temperature discharge is a complex system consisting of electrons, atoms, ionised species and excited atoms and molecules. These particles generate free radicals on the surface of the material as well as in the bulk upto a few microns depth. This method is limited to the surface only and can be used for surface modification of polymers in the form of fibre or film. Mastihuba et al.,[21] studied grafting of MMA or EA onto PP surface using this technique.

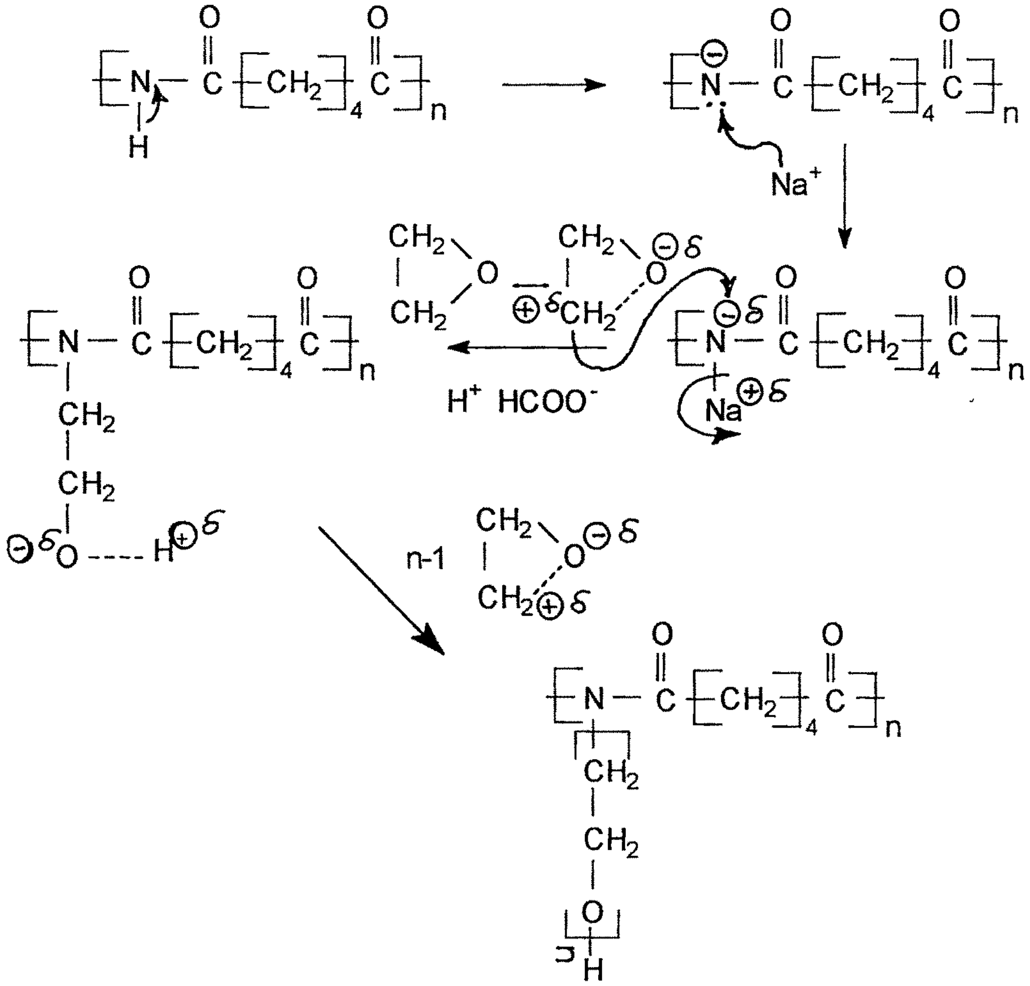
(v) Mechano chemical grafting

The successive mechanical and ultrasonic shearing forces cause bond scission or polymer degradation resulting into production of free radicals at the ruptured ends of the chain. The free-radicals generated in the presence of monomers initiate the grafting of the latter onto the polymer surface. The mechanical degradation may be carried out by mastication, milling, high speed stirring or shaking, extrusion, forcing the polymer solution through an orifice or freezing and thawing the polymer solution. Terada[22] carried out the graft copolymerisation of 1-phthalimido-1,3-butadiene onto PP by thermal mastication.

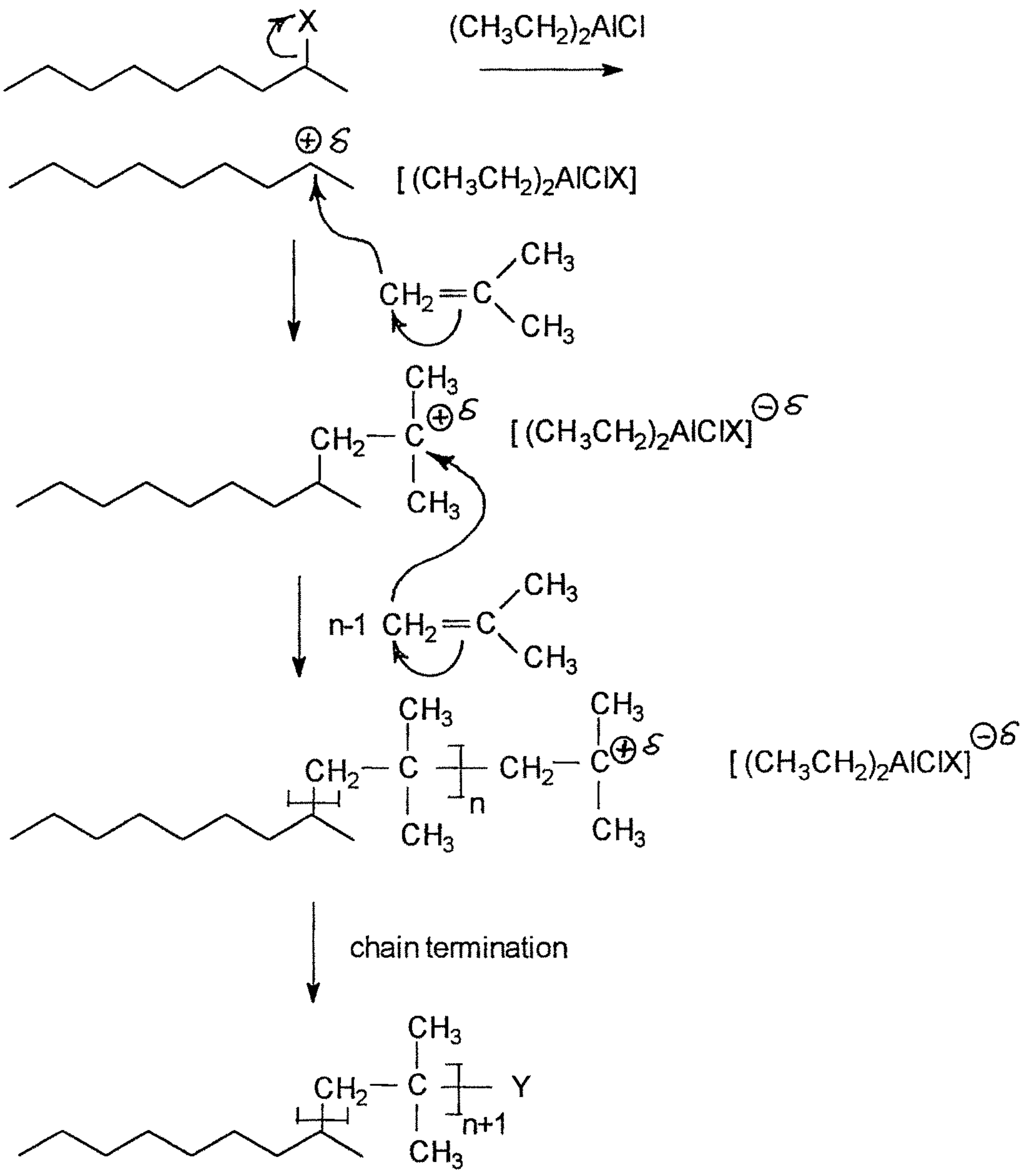
2.2.3.b Ionic polymerization

Graft copolymerization can also be carried out through anionic and cationic polymerization.

Anionic polymerization: Anionic polymerisation has become an excellent method for synthesis of block and graft copolymers. Graft copolymerisation is initiated by anions generated by the reaction of bases with acidic proton in the main polymer chain. For example polyamide metalated with sodium in liquor ammonia and then grafted with a monomeric unit [23,24].

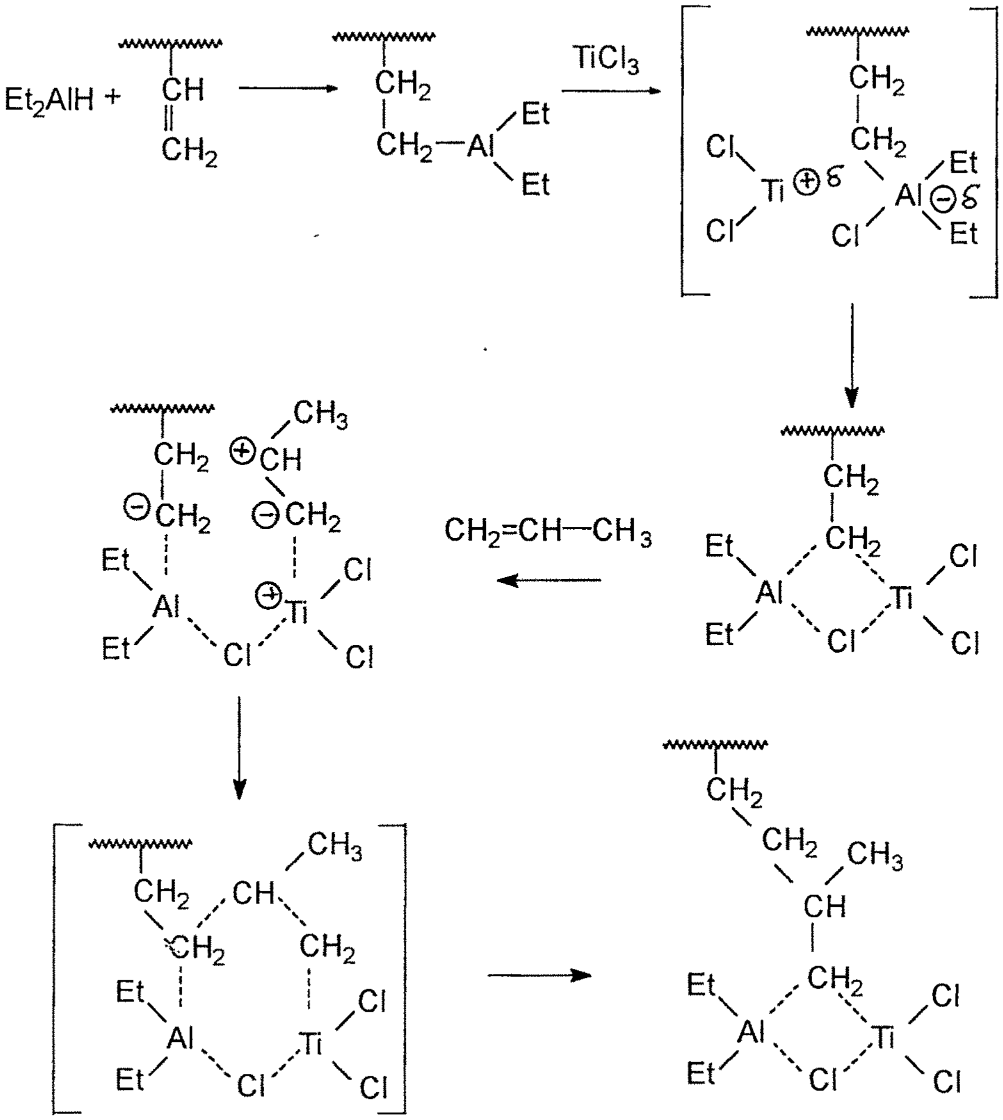

Na⁺
H⁺ HCOO⁻
n-1
n

- **Cationic polymerization :** The reaction between labile alkyl halide and Lewis acid has been utilised for the cationic grafting onto halogenated polymers[25] as follows.



2.2.3.c Co-ordination polymerization

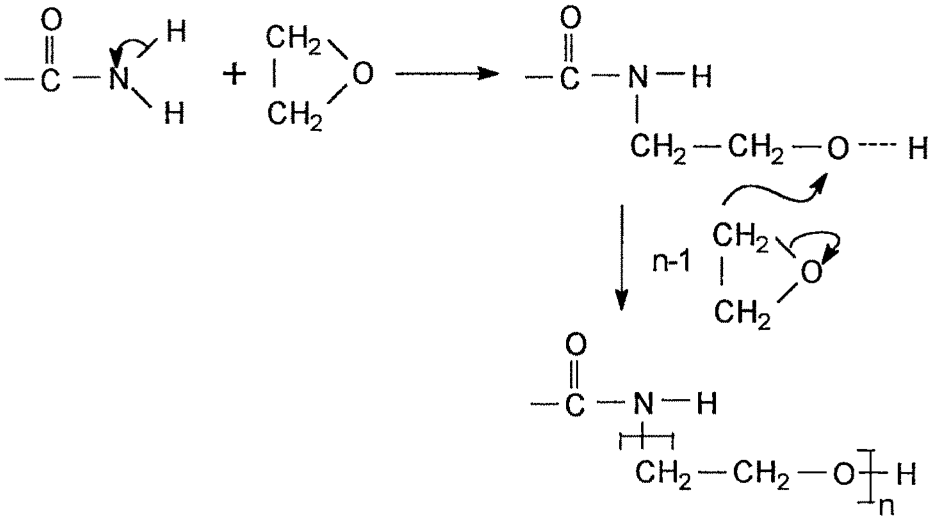
Stereospecific initiators can give stereo block copolymers which contain isotactic and heterotactic sequences. Greber[26] grafted olefins onto poly(styrene-co-butadiene) using a Ziegler-Natta co-ordination initiator system where diethylaluminium hydride reacts with pendant groups to form a macromolecular trialkylaluminium.



Trialkylaluminium units with $TiCl_4$ or $TiCl_3$ form a Ziegler-Natta initiator system which is used in the grafting of ∝-olefins onto the preformed macromolecular trialkylaluminium. By this technique, poly(styrene-co-butadiene)-g-ethylene or isotactic polypropylene was obtained.

2.2.3.d Coupling polymerisation

Polymers containing active hydrogen can be used for the synthesis of graft polymers. Poly(ethyleneoxide) is easily grafted onto nylon since the hydrogen atom of the amide nitrogen can be readily removed.



Graft copolymers can also be prepared by coupling two or more polymers containing suitable functional groups.

2.3 Review of the work done on graft copolymers of iPP

From the literature survey it is seen that the work carried out for the grafting of polypropylene through free radical mechanism is mainly composed of photochemical and high energy radiation methods. However, as the proposed work is in free radical polymerization through chemical initiation process, only work done in this area is discussed below.

2.3.1 Free radical polymerisation (Chemical initiation)

Graft copolymerisation by chemical initiation mainly takes place through (a) chain transfer (b) hydroperoxidation and (c) halogenation. Hence the work done earlier is further classified in these subsections.

2.3.1.a Chain transfer

(i) Solution grafting technique

Using various solvents for the dissolution of iPP, monomer and initiator the work carried out in the grafting of iPP is further classified according to the monomers used for grafting.

- **Maleic anhydride grafted onto iPP**

Maleic anhydride has been a preferred monomer for solution grafting of iPP. Wada, et al.[27] carried out grafting of maleic anhydride onto iPP at 120 °C temperature in the presence of benzoylperoxide as an initiator and found that the graft copolymer shows good bond strength to tin plate joints. Maleic anhydride was also grafted onto iPP by using di-tert-butyl peroxide as an initiator and chlorobenzene as a solvent[28]. The graft copolymer was reported to be useful for lamination. Use of benzoyl peroxide for grafting of maleic ahydride was also reported by Mitsubishi Petrochemical Co.[29]. They have carried out grafting at 220 °C and it was reported that graft copolymer had a good adhesion for aluminium as well as nylon. Ethylenically unsaturated carboxylic acid and/or maleic anhydride was grafted onto polypropylene by Toyo Ink Co. Ltd.[30-32] at 130 °C using benzoyl peroxide initiator and xylene as a solvent. The grafted product was reprecipitated using acetone as a non-solvent. 0.6 wt % grafting was reported and authors have reported that carboxy modified polyolefin has high bounding strength and is useful as an adhesive or as a base film in a laminate for food packing material. Dainippon Ink & Chemicals Ltd.[33] synthesized PP-g-maleic anhydride graft copolymer using xylene as a solvent and tert-butyl peroxide as a free radical initiator. The reaction carried out at 140 °C for one h, resulted into 65% conversion. Use of xylene and benzoyl peroxide for grafting of maleicanhydride was also reported by Kim et al.[34]. The graft copolymer was freed from monomer and homopolymer by using acetone.

Schulz and Hartmann[35] studied the effect of various solvents on grafting of maleic anhydride onto atactic polypropylene using free radical initiator, and they have observed that chain degradation and crosslinking can be controlled by controlling the reaction conditions such as initiator concentration and type of solvents. Park et al.[36] reported 3% grafting when maleic anhydride was grafted onto PP in xylene using benzoyl peroxide initiator for 4 h at 120 °C in nitrogen atmosphere. The effect of benzoyl peroxide concentration and reaction temperature on graft level of maleic-anhydride onto iPP was studied by Ligiang et al.[37] At lower concentration of initiator (<0.5%) and temperature (<100 °C) grafting was not observed. Extent of grafting was reported to depend on maleic anhydride concentration. Jiesheng, Su and Songbai[38] also studied the effect of organic peroxide as an initiator for the grafting of maleic anhydride onto polypropylene at 130 °C, using xylene as a solvent. Weihua, Li et al.[39,40] have synthesized PP-g-maleic anhydride, PP-g-trimethylol-propane and PP-g-ethylene glycol di-methacrylate. They also studied the effect of initiator concentration and reaction time on % of grafting.

- **Acrylic acid and methacrylic acid grafted onto iPP**

Solution grafting of isotactic polypropylene was carried out with acrylic acid in the presence of benzoyl peroxide at 140 °C in o-dichlorobenzene solvent. Highest grafting efficiency was observed for dilute solution of iPP and decreased melting point, heat of fusion and mol. wt. were reported for the products[41,42]. A membrane useful for reverse osmosis with good salt retention was prepared from two phase PP film containing grafted hydrophilic monomers[43]. Grafting of iPP with acrylic acid, ethylene glycol methacrylate and acrylamide was carried out at 120 °C in toluene. Membranes were prepared by solvent evaporation. Oomori and Iwata[44] have prepared PP-g-acrylic acid and methacrylic acid by using chlorobenzene as a reaction medium and t-butyle peroxide as an initiator. 10.5 wt % grafting was reported by them. They have reported 2.2 wt % grafting when p-chlorobenzene was changed to xylene as a reaction medium. Ulrich et al.[45] synthesized PP-g-acrylic acid under solution grafting technique, using 10-part acrylic acid in chlorobenzene and benzoyl peroxide as a radical initiator. Grafted product with 98% grafting was further used in PP/Nylon blend. PP-g-MAA copolymer was synthesized by Xiaoyan et al.[46] using xylene and benzoyl peroxide. They have studied the effect of reaction time, temperature and monomer concentration on percentage of grafting and have observed that grafting increased initially with increasing temperature but decreased with the further increase in temperature. The effect of grafting on growth of crystal was also studied using polarising microscope. In the grafting of MAA onto atactic-PP maximum grafting was reported by Chen and Xu[47] at 120 °C when 1% initiator and 0.25 : 1 (MAA:aPP) ratio was used. The prolonged reaction time resulted into increase in the rate of grafting.

- **Alkyl acrylates and methyl methacrylates grafted onto iPP**

Using solution grafting technique methyl methacrylate and diethylmethylmalonate were grafted onto polypropylene by Coover et al.[48]. While a mixture of alkyl acrylate was used by Canterino[49] for grafting onto polypropylene using benzoyl peroxide as an initiator. For a speciacity application in paint, chlorinated PP grafted with methyl methacrylate[50] was synthesized by Dainippon Ink & Chemical Ltd. According to their process 50 part chlorinated-PP (Cl = 28% with 30% solid), 80 part toluene, 59.5 part methyl methacrylate, 25.5 part iso-butyl methacrylate, 0.49 part benzoyl peroxide and 0.4 part azo bis-isobutyronitrile were heated to give a graft copolymer solution with 40% solid which was used for speciality coating applications. Klosiewicz[51] grafted butyl methacrylate onto PP in the presence of t-butyl peroxy benzoate at 135 °C temperature using chlorinated hydrocarbon as a solvent.

- **Miscellaneous**

Using solution grafting technique styrene monomer was grafted onto PP by Coover et al.[48]. Vinyl pyridine, acrylonitrile and vinyl caprolactam were grafted onto PP-fiber[52] by swelling the fiber in toluene containing 10 wt% benzoyl peroxide at 70 °C temperature. The tensile strength of the fiber was found to be unchanged after grafting but dyeing property was reported to improve. Badische and Soda[53] while grafting vinyl pyrolidone onto PP have reported excellent dyeability for the grafted samples. Oomori[54] grafted N-butyl maleimide onto PP by dissolving PP in chlorobenzene at 125 °C temperature and using dicumyl peroxide as an initiator. He has reported 10.5% grafting after 3 h reaction time. Polypropylene[55] grafted with bicyclo-(2,2,1) hept-5-ene-2,3-dicarboxylic acid anhydride at 130 °C temperature in o-dichlorobenzene using 1-butyl peroxide initiator gave 3.0 wt% of acid-anhydride in the copolymer. Unsaturated carboxylic acid or esters (ethylacetate) was grafted onto chlorinated polypropylene (Cl = 34.7%) by Tayo Chemicals Co. Ltd.[56]. The graft copolymer was reported to have excellent adhesive property. Grafting of vinyl monomers onto iPP was carried out by several workers using various methods and was reviewed by Mukherjee and Gupta[57]. Modification of polypropylene through functionalization has been reviewed by Guangxue and Shangan[58] with 597 references. Functionalisation of PP with vinyl triethoxysilane in solution as well as in melt grafting technique was studied by Nachtigall et al.[59] by using di-benzyol peroxide and di-cumyl peroxide as an initiator. The effect of silane and peroxide concentration on the degree of grafting was studied and it was reported that melt grafting is more efficient in accomplishing functionalisation, but the values of torque measurement and mol. wt. determined by GPC showed that chain scissoning took place during melt reaction.

(ii) Solid-phase grafting technique

The work carried out in the solid phases grafting of iPP is classified according to the monomers used for grafting.

- **Maleic anhydride grafted onto iPP**

The effect of interfacial agent and type and concentration of initiator on percentage of grafting of maleic anhydride onto iPP was studied by Rengarajan et al.[60-62]. It was reported that toluene works as a better interfacial agent as compared to tetraline and decalin. Using benzoyl peroxide or azo-bis-isobutyronitrile as an initiator maleic anhydride was grafted onto iPP by Enikolopov et al.[63]. Maximum 1 - 5% of grafting was reported and they observed that grafted polymer shows very good adhesion with metal surface and is also useful for paper and textile applications. At the same time, a review with 27 references on the functionalisation of PP-maleic anhydride with emphasis on the functionalisation methods like solution grafting, melt grafting, radiation and solid phase grafting and their characterization and application was published by Xue et al.[64]. Gu et al.[65] grafted maleic anhydride onto PP powder surface by using photo-initiated solid phase grafting technique. The degree of grafting which is influenced by factors like concentration of photo-sensitizer, reaction temperature, irradiation time and surface treatment of PP was also examined. The extent of grafting and crystalline structure of PP-g-MAH was characterized by XPS, WAXD and FTIR. A mechno-chemical solid-phase grafting of maleic anhydride onto PP was investigated by Cailin and Wang[66]. The structure and properties of the maleated-PP were studied by spectral, thermal and mechanical technique. The effect of load on pan-milling, rotation speed at the pan-milling, temperature, number of milling cycles, the content of monomer and filler etc. on the grafting was examined and maximum 30% of grafting was reported.

- **Acrylic acid and methacrylic acid grafted onto iPP**

In 1970, Eisuke, et al.[67] reported 42% grafting when acrylic acid was grafted onto iPP powder of 40 mesh size using fluidized bed reactor. They used this modified PP for asbestos reinforced polyolefin molded composites. Under pre-irradiation technique, acrylic acid and methacrylic acid were grafted onto solid-surface of polymer by Olenin, et al.[68,69]. Acrylic acid was grafted onto PP also by Enikolopov et al.[63]. They observed that grafted polymer shows very good adhesion with metal surface and is also useful for paper and textile application. PP-g-acrylic acid synthesized by Zhiyong, et al.[70] resulted into 58% of grafting. They used this product for PP/$CaCO_3$ composites preparation. Subramanian, et al.[71] have synthesized PP-g-acrylic acid copolymer which was used as a compatibilizer for preparation of thermoplastic blends. Kairong, et al.[72] grafted acrylic acid onto PP by means of suspension graft copolymerization technique. The reaction was carried out at 98 °C temperature with proper stirring, where water was used as a suspension medium. Benzoyl peroxide was used as an initiator and xylene as an interfacial agent, whose presence promoted the graft copolymerization. They have also observed that PP with lower isotacticity and smaller particle size was desirable for increasing graft extent. Jianying, et al.[73] have grafted methacrylic acid onto PP using benzoyl peroxide as an initiator. The influence of the reaction time, concentration of initiator and monomer on degree of grafting and MFI of graft copolymers was discussed. The effect of graft copolymer on mechanical properties of glass fiber reinforced PP composites was also studied and it was proved that graft copolymer could increase the interfacial adhesion between PP and glass fiber. PP-g-acrylic acid was synthesized by solid-phase grafting by Jingyunn et al.[74], where the effect of initiator concentration, reaction time and temperature on grafting was studied. Influence of grafting on % crystallinity was also examined.

- **Styrene grafted onto iPP**

Solid-phase graft copolymerization of styrene onto iPP was studied by Beenen, et al.[75]. They investigated the kinetics of polymerization through DSC and reported that the rate of conversion and grafting efficiency of styrene to be strongly influenced by styrene/PP ratio. Raetzsch, et al.[76,77] studied the basis of solid-phase grafting of styrene onto PP. The graft copolymer (iPP-g-PS) was used as modifier in PP/PS blend. They also studied the effect of diffusion and sorption of free radical initiator and solvent as an interfacial agent on grafting. The kinetics of the propagation and mechanism of polymerization as well as the termination of reaction of solid-phase grafting was also investigated. Grafting of styrene onto PP by Zhiyong, et al.[78] resulted into 17.5% grafting when reaction temperature was 90 °C, reaction time 4.0 h, free radical initiator (BPO) concentration 1.0%, styrene : PP ratio 0.25 : 1.0 and swelling time 4 h. Chungheng et al.[79] also synthesized PP-g-styrene copolymer which was used as a compatibilizer in PP/SEBS rubber blends.

- **Miscellaneous**

A review on newer techniques for surface modification of polymer through grafting with vinylic monomers appeared in 1979[80]. Anionic and cationic graft copolymerization on powder surface of polymer was reviewed with 24 references by Okita[81]. Grafting of vinyl chloride monomer onto crystalline PP powder was studied by Tokuyama Soda Co. Ltd.[82]. Grafting was carried out by using free radical initiator solution which was uniformly applied over the surface of PP powder, which was further placed in vapours of polymerizable monomer at 60 °C for 7.0 h. Surface grafting at polypropylene was reviewed by Singh[83] with 144 references.

Using γ-radiation technique, $CH_2 = CHSi(OEt))_3$ monomer was grafted onto PP powder of 50-250 μm size by Raetzsch, et al.[84]. A precise amount of monomer impregnated on PP powder in vapour form at 130 °C temperature resulted into 4.3% grafting. Monomers like maleic anhydride, acrylic acid, ethyl acetate and acrylamide were grafted onto pre-peroxidised as well as virgin polypropylene powder by Gu, et al.[85].

(iii) Melt grafting technique

Though in solution grafting maleic anhydride was a favoured monomer in the case of melt grafting it was observed that large amount of the work involves glycidyl methacrylate (GMA).

- **Glycidyl methacrylate grafted onto iPP**

Michel[86] grafted glycidyl methacrylate onto iPP after peroxidation of iPP by ozone. Peroxidized PP when extruded with precise amount of monomer (GMA) at 120 – 130 °C temperature at 100 rpm resulted into a product with m.p. 165 °C, mol. wt. 1,30,500 and more than 60% grafting. Same monomer was grafted onto PP by Showa[87], where 2 part GMA, 2 part aromatic peroxide and 100 part polypropylene were extruded at temperature 150 to 280 °C for 60 seconds. Shibata et al.[88] also grafted GMA onto PP, and styrene was also used to achieve higher % of grafting. They observed that this modified PP has very good adhesion with metal compared to virgin polypropylene. Free radical grafting of GMA onto iPP in the molten state was carried out in a batch mixture by Sun, et al.[89]. They have reported completion of grafting within 2-3 minute at 200 °C temperature. They also observed that grafting yield increased on the incorporation at styrene as a comonomer. The effect of peroxide concentration on % grafting was also studied. Melt grafting at GMA onto iPP was also studied by Chen and Baker[90,91]. They studied the structural influence of the graft copolymer on reactive compatibilization of rubber toughened PP. Unsaturated epoxidized monomer GMA was grafted onto PP using peroxide as an initiator by Kotlar, et al.[92,93]. They used this graft copolymer as a compatibilizer for PP/PBT blend system and they also studied the effect of initiator concentration, effect of chain transferring agent and copolymerisable monomer on degradation of PP through β-scissioning. Under melt grafting process, the reactive compatibilization of PP/PET blends on addition of PP-g-GMA graft copolymer was studied by Champagne and Peyrel[94]. They have observed that graft copolymer improves the compatibility between PP/PET and also improves mechanical properties. Surface polarity and change in other properties of PP during melt grafting with monomers like glycidyl methacrylate (GMA), 2-hydroxy ethylemethacrylate (2-HEMA) styrene and mixture of these monomers was reported by Chen and Xie[95,97]. Extensive degradation of PP and competition between grafting and β-scissioning of PP chains was reported. Addition of styrene was reported to increase the percent grafting and reduce the chain scissioning of PP. Pan and coworkers[96] have synthesized iPP-g-GMA copolymer by the use of single screw as well as twin-screw extruder process, DCPO was used as a free radical initiator. The influence of some reaction conditions and the composition of the reaction mixture on the degree of grafting has been investigated. The degradation of PP was indirectly monitored by means of torque measurement.

In a co-rotating twin screw extruder GMA was grafted onto PP by Hu and Cartier[98]. They investigated the influence of feeding on percent grafting. Mizutani and Nago[99] synthesized PP-g-GMA copolymer fibers with improved dyeability under a composition of 100 part PP, 5 to 15 part mixture containing 100 part GMA and 3 part di-terbutyl peroxide in extruder at 190 - 240 °C temperature. The same monomer was grafted onto PP by Claudine, et al.[100]. Here, they investigated the effect of initiator and comonomer concentration on percent grafting. Reaction was carried out in a twin-screw extruder. They also reported that addition of styrene as a comonomer can increase the graft level and reduce the chain scissioning of PP. Champagne and Peyree[101] also synthesized PP-g-GMA copolymer and used it as a reactive compatibilizer for PP/PET blend styrene. They used 0.2 and 1.2 wt% of grafted copolymer as interfacial agent for 10 wt% PP/PET blends. While, Gao, et al.[102] have used PP grafted GMA copolymer as a compatibilizer for PP/Nylon blend.

Crystallisation behaviours at melt grafted PP with GMA was studied by Pan and coworkers[103]. The crystallinity of the samples was determined by WAXS and DSC measurement. The speed of isothermal crystallisation of the samples was also measured. The effect of graft level on crystallinity was also investigated.

- **Acrylic acid and similar carboxylic acids grafted onto iPP**

Using melt grafting technique, crotonic acid was grafted onto polypropylene by Ames[104] at 160 °C temperature using di-tertbutyl peroxide initiator. Using benzoyl peroxide or dicumyl peroxide as an free radical initiator acrylic acid was grafted onto PP by Sasaki et al.[105]. They observed that only with 0.5% of grafting the thermal and mechanical properties of modified polymers showed considerable improvement. Acrylic acid was also grafted onto iPP by Ludwing[106], which was further used for metal-plastic laminates, coatings, hot-melt adhesives and coupling of reinforcing materials. Preparation and characterization of PP-g-acrylic acid formed during extrusion was studied by Zhang et al.[107] also. Polypropylene or amorphous propylene-1-butene copolymer was grafted with unsaturated $C_{3\text{-}10}$ carboxylic acid by Okamolo, et al.[108]. The graft copolymer was reported to show good adhesive, printing and dyeing properties. Factors affecting the grafting of acrylic acid and methacrylic acid onto melt-blown non woven-PP initiated by BPO as free radical initiator were studied by Qinfei, et al.[109]. They investigated the relation between % grafting, reaction time and monomer and initiator concentration. The structural and related performance of grafted non woven-PP was examined and it was observed that wettability of non woven-PP is greatly improved on grafting.

- **Anhydride, amide and imide functional monomer grafted onto iPP**

Using melt grafting technique, maleic anhydride was grafted onto PP by Sasaki, et al.[105]. Benzoyl peroxide or dicumyl peroxide was used as a free radical initiator. PP-g-MAH was synthesized by Mitsubishi Petrochem. Co. Ltd.[110], using 100 part PP, 1 part MAH and 0.5 part benzoyl peroxide. Mixture was palletised at 220 °C. Maximum 0.3% grafting was reported. Morita, et al.[111] synthesized PP-g-MAH under extrusion process, using 0.05 part an organic peroxide and 6000 ppm (based on PP) maleic anhydride. The modified PP showed good compatibility with polyamide. The effect of comonomer on PP grafted with maleic anhydride was studied by Samay et al.[112] and the mechanism of melt grafting of maleic anhydride onto PP was reported by Shen[113]. Under the same technique, acrylamide[114] and maleimide[115] were also grafted onto PP and structural and morphological properties of grafted products were studied through IR, WAXD and DSC. Synthesis and characterisation of PP-g-acrylamide using benzoyl peroxide as free radical initiator in the melt condition was studied by Zhihui, et al.[116]. They studied the effect of various parameters such as monomer and initiator concentration, reaction time and reaction temperature on degree of grafting. Grafting of maleic anhydride onto PP in a single screw extruder was studied by Qing, et al.[117]. They investigated the effect of types of PP, added amount of DCPO, the ratio of MAH/DCPO and extrusion conditions on percent grafting and melt viscosity of products. They observed that concentration of DCPO and value of MAH/DCPO would substantially influence the percent grafting and thermal and oxidative degradation of PP macromolecules and have concluded that by the selection of suitable extrusion conditions and use of some additives one can control the degradation of PP to some extent. Comberlin and Gonzalez[118] synthesized PP-g-maleimide copolymer which was used for the manufacturing of polymer blends, extruded plastics and multi layer materials and adhesions and coatings.

- **Miscellaneous**

Tokuyama Soda Co. ltd.[119] synthesized PP-g-vinyl pyridine copolymer by melt grafting technique, where 100 part ethylene-propylene block copolymer, 1 part vinyl pyridine and 0.1 part di-cumyl peroxide were melt kneaded at 220 °C to produce a graft copolymer. This grafted polymer showed very good impact properties than polypropylene. Using benzoyl peroxide as an initiator, 2-hydroxyethyle acrylate[120] and 2-hydroxypropylen methacrylate[121] were grafted onto polypropylene. Extrusion was conducted at 230 °C temperature. Tung and coworkers[122] synthesized PP-g-dibutyl maleate graft copolymer. They studied the effect of monomer concentration as well as initiator concentration on percentage grafting. Maximum grafting was reported to be at 180 °C within 10 minutes reaction time. Using same technique maleic acid and its anhydride and itaconic acid were grafted onto PP[113]. Buchler and Gebauer[123], grafted glycidyl methacrylate and di-allyl adipate or maleate / penta-arythritol tri-acrylate / tri-allyl cyanurate monomers onto PP under extrusion process. Maximum 7.2% grafting was observed. While, m-isopropenyl-2-2-dimethyl benzyl isocyanate (TMI) was grafted onto PP by Barun and Schmi[124]. Silane monomer was grafted onto polypropylene by Lu and Lui[125]. They studied the effect of type and content of silane monomer and initiator on % grafting. The effect of reaction conditions on the gel fraction was also examined. The synthesis of polyolefin graft copolymers by melt grafting process and/or other forms of melt phase process is reviewed by Moad[126]. In this review, primary concerns are the structure of the graft copolymers formed, the mechanism of graft formation and their relationship to processing conditions.

2.3.1.b Hydroperoxidation

The oxidation of iPP is an autocatalytic process and controlled oxidation results in the formation of hydroperoxide linkages[127]. Introduction of active sites onto iPP backbone through oxidative reaction is commercially viable process. The process can produce graft copolymers with lesser homopolymer[57]. The hydroperoxidation of iPP was carried out by heating in an air/oxygen current at 70 - 80 °C or by initiating oxidation with initiator (tert-butyl peroxide, benzoyl peroxide, dicumyl peroxide) in air or with a cationic surfactant / potassium persulfate in an aqueous slurry. To attain the peroxide content adequate for desirable graft level, the five oxidation variables (i.e. temperature, time, oxygen pressure, concentration of initiator and surfactant) are reported to be important[128]. Hydrperoxidation is reported to be restricted to the surface or inter crystalline amorphous regions.

Number of monomers have been grafted onto PP films or fibers through this technique. To name a few of them : acrylic acid[129], MMA / styrene[130], various methacrylic ester derivatives containing aromatic amines or phenols[131], N,N'-di-methylaminoethyl methacrylate, butyl acetate[132], acrylonitrile, vinyl chloride, acrylamide, 2-vinyl pyridine monomers were grafted onto PP films or fibers[133], various azadyes (polymerizable dyes)[131], acrylic acid, acrylamide, ethyleneglycol methacrylate[134], C_{1-15}-alkyl methacrylate[135], glycidyl methacrylate[86] and 2-hydroxyethyl methacrylate[136].

Redox catalysts were also used as an activators to prepare a graft copolymers. Benzoin and ferric-stearate or ferric acetyl acetonate were used as redox catalysts[132]. Chitoricky et al.[137] grafted water soluble monomer onto oxidized PP at 30 °C in an aqueous medium. Oxonolysis has been confirmed to be a more effective means to produce active species on iPP backbone than air oxidation, which provides a water range of choice for the graft copolymerization of various monomers onto a PP surface with higher grafting efficiency and grafting rate due to the formation of other active species such as peroxides and hydroperoxides[57]. By means of this technique number of monomers listed above were grafted onto PP film or fibers. Recently, Yamauchi and coworkers[137] grafted methyl methacrylate onto PP oxidized with ozone. The active species, peroxyl radical determined by ESR spectroscopy was converted to the hydroperoxide and then the hydroperoxide was decomposed by heating to produce alkoxyl and hydroxyl radicals. The former of which initiated graft copolymerization as active site.

2.3.1.c Halogenation

Halogenation provides another method to introduce functional group onto a polypropylene. Non-polar PP is turned into a polar polymer by introduction of chlorine atom, and the polarity is directly proportional to the chlorine content onto PP. On the one hand, increased polarity of polypropylene can be used to improve its surface properties for dyeing and adhesion and on the other hand, activating the chlorinated PP molecules with different chemicals it can be used to initiate the grafting of various monomers. Not much work has been done on chlorination of PP[57]. The most general method of chlorination is to heat a polymer upto 60 °C in chlorinated hydrocarbon. Generally carbon tetra chloride is used as a medium, while tertbutyl hydroperoxide and titanium tetrachloride is used as a catalyst for the chlorination of iPP[138]. Aoki[139] studied various methods of chlorination of iPP and modified product was used as an adhesive. Omichi, et al.[140] have proposed a free radical mechanism taking place during chlorination of iPP under γ radiation. The graft copolymerization of styrene and 2,4,6-trimercapto-5-triazine onto chlorinated iPP was reported by Denes et al.[141], while chlorination of iPP in CCl_4 using UV-light or natural light was reported by Sharma and coworkers[142]. iPP was also chlorinated in the presence of di-tert-butyl peroxide and chlorobenzene by Park[143].

2.4 Experimental

Isotactic polypropylene was modified by solution as well as solid phase free radical polymerization technique. 4-Vinyl pyridine, glycidyl methacrylate (GMA), methacrylic acid (MAA) and styrene-methyl methacrylate (STY-MMA) were grafted onto iPP. Benzoyl peroxide (BPO) was used as a free radical initiator and toluene was used as an interfacial agent for solid-phase grafting and as a solvent for solution grafting. Repeatibility of the method was tested by carrying out experiments at least in three sets.

2.4.1 Materials

- Isotactic polypropylene (iPP) of M0030 grade and melt flow index 10g/10 min at 220 °C and 2.16 kg load in the form of 375 - 500 μm size powder was supplied by Indian Petrochemical Corporation Ltd., Vadodara, India. It was washed several times with acetone and dried under vacuum at 60 °C prior to use.
- Glycidyl methacrylate (GMA), 4-vinyl pyridine (4-VP), methylmethacrylate (MMA) from Fluka, Switzerland were used after vacuum distillation. Styrene from National Chemicals, Vadodara, India was made free from inhibitor by washing with 5.0% w/v sodium hydroxide solution and then dried over anhydrous calcium chloride. It was further purified by vacuum distillation and was stored at 4 °C.
- 2,2'-Azo bisisobutyronitrile (AIBN) was received from Trizma Chemicals, Vadodara, India and was used after recrystallization from methanol. Benzoyl peroxide (BPO) was received from Fluka, Switzerland and was used after recrystallization from chloroform. Dicumyl peroxide (DCPO) from National Chemicals, Vadodara, India was used after recrystallization from toluene.
- Nitrogen gas of high purity grade was used after passing through sulphuric acid traps.
- Xylene, toluene, decalin and chlorobenzene were received from Qualigens, Mumbai, India and were dried over sodium metal in vertical distillation column. Benzene, dichloroethane, dimethyl formamide (DMF), acetone, methanol and chloroform of LR grade from Qualigens, Mumbai, India were used after distillation. Double distilled, deionized water was used through out the work.

At all the stages attempts were made to ensure that all the glass wares were scrupulously clean and all transfer operations were performed with uniformity. The samples given for instrumental analysis were ensured to be in the most suitable form.

2.4.2 Synthesis of isotactic polypropylene (iPP) based graft copolymers

2.4.2.a Synthesis of isotactic polypropylene-g-4-vinyl pyridine (iPP-g-4VP)

Synthesis of iPP-g-4VP was carried out through solid phase grafting technique. Prior to the grafting reaction the iPP was kept in acetone for 72 h in order to remove various additives and/or an impurities. The grafting reaction was carried out in a reaction kettle equipped with twin blade mechanical stirrer, condenser, nitrogen gas inlet and thermometer. The temperature of the kettle was maintained with an accuracy of ± 1 °C. The precise amount (4%, w/w) of iPP powder (>40 mesh size) was charged in the reaction kettle at 100 ± 1 °C temperature under inert atmosphere. After 10 to 15 minutes 5 ml of 0.413 mM initiator solution (BPO) in toluene was added to it under constant flow of nitrogen. After homogeneous coating of iPP with initiator solution, 19.05 mM of monomer (4-VP) was added over 10 minutes and then reaction was further continued for 30 minutes. Homopolymer of 4-vinyl pyridine was removed by Soxhlet extraction with DMF until constant weight. Excess of DMF was removed by Soxhlet extraction with methanol for 2 to 3 h. Graft copolymer was dried under pressure at 60 - 70 °C till constant weight.

Degradation of iPP due to benzoyl peroxide was examined through a controlled experiment, carried out under identical conditions without addition of monomer.

2. 4.2.b Synthesis of isotactic polypropylene-g-glycidyl methacrylate (iPP-g-GMA)

Grafting of iPP with GMA was carried out through solution method. Grafting was carried out in a five neck reaction kettle equipped with stirrer, condenser, thermometer and nitrogen inlet. The reaction temperature was maintained with an accuracy of ± 1 °C. Nitrogen gas was purged through the reaction mixture for 10 - 15 minutes. A precise amount of iPP (2.0 %, w/v) was dissolved in 100 ml of toluene at 110 ± 1 °C in the reaction kettle. A mixture containing 14.07 mM of monomer and 0.619 mM of initiator in 50 ml toluene was added to the reaction mixture over 15 minutes. The reaction was further continued for 4 h. After completion of reaction the reaction mixture was purged into four fold acetone under vigorous stirring. The graft copolymer was isolated and Soxhlet extracted using acetone, to remove homopolymer and unreacted monomer. The grafted product was dried under reduced pressure at 80 °C to constant weight. Degradation of iPP during grafting was examined through controlled experiment.

2. 4.2.c Synthesis of isotactic polypropylene-g-methacrylic acid (iPP-g-MAA)

The graft copolymer was synthesised using the procedure mentioned for iPP-g-GMA copolymer. The reaction temperature was maintained at 110 °C. The reaction was carried out for 7.0 h, using 50 ml of 0.524 mM of benzoyl peroxide in toluene.

2. 4.2.d Synthesis of hydroperoxidized polypropylene

Hydroperoxidized-PP (HPP) itself contains an active species in the form of peroxide, which on decomposition provides free radicals on polymer backbone. In a typical procedure of hydroperoxidation, in a three neck reaction kettle equipped with mechanical stirrer with twisted blade and air purger, 100 g of 375 - 500 μm size PP powder was taken. To it 20 ml of 0.46 M benzoyl peroxide solution in toluene was added and the reaction mixture was stirred, for 15 minutes. This was followed by the removal of toluene by evacuation. The reaction kettle was placed in an oil bath at 80 ± 1 °C and the dry air prepared by passing through sulfuric acid, caustic soda and calcium chloride traps, was passed at a constant rate of one bubble/sec from 0.2 mm diameter orifie for an hour with vigorous stirring. The reaction mixture was then cooled to room temperature under nitrogen atmosphere and the product in powder form was soaked in acetone for 12 hours to remove any unreacted benzoyl peroxide. This was followed by filtration, washing with acetone and drying under vacuum prior to its storage at 4 °C until further use. The peroxide content (active oxygen) of the HPP was determined by iodometry as per the method suggested by Citovicky et al.[144], which showed 3.2 meq. of hydroperoxide in PP.

Grafting of various monomers onto hydroperoxidized PP was carried out in three neck reaction kettle equipped with mechanical stirrer and nitrogen purger. 25% w/v HPP powder of 3.2 meq peroxide value was suspended along with 1 % w/w monomer or monomer mixture in various reaction media of different polarity. The grafting was carried out at 70 ± 1 °C for 7 h. The product in the powder form was taken in methanol, filtered and dried at 60 °C under vacuum. The graft copolymers were further purified by removing the unbound homo or copolymers formed, through soxhlet extraction in a suitable solvent till constant weight.

Grafting through thermal cleavage though is easiest and more convenient, formation of homopolymerization is also high. This can be over come by choosing proper reaction medium for grafting. Grafting of various monomers and monomer pairs on HPP under thermal cleavages of hydroperoxide group is reported[145]. The various monomer and monomer pairs used were styrene, methyl methacrylate (MMA), ethyl methacrylate (EMA), styrene-acrylonitrile (STY-AN), ethylmethacrylate – acrylonitrile (EMA-AN), methyl methacrylate-acrylonitrile (MMA-AN) and styrene-methyl methacrylate (STY-MMA). According to our experimental observation, grafting was observed to increase as polarity of medium increases. Highest % of grafting for all the monomers under study was obtained in acetone and water which is given in Table 2.3. More than 90% of grafting efficiency in all the media. Table 2.3 indicated lower extent of homopolymer formation. This is because on

Table 2.3 : Effect of reaction medium on % grafting of hydroperoxidized- PP

Reaction Medium	% Grafting						
	Styrene	STY-AN	MMA-AN	MMA	EMA-AN	EMA	STY-MMA
Toluene	0.5 (100)	0.6 (100)	0.3 (100)	--	--	--	--
Chlorobenzene	4.3 (97.6)	4.6 (93)	3.7 (86)	3.8 (100)	4.1 (94.1)	4.2 (95.2)	3.8 (92.1)
Dichloroethane	7.4 (94.6)	7.1 (91.5)	7.7 (94.5)	8.3 (96.3)	9.1 (93.4)	9.55 (96.8)	8.5 (98.5)
Acetone	19.3 (95.3)	18.4 (97.8)	18.8 (98)	18.81 (98.3)	16.5 (89)	14.6 (97.2)	19.8 (95.9)
Water	18.63 (95)	19.4 (92.8)	21.4 (89.6)	21.8 (92.6)	21.4 (91.5)	18.4 (89.2)	19.7 (92.3)

Values in brackets indicate % grafting efficiency.

decomposition of hydroperoxide group, one free radical is generated on PP backbone and the other free radical enters the polar solvent medium. In the case of hydrophobic solvents due to the insolubility of generated hydroxyl radical mutual termination takes place.

However, in hydrophilic solvent such as acetone and water the free radical induces homopolymerisation of the monomer dissolved in the medium. If monomer has no solubility in the medium no homopolymerisation is observed inspite of the availability of the free radical in the polar medium.

The observed higher % of grafting in polar solvents can be explained on the basis of higher affinity of nonpolar solvents to HPP surface resulting into decreased possibility of monomer availability at peroxide group.

Lower affinity of polar solvent towards HPP surface resulted into more adsorption of hydrophobic monomers, and hence at the thermolytic cleavages of hydroperoxide groups the grafting of monomers is favoured. Hence, further studies were carried out using water as a reaction medium.

It should be noted that the % grafting determined gravimetrically is an apparent value as the weight of grafted iPP also consists ungrafted iPP. However, our aim of synthesis of graft copolymer is for their utility as compatibilizer in iPP/ABS blends. We have undertaken the compatibilization of PP/ABS blends using iPP-g-methacrylic acid and HPP-g-STY-MMA copolymer. Both the systems give higher level of percent grafting. Synthesis of such a graft copolymer is economically cheaper and polar groups of graft copolymer also provide higher miscibility with ABS.

2. 4.2.e Percentage grafting and grafting efficiency

The percentage grafting and grafting efficiency were determined gravimetrically. Rate of polymerisation (R_p) rate of grafting (R_g) and rate of

2.4.3.a Solid phase grafting technique (iPP-g-4-VP)

Effect of monomer concentration

To study the effect of monomer concentration on the grafting of 4-vinyl pyridine, all other parameters except monomer concentration were kept constant. The reaction was carried out for 90 min. at 110 ± 1 °C using 4.0 % (w/w) of iPP powder (> 40 mesh size) and 5 ml of 0.413 mM benzoyl peroxide solution in toluene. 4-Vinyl pyridine concentration was varied from 9.524 mM to 28.571 mM. Further treatment of the products for the separation of graft and homopolymers was as discussed in section 2.4.2. The optimized monomer concentration was used in further studies.

Effect of reaction time

To study the influence of reaction time on the grafting, the reaction was carried out using optimized concentration of monomer, using 0.413 mM of benzoyl peroxide as an initiator. The reaction temperature was kept at 110 ± 1 °C. The reaction time was varied from 15 to 90 min. The method of precipitation of graft copolymers, separation and isolation of homopolymers from graft copolymers was similar to the one discussed in section 2.4.2.

Effect of types and concentration of initiator

To study the effect of various types of initiators on percentage of grating, benzoyl peroxide, 2,2'-azobisisobutyronitrile and dicumyl peroxide were used during grafting reaction. The initiator resulting into maximum % grafting was used in further studies.

In order to study the effect of initiator concentration on percentage grafting of 4 -vinyl pyridine (4VP), the reaction was carried out with 4 % (w/w) of iPP powder (>40 mesh size) with 19.05 mM of 4 - vinyl pyridine. Toluene was used as an interfacial agent and the reaction period was kept 30 min. The reaction temperature was kept at 110 ± 1 °C. The initiator concentration was varied from 0.103 mM to 0.516 mM in 5 ml of toluene. Isolation and drying of graft copolymers and homopolymers was done as per the procedure discussed in section 2.4.2.

2. 4.3.b Solution grafting technique (iPP-g-GMA)

Effect of types and concentration of initiator

To study the effect of various types of initiators on percentage of grating, benzoyl peroxide, 2,2'-azobisisobutyronitrile and dicumyl peroxide were used during grafting reaction. The initiator resulting into maximum % grafting was used in further studies.

In order to study the effect of initiator concentration on percentage grafting of glycidyl methacrylate (GMA) on to iPP, the reaction was carried out with 2 % (w/v) of iPP and 14.07 mM of GMA. Toluene was used as a solvent and the reaction was carried out for 6 h. The reaction temperature was kept at 110 ± 1 °C. The initiator concentration was varied from 0.206 mM to 2.064 mM in 50 ml of toluene. Isolation, purification and drying of graft copolymers and homopolymers was done as per the procedure discussed in section 2.4.2.

Effect of reaction time

To study the influence of reaction time on the grafting, the reaction was carried out using optimized concentration of initiator, using 14.07 mM of GMA as monomer. The reaction temperature was kept at 110 ± 1 °C. The reaction time was varied from 2 to 12 h. The method of precipitation of graft copolymers, separation and isolation of homopolymers from graft copolymers were similar to the one discussed in section 2.4.2.

Effect of monomer concentration

To study the effect of monomer concentration on the grafting of GMA, 2.0 % (w/v) of iPP was taken in the reaction mixture of 100 ml. The reaction was carried our for 4 h. at 110 ± 1 °C, using 0.619 mM benzoyl peroxide and toluene was used as a solvent. GMA concentration was varied from 7.04 mM to 28.15 mM. Further treatment of the product for the separation of graft and homopolymers was as discussed in section 2.4.2.

The optimized concentration of monomer, initiator and time was used to study the effect of reaction temperature and medium for both the systems (iPP-g-GMA and iPP-g-4-VP).

Effect of reaction temperature

The effect of temperature on the grafting of GMA and 4-VP onto iPP was studied by varying the reaction temperature from 90 ^{0}C to 110 ^{0}C using optimised concentration of monomer, initiator and time. Precipitation, separation and drying of graft copolymers and homopolymers was carried out as discussed in section 2.4.2.

Effect of reaction medium

Grafting of GMA onto iPP was carried out at optimised conditions using different solvents such as xylene, decalin, dichlorobenzene and toluene. For 4-VP system toluene was used as an interfacial agent. The reaction was also carried out in nitrogen and air atmosphere.

2. 4.4 Characterisation of graft copolymers

2.4.4.a Infrared analysis

IR-Spectroscopic information of the graft copolymers was recorded on a Shimadzu IR-408 Spectrophotometer using compression moulded films of graft copolymers prepared on a "metro" (India) compression moulding machine, at 190 °C under 100 kg/cm^2 pressure. Care was taken to ensure uniformity in the thickness of the films.

2. 4.4.b Thermal analysis

Differential Scanning Calorimetery

DSC thermograms of the selected samples were recorded on Du-Pont-2000 DSC analyser. The analysis was carried out at a constant heating rate of 10 °C/min in the temperature range 50 - 200 °C under nitrogen atmosphere. The samples were kept for 2 minute at the annealing temperature then they were cooled to room temperature. The next heating run was carried out at 10 °C/min. The ΔH values of the samples were used for further calculations. The percent crystallinity was calculated by using following expression[147].

$$\% \text{ crystallinity} = \Delta H_f^{*} \times 100 \ / \ \Delta H_f^{o} \qquad (3)$$

where ΔH_f^0 is the heat of fusion for 100 % crystalline polypropylene and ΔH_f^* is the heat of fusion for the graft copolymer.

Thermogravimetry

Thermogravimetric analysis was carried out on the Shimadzu DT-30 thermal analyser at the heating rate of 10 °C/min in an air atmosphere in the range of 30 to 600 °C. The initial decomposition temperature (IDT) and temperature at which samples undergo 50% decomposition (T_{50}) were calculated from the thermograms.

2.5 Results and discussion

2.5.1 Solid-phase grafting technique

In the proposed method of solid-phase grafting toluene is used as an interfacial agent which acts as medium for the formation and transportation of free radicals to iPP back-bone. Optimisation of conditions for maximum percentage of grafting was done by varying the concentration of initiator, interfacial agent, time temperature and monomer concentration.

2.5.1.a Effect of initiator concentration

Fig. 2.2 illustrates the effect of initiator concentration on percentage grafting. Observed initial increase in percentage grafting with increased concentration of initiator may be attributed to the increase in population of free radicals generated and transported to iPP through toluene as an interfacial reagent. However, further increase in concentration of initiator gives rise to more free radicals in the interfacial reagent but, the concentration being too high, the mutual termination rate is faster than the rate of transportation to the iPP surface. As a result the number of free radicals generated on the iPP surface decreases and hence percentage grafting decreases. Similar results were reported by Pan, et al.[148].

2.5.1.b Effect of monomer concentration

The effect of monomer concentration on the graft level is shown in Fig. 2.3. Solid-phase grafting being mainly a surface grafting process, the mechanism of grafting differs from that in solution grafting. In solution grafting reactions are taking place at molecular level whereas in solid-phase grafting, the decomposition of initiator to form free radicals is taking place at the solid-

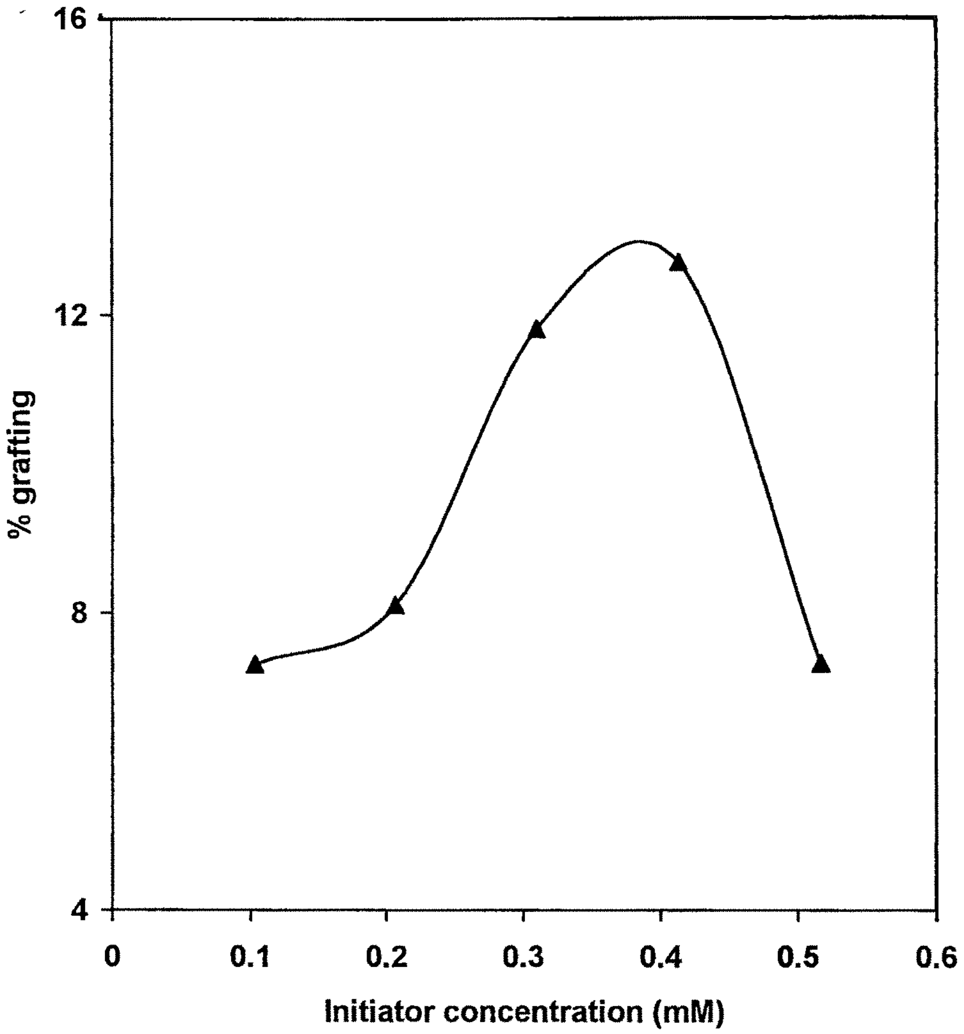


Figure 2.2: Effect of initiator concentration on % grafting of 4-vinyl pyridine on iPP

Polypropylene: 4.0 % (w/w), reaction temperature: 110 °C, reaction time: 30 min, monomer concentration: 19.02 mM, reaction atmosphere : N_2 Interfacial agent: toluene (5.0 ml)

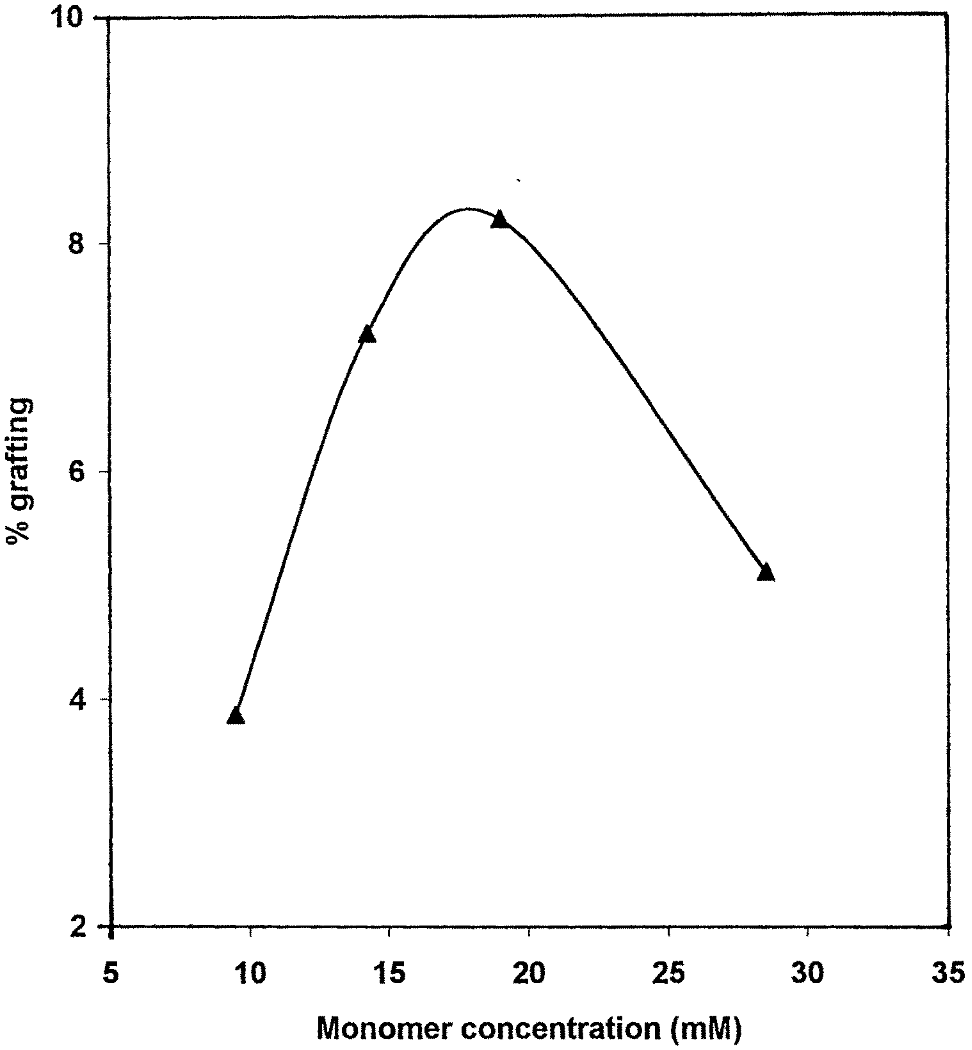


Figure 2.3: Effect of monomer concentration on % grafting of 4-vinyl pyridine on iPP

Polypropylene: 4.0 % (w/w), reaction temperature: 110 °C, reaction time: 90 min. initiator concentration: 0.413 mM in 5 ml toluene, reaction atmosphere: N_2, Interfacial agent: toluene liquid interface. As the total time for the grafting does not exceed 30 minute generation of free radicals in the PP-bulk and diffusion of monomer into iPP powder is assumed to be negligible. Percentage swelling of iPP in toluene and monomer was observed to be <30% within 30 minutes.

The grafted chains in solution grafting are freely suspended whereas in solid-phase once they grow to optimum size they spread on the surface of the iPP, inhibiting further growth due to unused free radicals from the iPP coming into contact and terminating the growing chains. With increased monomer concentration, unused free radicals in interfacial reagent increase the tendency of homopolymerisation. As an overall effect percentage grafting passes through maxima with increase in monomer concentration.

2.5.1.c Effect of reaction time

Effect of reaction time on the percentage grafting of 4-VP onto iPP is illustrated in Fig. 2.4. It was observed that grafting increases initially with increasing time up to 30 minutes and then decreases to some extent. The observed decrease in percentage grafting may be due to β-scissioning of the iPP back-bone.

The amount of interfacial agent (toluene) also plays an important role in solid-phase grafting. With increase in the volume of toluene from 5 to 15 ml, percentage grafting decreases from 12.7 to 4.3 percent. This may be due to a favoured chain transfer mechanism of termination in the solvent.

2.5.1.d Effect of reaction temperature

The effect of reaction temperature on the grafting level is shown is Fig. 2.5. With increase in temperature grafting level increases due to increased decomposition rate of initiator. This results in the increased number and mobility of the free radicals. At higher temperature, the swelling of the

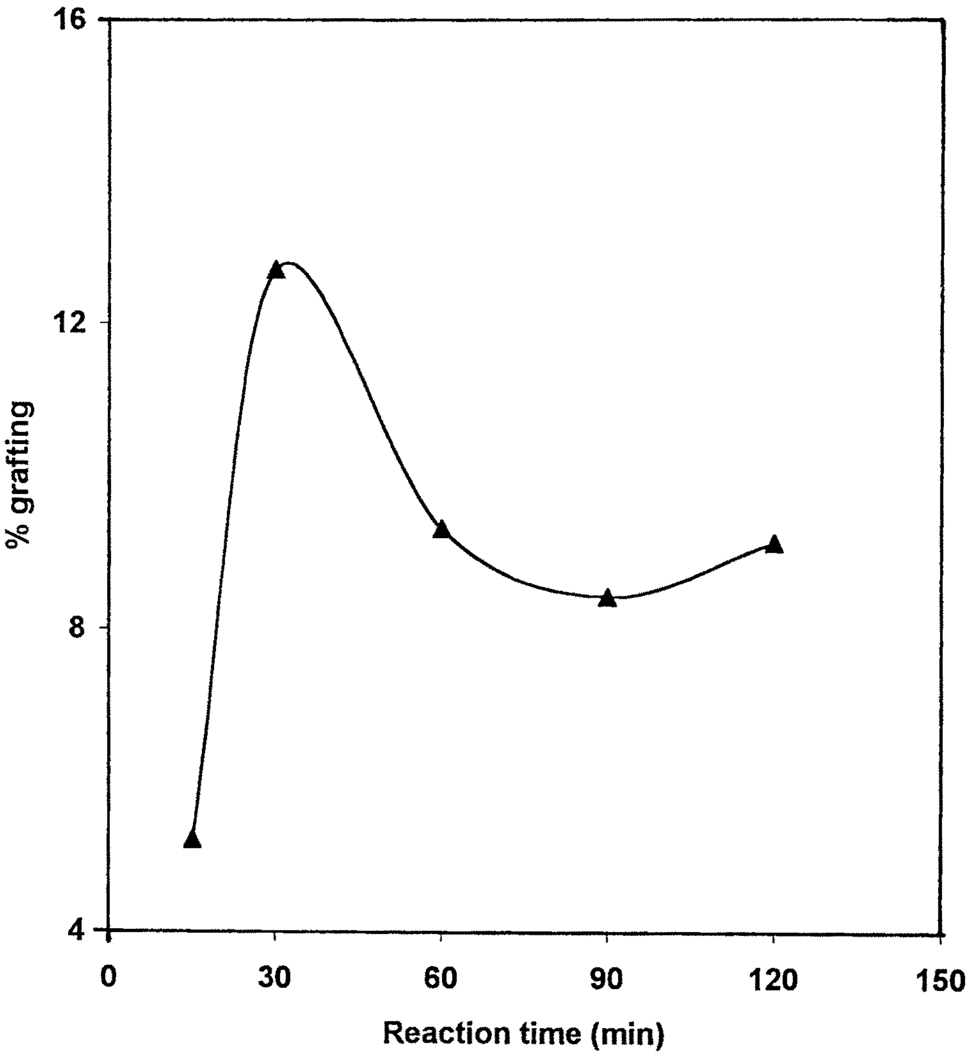


Figure 2.4: Effect of reaction time on % grafting of 4-vinyl pyridine on iPP

Polypropylene: 4.0 % (w/w), reaction temperature: 110 °C, monomer concentration: 19.02 mM, initiator concentration: 0.413 mM in 5 ml toluene, reaction atmosphere: N_2, Interfacial agent: toluene

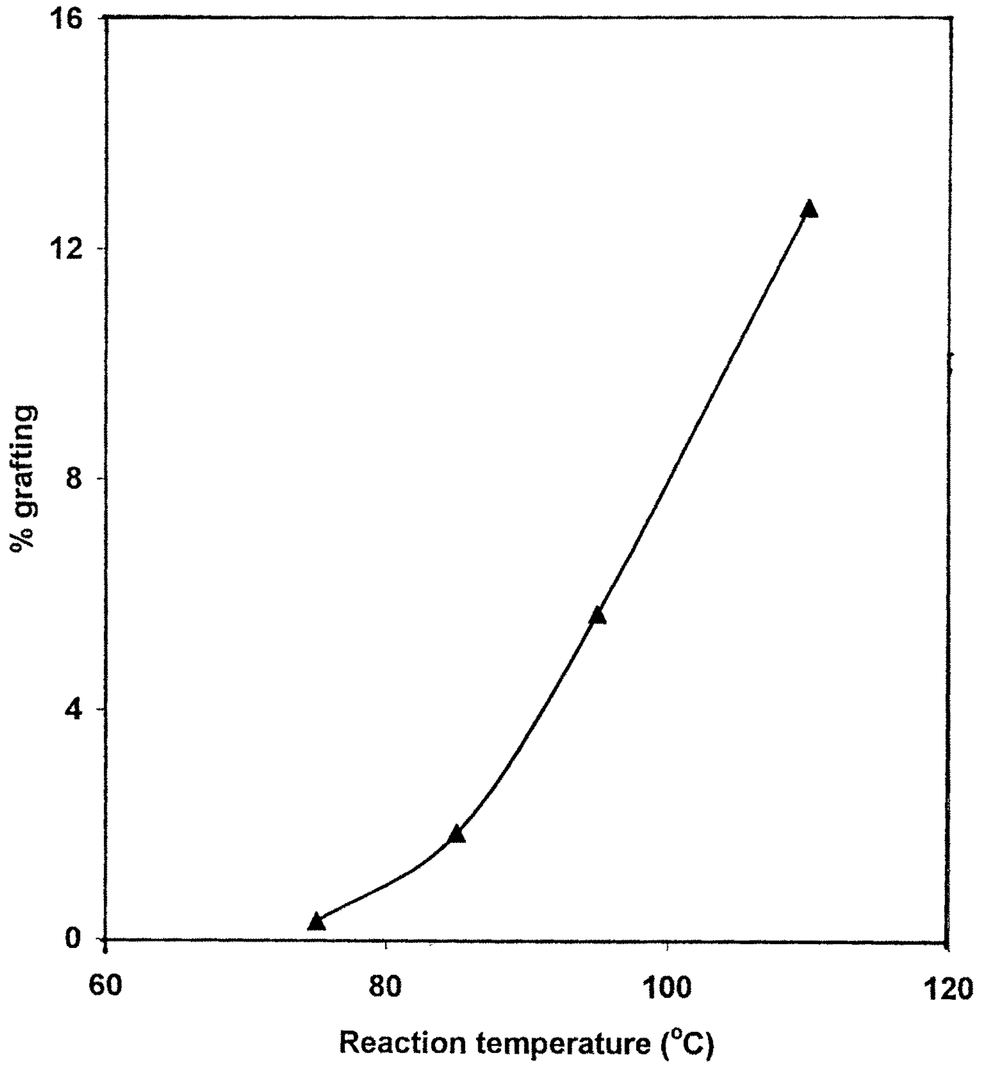


Figure 2.5: Effect of reaction temperature on % grafting of 4-vinyl pyridine on iPP

Polypropylene: 4.0 % (w/w), monomer concentration: 19.02 mM, reaction time: 30 min. initiator concentration: 0.413 mM in 5 ml toluene, reaction atmosphere: N_2, interfacial agent: toluene polypropylene surface also increases which provides more surface area for generation of free radical sites on the iPP-backbone. As a result, increased percentage of grafting is observed.

2.5.1.e Effect of particle size

Grafting was carried out by using commercial grade iPP with a 40 and above mesh size and 4.96 m^2/g surface area. The maximum extent of grafting was observed to be 12.7%. However, commercial grade iPP was sieved to get samples with 40-80, 80-120 and >120 mesh size. The percentage grafting was observed to be 6.9, 9.7 and 9.0 % respectively, under identical conditions. Solution grafting of iPP at optimised conditions resulted in 6.0% grafting.

2.5.2 Solution grafting technique

2.5.2.a Effect of type and concentration of initiator

To study the effect of different initiators on the percentage grafting of GMA onto iPP, reaction was carried out in toluene at 110 ± 1 °C in nitrogen atmosphere. Benzoyl peroxide(BPO), dicumyl peroxide(DCPO) and 2,2'-azobis-isobutyronitirile(AIBN) were used to study the effect of type of initiator on % grafting. The results obtained are given in Table 2.4. Here, the lowest % grafting was observed with AIBN which can be attributed to the steric hindrance generated at the free radical causing decreased efficiency of hydrogen abstraction from tertiary carbon of iPP. The observed higher % grafting with BPO can be attributed to the generation of more free radicals by BPO than DCPO at 110 °C, as the energy required for the decomposition of benzoyl peroxide is much lower than that of dicumyl peroxide[149]. Hence, further work was carried out by using BPO as an initiator.

The results obtained for iPP-g-GMA system with variation in initiator concentration are shown in Fig. 2.6. With increasing initiator concentration %

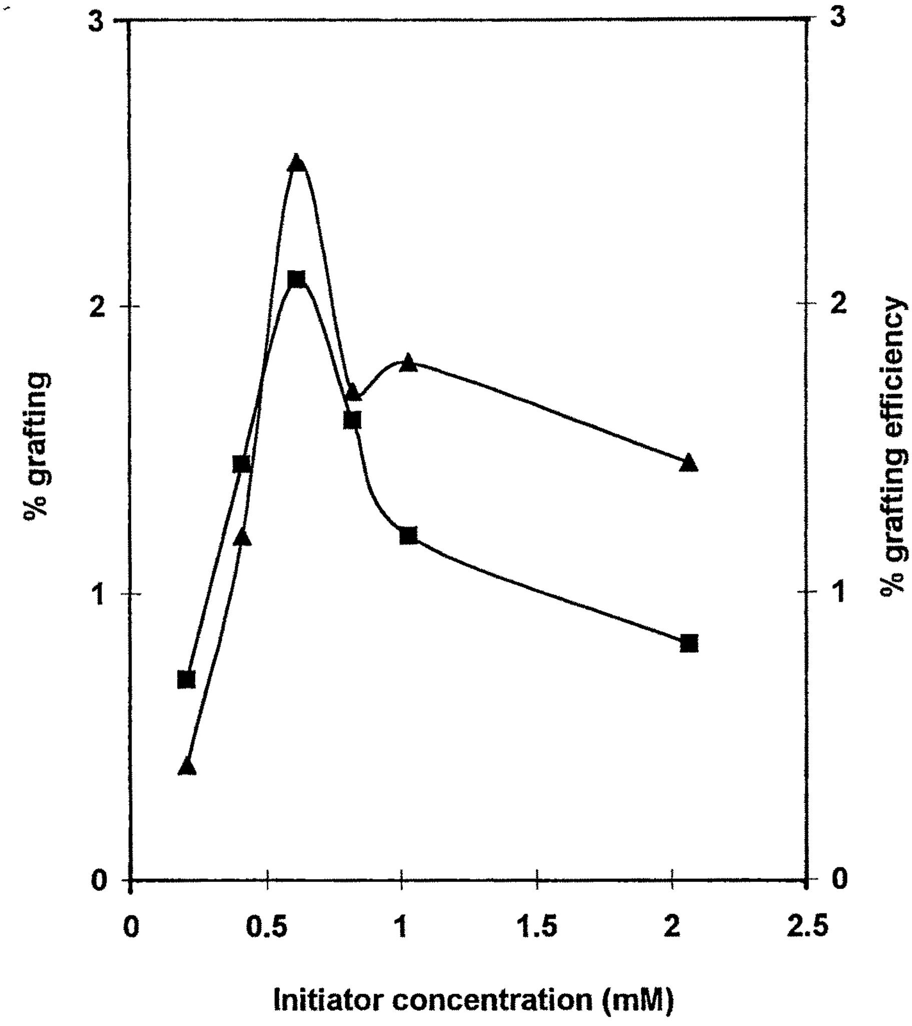


Figure 2.6: Effect of initiator concentration on % grafting and % grafting efficiency of glycidyl methacrylate on iPP

Polypropylene: 2.0 % (w/v), monomer concentration: 14.07 mM, reaction time: 6h, reaction temperature: 110 °C, reaction atmosphere: N_2, reaction medium : toluene

(▲) % grafting (■) % grafting efficiency

Table 2.4 : Effect of initiator type on grafting

Polypropylene : 2.0 %(w/v), monomer concentration : 14.07 mM, reaction time : 6.0 h, reaction atmosphere : N_2, reaction medium : toluene, reaction temperature : 110 °C

Initiator	Initiator concentration (mM in 50 ml toluene)	Percent of grafting	$t_{1/2}$ value (min)
AIBN	0.915	0.9	4.4
BPO	0.619	2.5	45
DCPO	0.555	1.9	110

Table 2.5 : Effect of initiator concentration on grafting

Polypropylene : 2.0 % (w/v), reaction time : 6.0 h, monomer concentration : 14.07 mM, reaction temperature: 110 °C, medium : toluene, atmosphere: N_2

Initiator concentration (mM in 50 ml toluene)	% Grafting	R_g X 10^7 (mol.litre^{-1}.s^{-1})	R_hX10^6 (mol.litre^{-1}.s^{-1})	R_p X 10^6 (mol.litre^{-1}.s^{-1})
0.206	0.4	0.26	3.70	3.70
0.413	1.45	0.94	6.23	6.30
0.619	2.5	1.62	7.92	8.08
0.826	1.79	1.17	8.79	8.91
1.032	1.45	0.94	10.07	10.02
2.064	1.45	0.94	11.40	11.46

grafting initially increases and then decreases, which is a typical behaviour of copolymerisation through either chain transfer mechanism or due to mutual termination[150]. A similar trend was observed in solid-phase grafting also. Initial increase in % grafting and grafting efficiency with increasing concentration of initiator can be attributed to the increased number of free radicals generating more active sites on the polymer back-bone. Further increase in initiator concentration decreases the average molecular weight of side chain, and increases the consumption of monomer in the process of homopolymerisation. It is observed from Table 2.5 that R_p, R_g and R_h initially increase and then R_g decreases with increasing concentration of initiator where as R_p and R_h increase with increasing concentration of initiator.

2.5.2.b Effect of monomer concentration

The results obtained in the study of effect of monomer concentration on % grafting and grafting efficiency for iPP-g-GMA system are given in Fig. 2.7. It is observed that with increase in monomer concentration % grafting increases initially while further increase in monomer concentration causes decrease in grafting. With increase in monomer concentration rate of homopolymerisation increases. At lower concentration, monomer molecules have been consumed preferentially for grafting. The number of free radical sites available on iPP-back-bone being a limiting factor, the free radicals in the solution initiate homopolymerisation to a greater extent. Hence the grafting efficiency also goes on decreasing as concentration of monomer increases. It is clearly indicated also by the growth in the rate of homopolymerisation R_h (Table 2.6). A similar trend was observed by Mehta et al.[150] and Kaul et al.[151] for grafting of 4-VP and methacrylonitrile onto iPP fibre.

2.5.2.c Effect of reaction time

Fig. 2.8 illustrates the results obtained in the study of the effect of reaction time on the % grafting and grafting efficiency for iPP-g-GMA system.

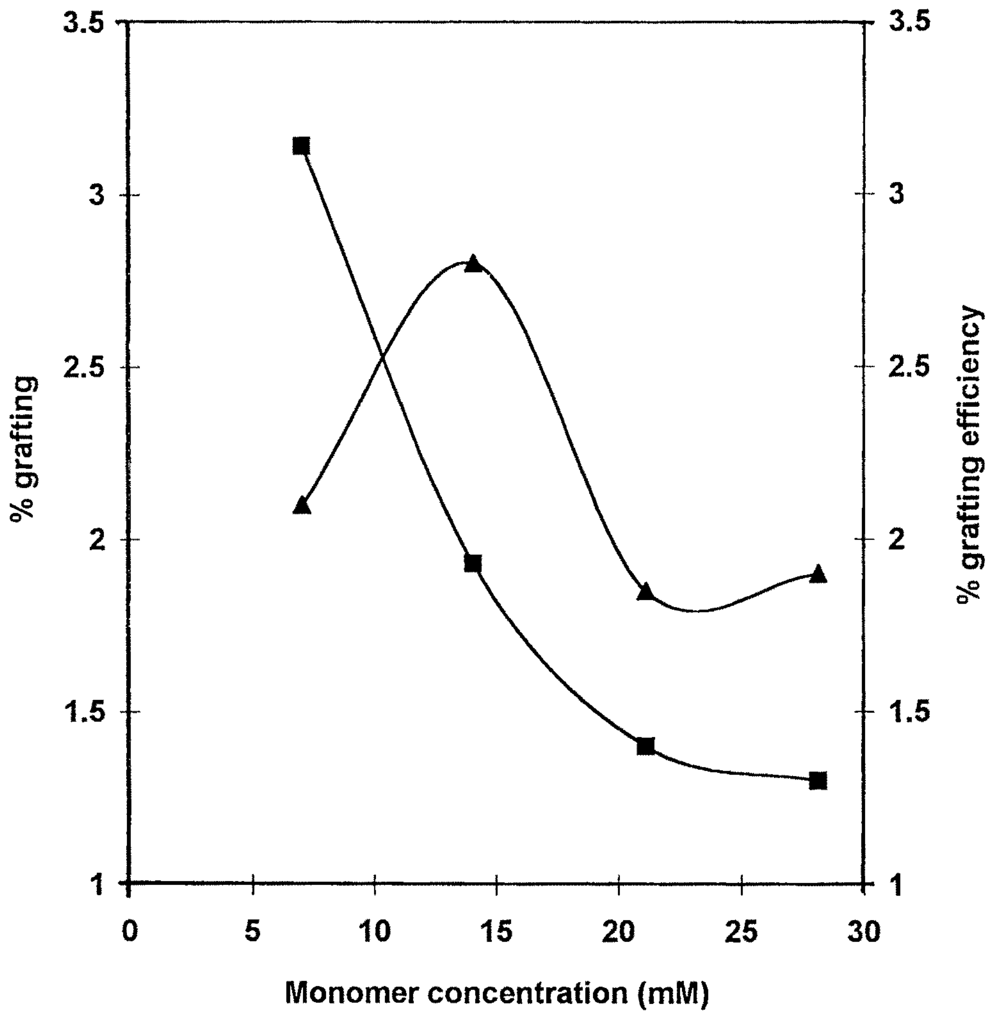


Figure 2.7: Effect of monomer concentration on % grafting and % grafting efficiency of glycidyl methacrylate on iPP

Polypropylene: 2.0 % (w/v), initiator concentration: 0.619 mM in 50 ml toluene, reaction time : 4h, reaction temperature: 110 °C, reaction atmosphere: N_2, reaction medium : toluene

(▲) % grafting (■) % grafting efficiency

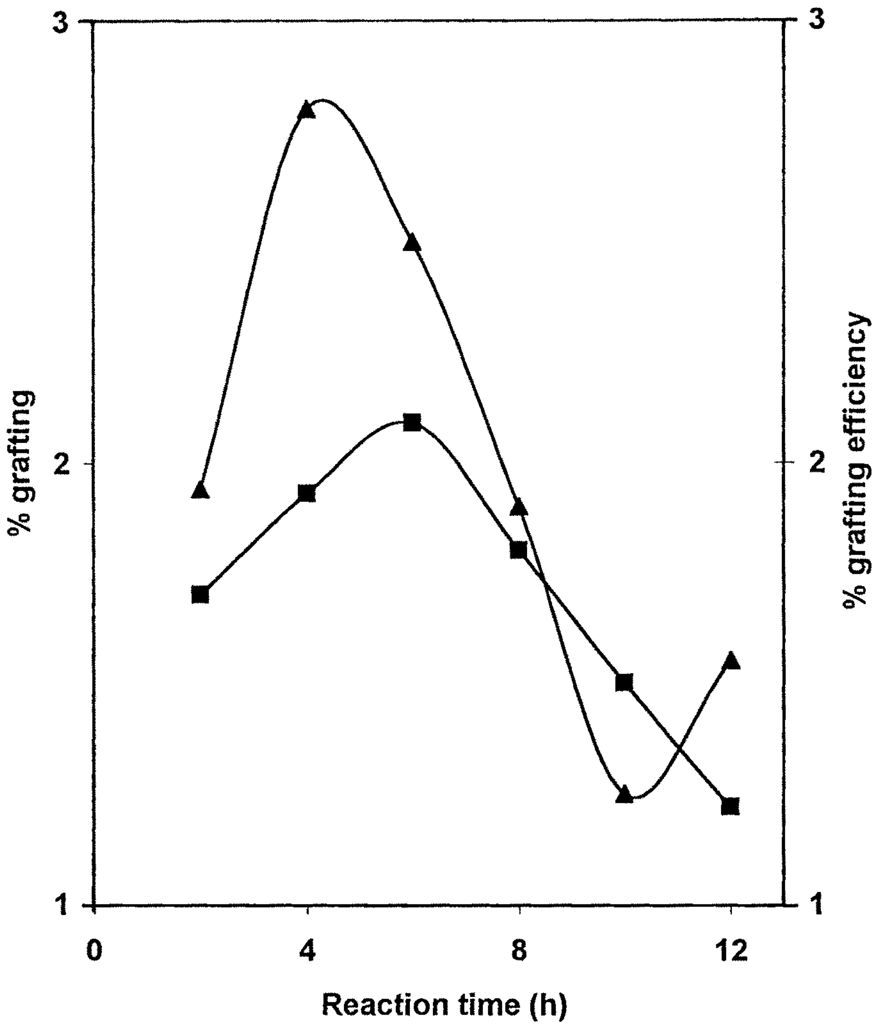


Figure 2.8: Effect of reaction time on % grafting and % grafting efficiency of glycidyl methacrylate on iPP

Polypropylene: 2.0 % (w/v), initiator concentration: 0.619 mM in 50 ml toluene, monomer concentration: 14.07 mM, reaction temperature: 110 °C, reaction atmosphere: N_2, reaction medium . toluene

(▲) % grafting (■) % grafting efficiency

Table 2.6 : Effect of monomer concentration on grafting

Polypropylene : 2.0 % (w/v), initiator concentration (BPO) : 0.619 mM in 50 ml toluene, reaction time : 4.0 h, reaction temperature : 110 °C, atmosphere : N_2, medium : toluene

GMA (mM)	% Grafting	$R_g \times 10^7$ (mol.litre^{-1} s^{-1})	$R_h \times 10^5$ (mol. litre^{-1} s^{-1})	$R_p \times 10^6$ (mol.litre^{-1} s^{-1})
7.035	2.10	2.05	0.07	6.98
14.070	2.80	2.83	1.19	12.20
21.105	1.85	1.80	1.27	12.90
28.139	1.5	1.51	2.38	23.00

Table 2.7 : Effect of reaction time on grafting

Polypropylene : 2.0 %(w/v), initiator concentration (BPO) : 0.619 mM in 50 ml toluene, reaction temperature : 110 °C, monomer concentration : 14.07 mM, medium : toluene, atmosphere : N_2

Reaction time (h)	% Grafting	R_g X 10^7 (mol.litre^{-1}.s^{-1})	R_h X 10^6 (mol.litre^{-1}.s^{-1})	R_pX 10^6 (mol.litre^{-1}.s^{-1})
2.0	1.94	3.81	23.56	23.94
4.0	2.80	2.83	11.90	12.20
6.0	2.5	1.62	7.92	8.08
8.0	1.90	0.92	5.33	5.43
10.0	1.29	0.50	3.90	4.00
12.0	1.55	0.5	3.67	3.72

It was observed that initially grafting increases with increase in time up to 4 hours, but with further increase in reaction time % grafting decreases. This may be due to the β-scissioning of side chains from the iPP-backbone. Similar observation was reported by Sivakumar et al.[152] and Sathe et al.[153]. With increase in time R_p and R_h were observed to decrease where as % grafting initially increased and then decreased. R_p, R_g and R_h were also observed to decrease with reaction time (Table 2.7).

2.5.2.d Effect of reaction temperature

In the study of effect of temperature on the grafting level and grafting efficiency for iPP-g-GMA system, it was observed that with increase in temperature % grafting and grafting efficiency increase due to increased decomposition rate of initiator, which increases the number and mobility of free radicals. Results are given in Table 2.8. This also increases the rate of homopolymerisation R_h and rate of grafting R_g. The grafting was also carried out in air and nitrogen atmosphere resulted into 1.2 and 2.8 % respectively. The decrease in % grafting in air may be due to the deactivation of initiator[154]. This can be explained from the following

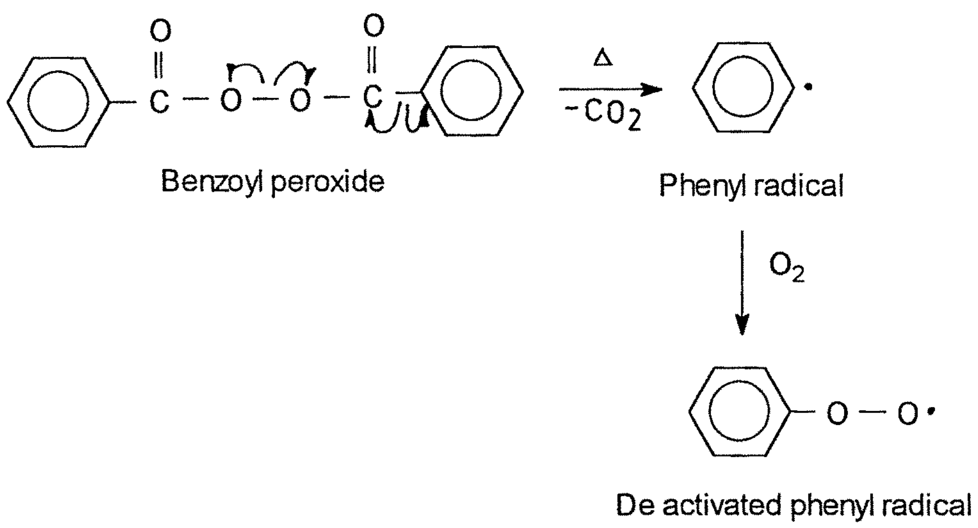


Table 2.8 : Effect of temperature on grafting

Polypropylene : 2.0 %(w/v), initiator concentration : 0.619 mM in 50 ml toluene, reaction time : 4.0 h, monomer concentration : 14.07 mM, medium : toluene, reaction atmosphere : N_2

Reaction Temperature (°C)	% Grafting	% Grafting Efficiency	R_g X 10^7 (mol.litre^{-1}.s^{-1})	R_h X10^6 (mol.litre^{-1}.s^{-1})	R_p X 10^6 (mol.litre^{-1}.s^{-1})
90	-	-	-	-	-
100	0.7	0.9	0.68	7.53	7.60
110	2.8	1.93	2.83	11.90	12.20

Table 2.9 : Effect of reaction medium on grafting

Polypropylene : 2.0 % (w/v), initiator concentration (BPO) : 0.619 mM in 50 ml toluene, monomer concentration : 14.07 mM, reaction time : 4.0 h, reaction temperature : 110 °C, atmosphere : N_2, medium : toluene

Reaction Medium	Dipole Moment	% Grafting
toluene	0.42	2.8
xylene	2.57	1.2
chlorobenzene	1.72	0.7
decalin	0.00	-

2.5.2.e Effect of reaction medium

Effect of reaction medium on % grafting was studied by using various solvents with different polarity like toluene, xylene, chlorobenzene and decalin at the optimised conditions for grafting of GMA on iPP. From the results in Table 2.9 there seems to be no apparent correlationship between polarity of the medium and grafting extent. However, maximum % grafting was achieved in toluene and hence further studies were carried out in toluene.

2.5.3 Evidence of grafting

iPP-g-GMA, iPP-g-methacrylic acid copolymers were colourless, whereas iPP-g-4-VP graft copolymer showed light brown colour. All graft copolymers showed solubility behaviour similar to that of iPP.

2.5.3.a IR-analysis

Figs. 2.9, 2.10, 2.11 and 2.12 illustrate the ir spectra of iPP, iPP-g-4VP, iPP-g-GMA and iPP-g-MAA graft copolymers respectively. Fig. 2.10 shows a band at 1610 cm^{-1} which is a characteristic of the aromatic ring from vinyl pyridine. This band was observed to be absent In the ir-spectra of iPP (Fig. 2.9). In Fig. 2.11 the ir-spectra of iPP-g-GMA graft copolymer shows a band at 1730 cm^{-1} which can be assigned to the carbonyl group of GMA which is grafted onto iPP. Fig. 2.12 shows the ir-spectra of iPP-g-MAA copolymer where appearance of a new strong band at 1730 cm^{-1} which is a characteristics of carbonyl group of acrylate in iPP-g-MMA on iPP confirms the grafting.

2.5.3.b Differential scanning calorimetry

The results of the DSC measurements carried out for iPP, iPP-g-4-VP and iPP-g-GMA and iPP-g-MAA copolymers are given in Table 2.10 and Table 2.11, respectively. From the DSC thermograms (Fig. 2.13 and Fig.

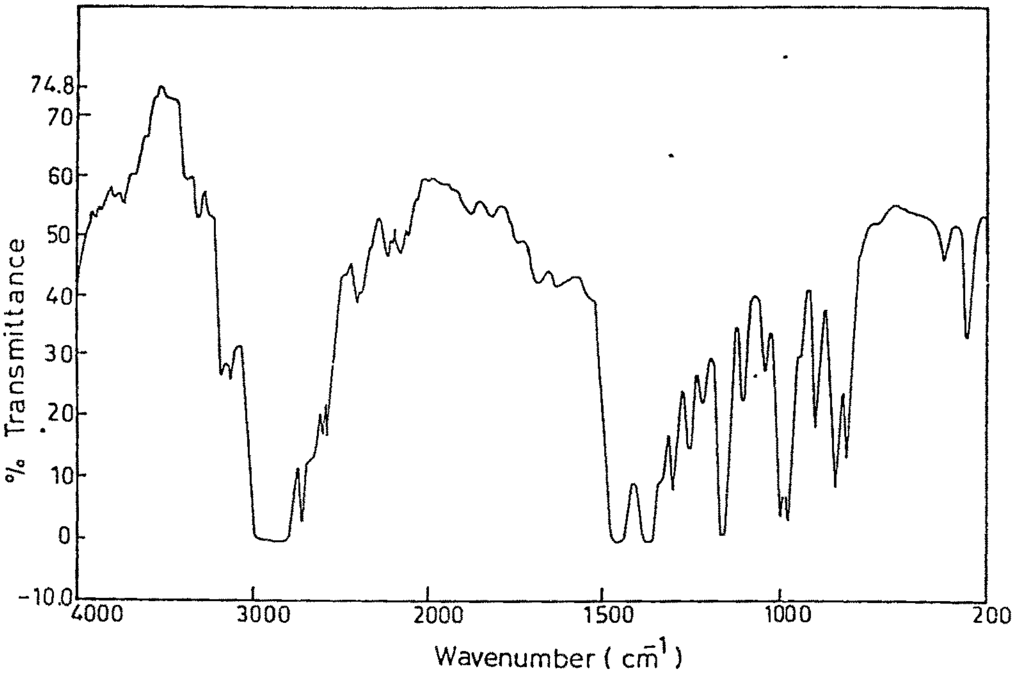


Figure 2.9 : FTIR spectra of isotactic polypropylene (iPP)

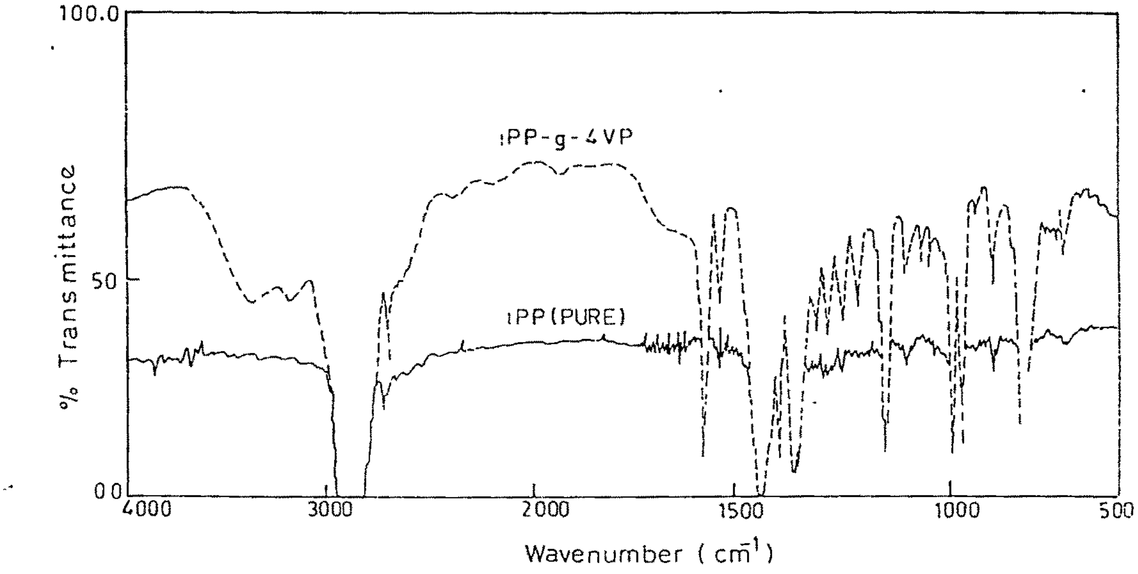


Figure 2.10 : FTIR spectra of iPP and iPP-g-4-VP

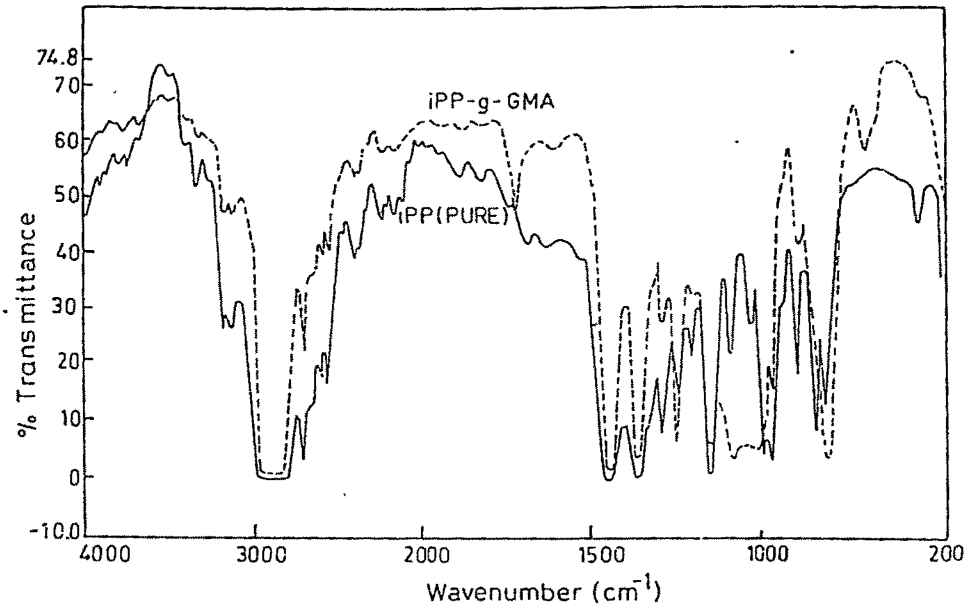


Figure 2.11 : FTIR spectra of iPP and iPP-g-GMA

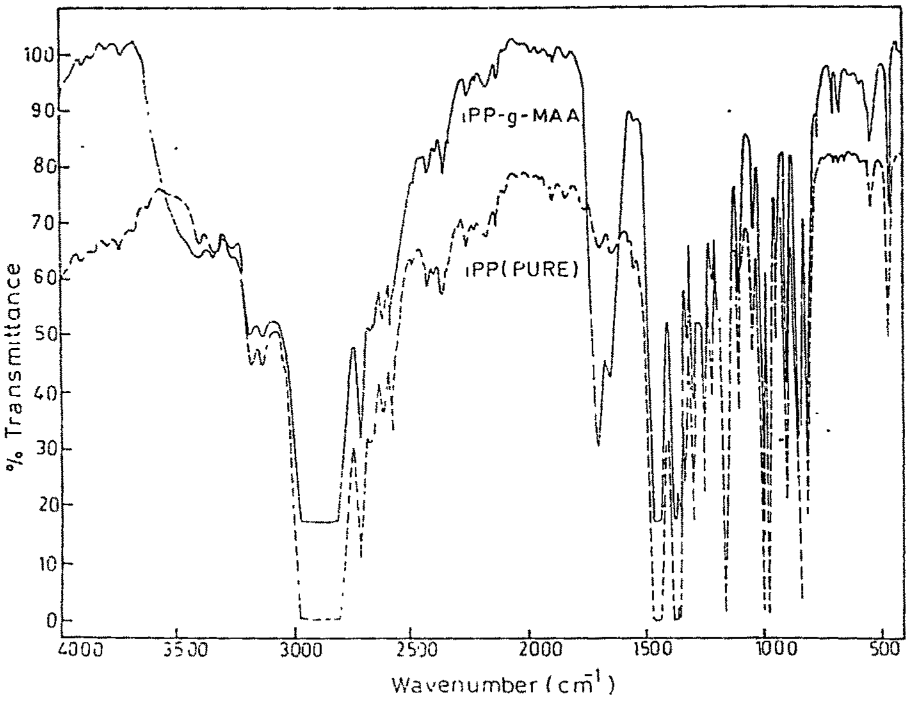


Figure 2.12 : FTIR spectra of iPP and iPP-g-4-MAA

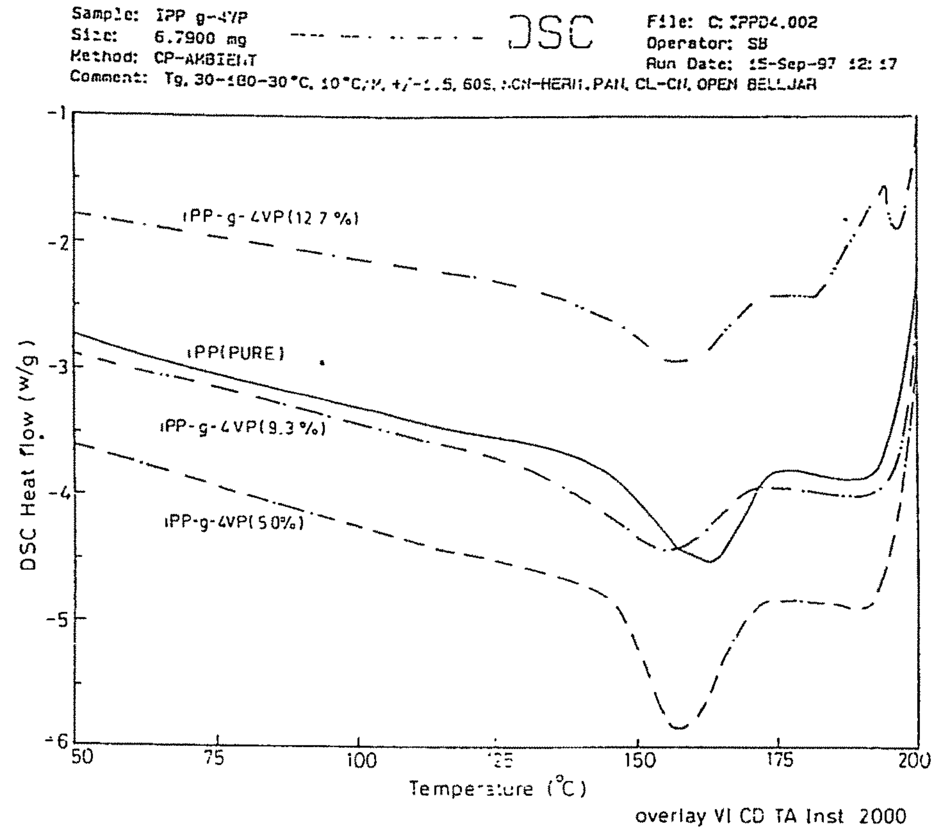


Figure 2.13 : DSC thermograms for iPP-g-4-VP

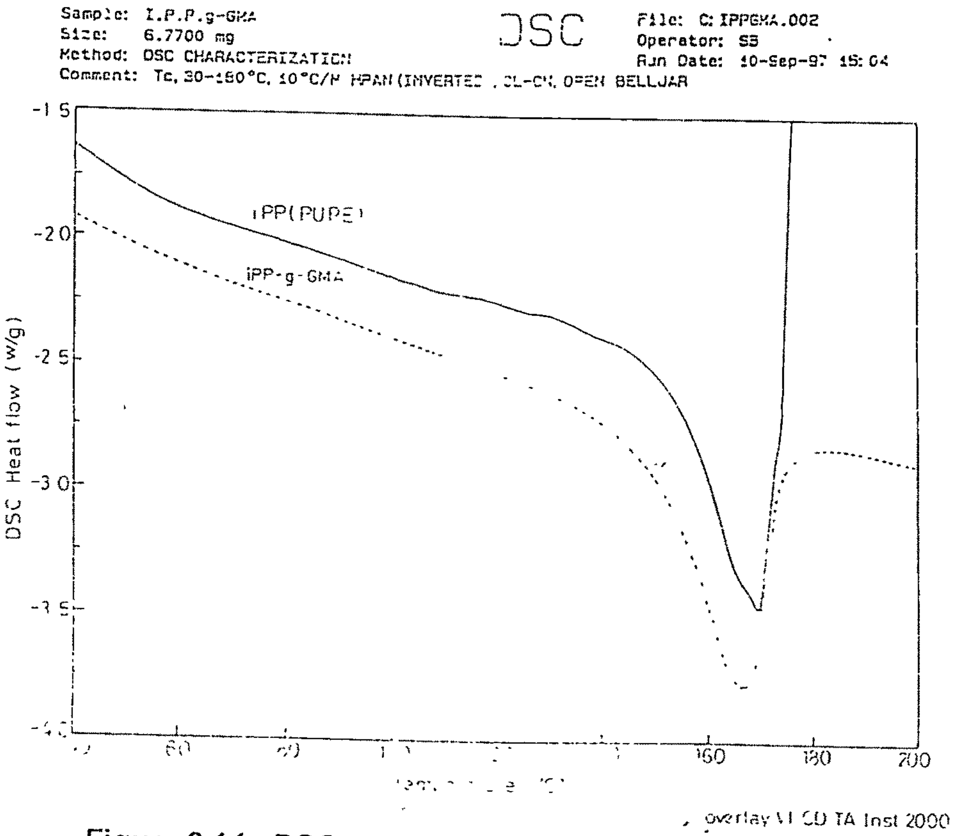


Figure 2.14 : DSC thermograms for iPP-g-GMA

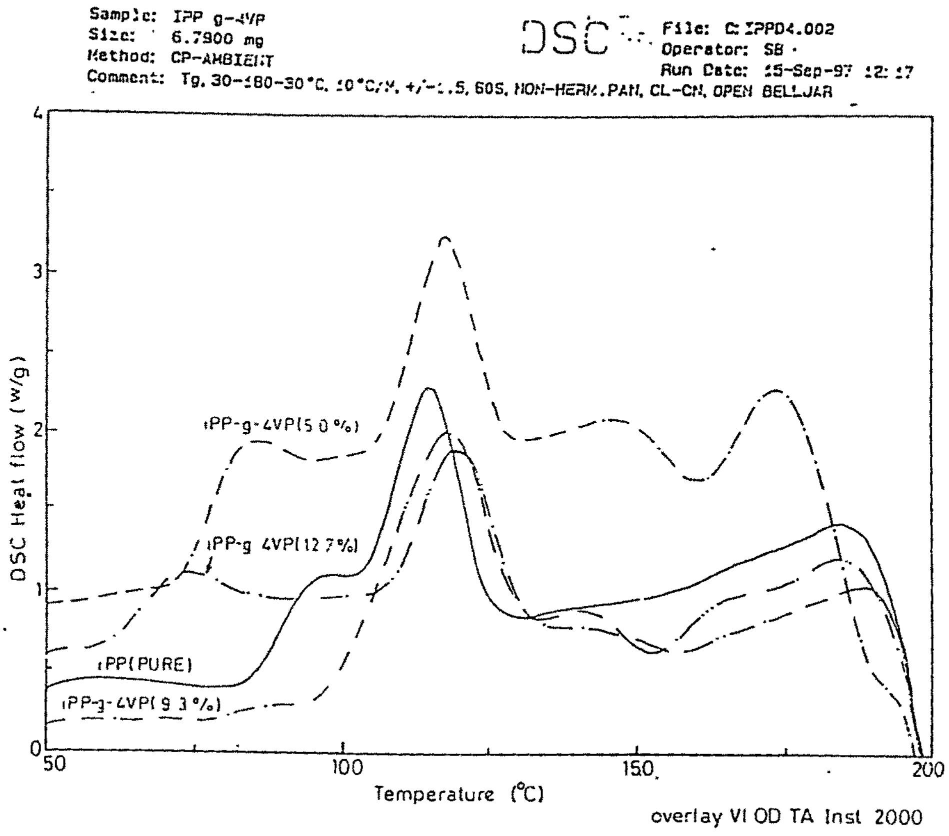


Figure 2.15 : DSC cooling curves for iPP-g-4-VP

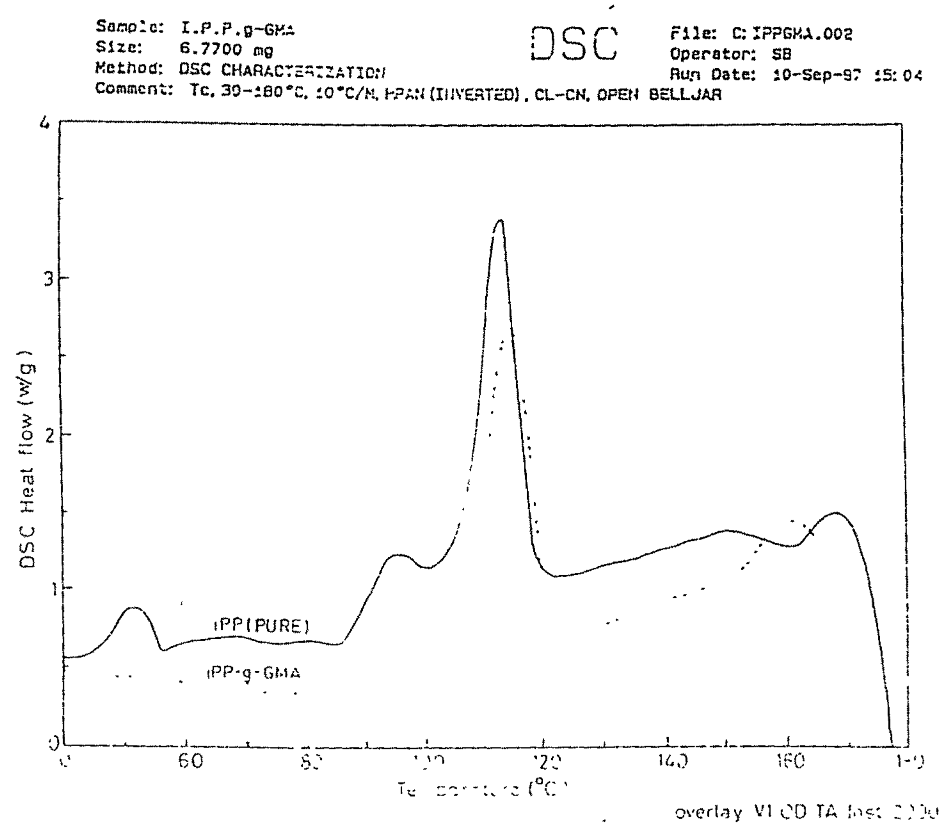


Figure 2.16 : DSC cooling curves for iPP-g-GMA

2.14), it can be observed that the melting temperatures (T_m) for grafted samples are some what lower than that of virgin iPP. From the DSC cooling curves Fig. 2.15 and Fig. 2.16, crystallisation temperature for the grafted samples were observed to be somewhat higher than that of iPP. Higher crystallisation temperature (T_c) for grafted samples may be due to nucleating effect of pyridine ring and carbonyl and /or epoxy group which is incorporated in the grafted chains. Xiaomin, et al.[155] and Rybnikar, et al.[156] have also found nucleation effect due to incorporation of carbonyl and/or epoxy group in iPP.

From the heat of fusion (ΔHf^*), percentage crystallinity was calculated on the assumption that the heat of fusion (ΔHf^0) of 100 % crystalline iPP is 50 cal/g[165]. As the heat of fusion is directly proportional to the amount of crystalline iPP in the sample, it decreases linearly with increase in percent grafting. An apparent decrease in heat of fusion was due to the decrease in weight fraction of crystalline iPP in copolymer due to incorporation of amorphous poly vinyl pyridine and poly glycidyl methacrylate in iPP. Similar trend was observed by Mukherjee[157] and Agrawal and Horrison[158] for iPP-g-MAA and PE-g-AA, respectively.

2.5.3.c Thermogravimetry

Figs. 2.17, 2.18 and 2.19 show the TGA curves for iPP-g-4VP, iPP-g-GMA and iPP-g-methacrylic acid copolymers with different percentage of graft level along with iPP. From the thermograms it is observed that increase in initial decomposition temperature (IDT) and temperature for 50% decomposition (T_{50}) takes place with increase in grafting and it is also evident that grafted samples have improved thermal stability. Initial decomposition temperature (IDT) and 50% decomposition temperature (T_{50}) for the iPP and grafted iPP are given in Table 2.10 and Table 2.11 for iPP-g-4VP, iPP-g-GMA, iPP-g-MAA graft copolymer systems, respectively.

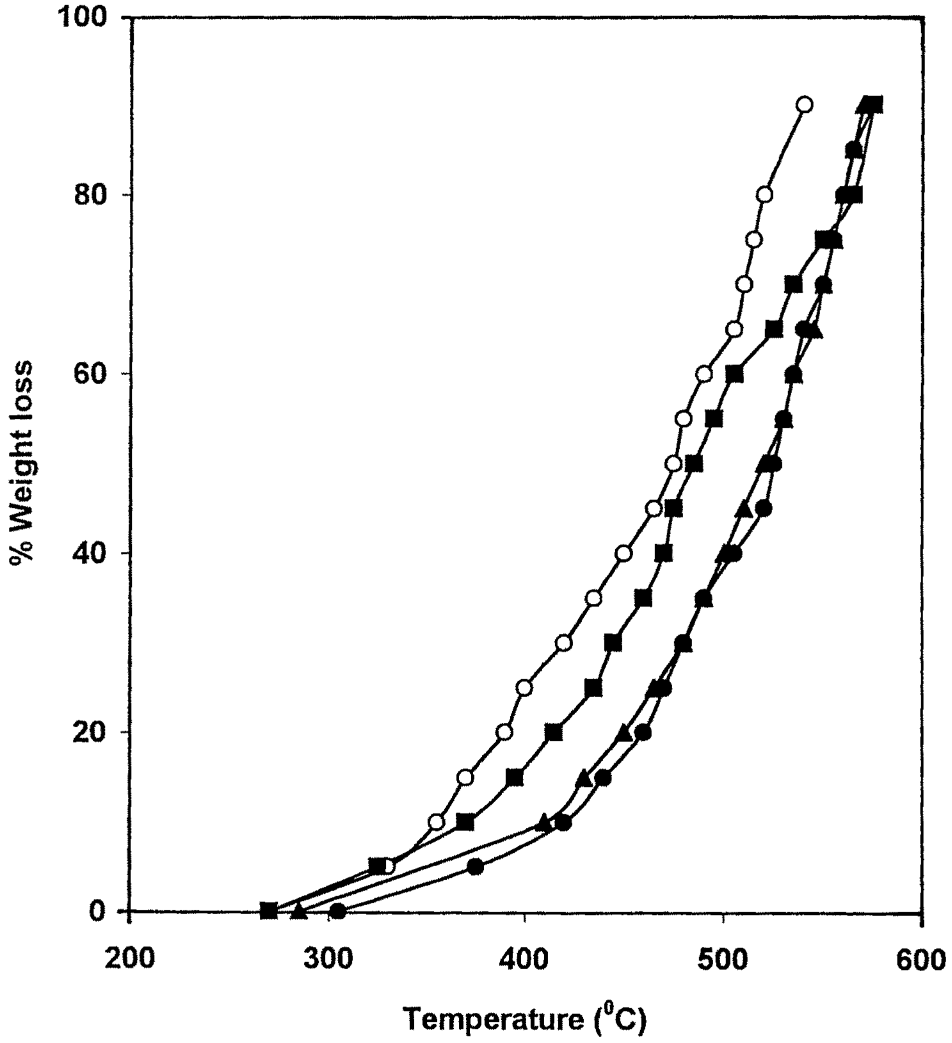


Figure 2.17 : TGA plots of iPP-g-4-VP

(o) : iPP
(■) : iPP-g-4-VP (5.0% grafting)
(▲) : iPP-g-4-VP (9.3% grafting)
(●) : iPP-g-4-VP (12.7% grafting)

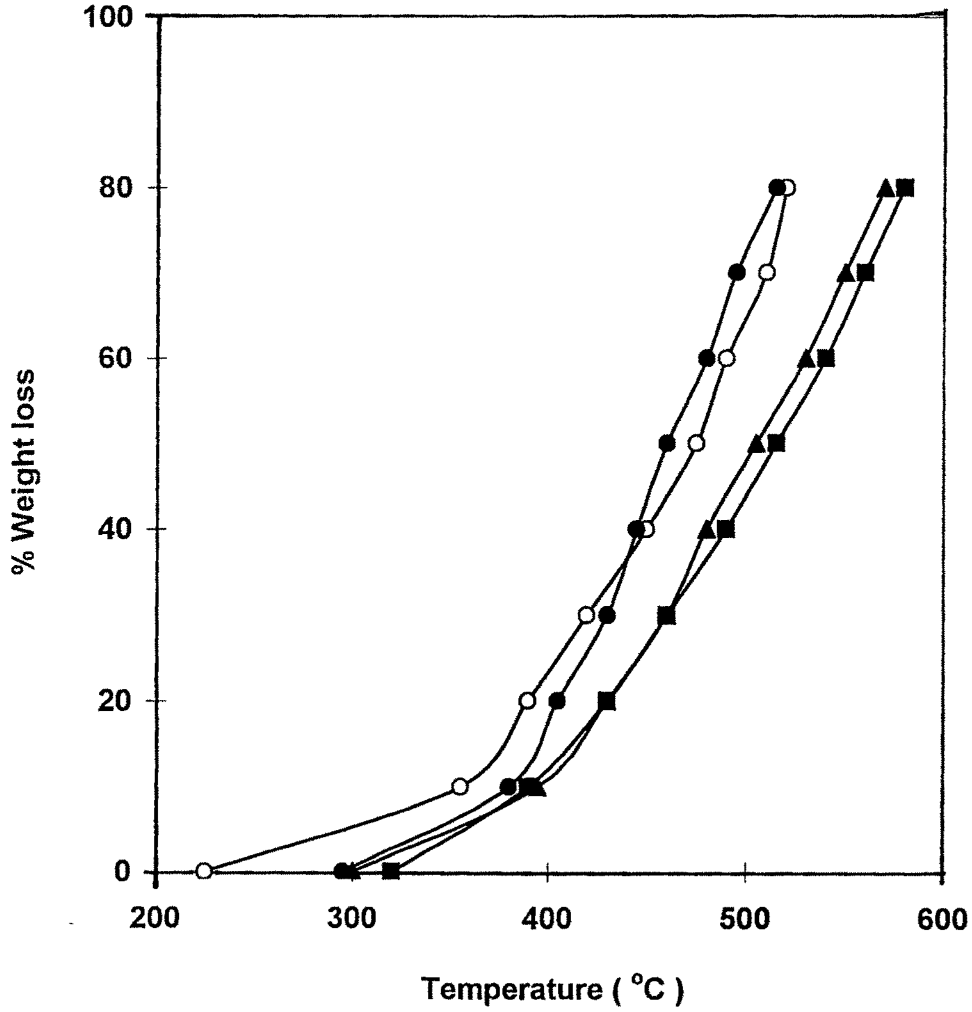


Figure 2.18 : TGA plots of iPP-g-GMA

(o) : iPP

(●) : iPP-g-GMA (1.05% grafting)

(▲) : iPP-g-GMA (1.80% grafting)

(■) : iPP-g-GMA (2.80% grafting)

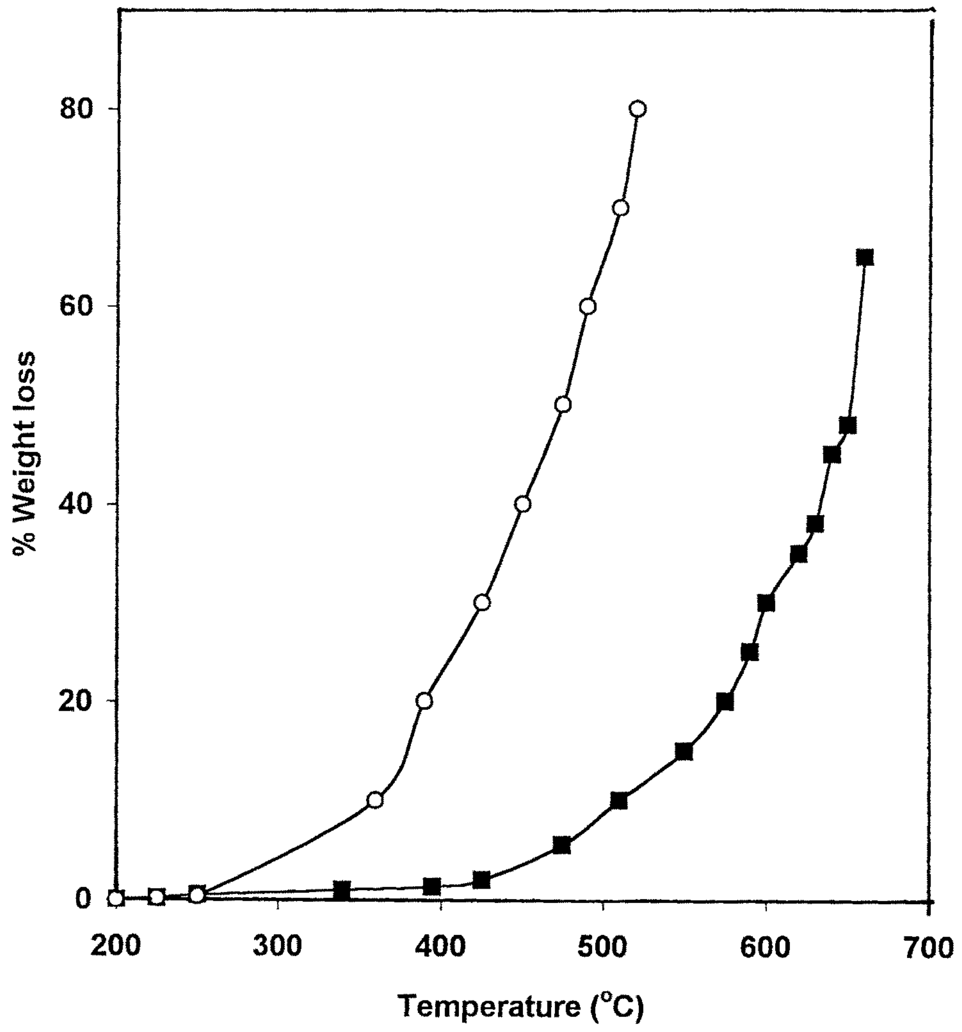


Figure 2.19 : TGA plots of iPP-g-MAA

(○) : iPP

(■) : iPP-g-MAA (7.0% grafting)

Table 2.10 : Thermal properties of iPP and iPP-g-4-VP

	% grafting	T_m (^{0}C)	Crystallisation Temperature (^{0}C)	ΔH_f* (Cal/g)	% Crystallinity	IDT (^{0}C)	T_{50} (^{0}C)
iPP	-	161.9	113.85	50.0	-	225	475
iPP-g-4-VP	5.0	156.7	116.90	19.8	39.6	270	485
iPP-g-4-VP	9.3	154.1	116.99	15.5	31.2	285	520
iPP-g-4-VP	12.7	157.3	119.59	15.6	31.3	305	525

Table 2.11 : Thermal properties of iPP and iPP-g- GMA and iPP-g-MAA

	% grafting	T_m (°C)	Crystallization Temperature (°C)	ΔH_f* (Cal/g)	% Crystallinity	IDT (°C)	T_{50} (°C)
iPP	-	167	114	-	-	225	475
iPP-g-GMA	1.0	163	115	11.24	22.4	295	460
	1.8	163	115	8.27	16.5	300	505
	2.8	164	118	6.75	13.5	320	515
iPP-g-MAA	6.0-7.0	159	121	6.40	12.8	260	630

2.6 Conclusion

Grafting of 4-vinyl pyridine onto isotactic polypropylene using solution as well as solid-phase grafting techniques resulted into 6.0 and 12.7% of grafting at optimized conditions. Grafting of 4-VP onto iPP using benzoyl peroxide as initiator, 4 h reaction time at 110 °C in toluene resulted into 6.0% of grafting, where as for the same monomer in solid-phase grafting technique at 110 °C temperature with 30 min. reaction time with 1:2 polymer to monomer ratio resulted into 12.7% of grafting. The higher % of grafting in solid phase is attributed to more reactive sites on iPP surface and solvent playing an important role for governing the grafting in both techniques by acting as chain transferring agent and reducing the % grafting with an increased concentration of solvent.

The graft copolymers were characterized by FTIR, TGA and DSC analysis. FTIR spectra of iPP-g-4-vinyl pyridine showed stretching band of aromatic ring at 1010 cm^{-1} confirming the incorporation of 4-VP in graft copolymer. The TGA data showed improved thermal stability of graft copolymers compared to iPP. Thermal stability was observed to increase with % grafting. Through DSC analysis % crystallinity was observed to decrease with increased % grafting of 4-VP onto iPP.

Using solution grafting technique, at optimized condition 2.8 and 6.8 % of grafting was observed for glycidyl methacrylate and methacrylic acid monomers respectively. FTIR spectra of grafted samples showed >C=O stretching band at 1730 cm^{-1} confirming the presence of GMA in iPP-g-GMA and MAA in iPP-g-MAA graft copolymers. The thermal stability of grafted samples and crystallization temperature (Tc) were observed to increase in modified iPP due to the nucleating effect of grafted monomers, while % crystallinity was observed to be decreased because of the incorporation of grafted monomer in iPP.

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