Chapter 2

Graft copolymers : Synthesis and Characterisation

CONTENTS

Polymers are classified according to their chemical structure as homopolymers, graftcopolymers, random copolymers and block copolymers[1]. **Fig.2.1** illustrates the structures of these polymers.

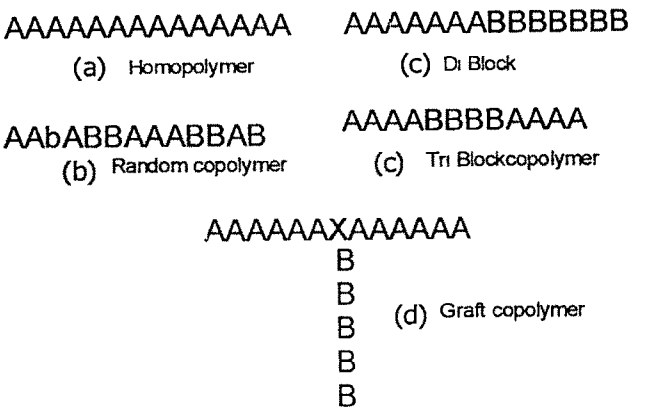

Fig. 2.1 Some structures of polymers

In earlier chapter various types of polymers useful as compatibilizers are discussed. However, the present work of development of compatibilizers for PP / ABS blends involves synthesis of graft copolymers, details of which are discussed here. In graft copolymers, sequences of one monomer are grafted onto a backbone of the other monomer and can be represented as shown in **Fig.2.1 d**. Thus a graft copolymer is a polymer comprising molecules with one or more species of block connected to main chain as side chains, having constitutional or configurational features that differ from those in the main chain[1, 2]. In graft copolymers the backbone and side chains may both be homopolymeric or the backbone may be homopolymeric and side chains copolymeric or vice a versa. Or both

backbone and side chains may be copolymers but of different chemical compositions[2-4]. The simplest case of a graft copolymer can be represented by the structure in **Fig.2.1 d.**

Graft copolymers can be produced by three different ways[5]

1. By first synthesising the main chain, and then polymerising the pendant chains at the active sites on the polymer back bone. This is termed as **'growing from'** route for the synthesis of graft copolymers.

2. By first synthesising the pendant chains with reactive groups on their ends, which then participate in the polymerisation with monomer(s) of the side chain. This route is termed as **'growing through'** for the synthesis of graft copolymers.

3. Alternatively the pendant and main chains each containing active sites are polymerised separately, which then react in a subsequent step to form the graft copolymer. This method for the synthesis of graft copolymers is termed as **'grafting onto'**.

The methods of synthesis of graft copolymers have been well reviewed by Ceresa[1], Sperling[4], Aggrawal[6], Matzener et.al.[7], Goodman[8], Meier[9], Xu and Lin[10] and Mukharjee and Gupta[11].

In graft copolymers the main chain and the branch chains with different characters and thermodynamically incompatible nature are joined by

covalent bonds. According to Molau such micro phase separated graft copolymers exhibit many of the unique thermal and mechanical properties[12].

'Grafting from' and 'grafting through' methods are most widely applicable for the synthesis of graft copolymers.

2.2 Methods of Grafting

Based on the mechanism, grafting methods can be classified as free radical, ionic and co-ordination coupling grafting.

2.2.1. Grafting through free radical

Free radical grafting involves either radical chain transfer or addition of monomer to the polymer backbone containing active sites. It is used to synthesise commercial multiphase polymeric materials, such as high impact polystyrene (HIPS) and acrylonitrile - butadiene - styrene (ABS) [13, 14].

The general mechanism of free radical graft copolymerisation is as illustrated below (**Fig.2.2**) which involves the generation of free radicals at polymer backbone and successive attack on monomer.

The macro radical either adds to double bond as in the case of polydiene[16], shown in **Fig.2.3** or abstracts labile hydrogen from allylic carbon or from tertiary carbon as in the case of PP, PE. This leads to the grafting as shown in **Fig. 2.4 a** and **b**.

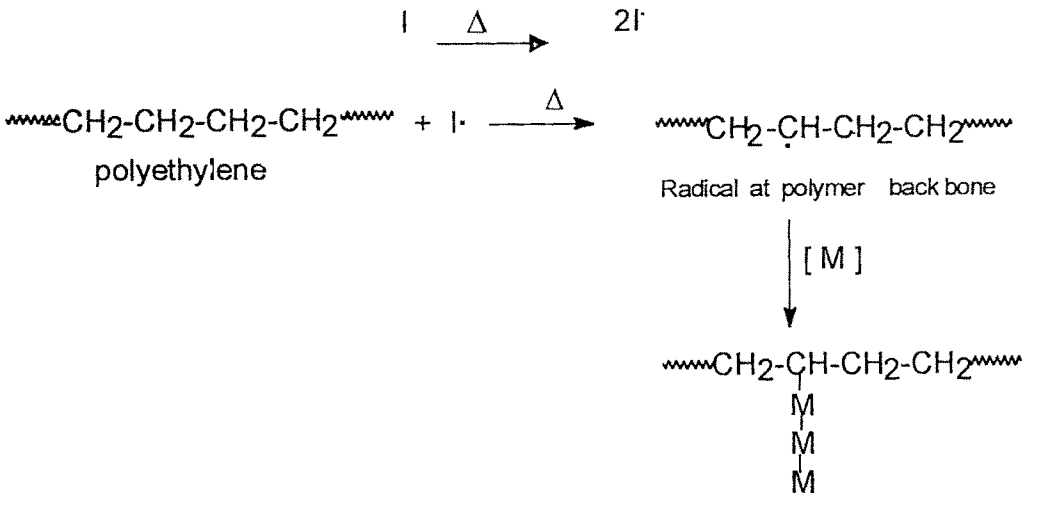

Fig.2.2 General mechanism of graft copolymerisation

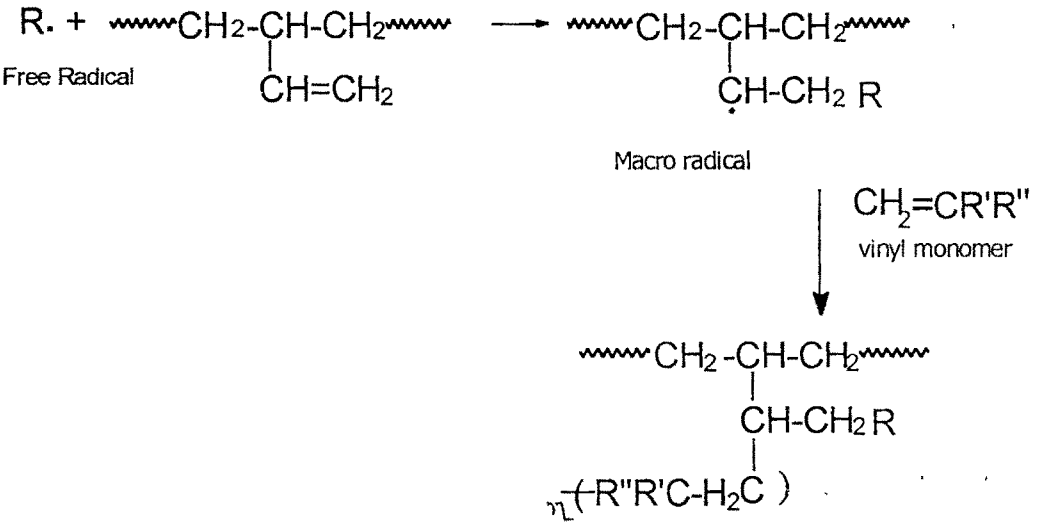

Fig.2.3 Grafting on polydiene through cleavage of double bond

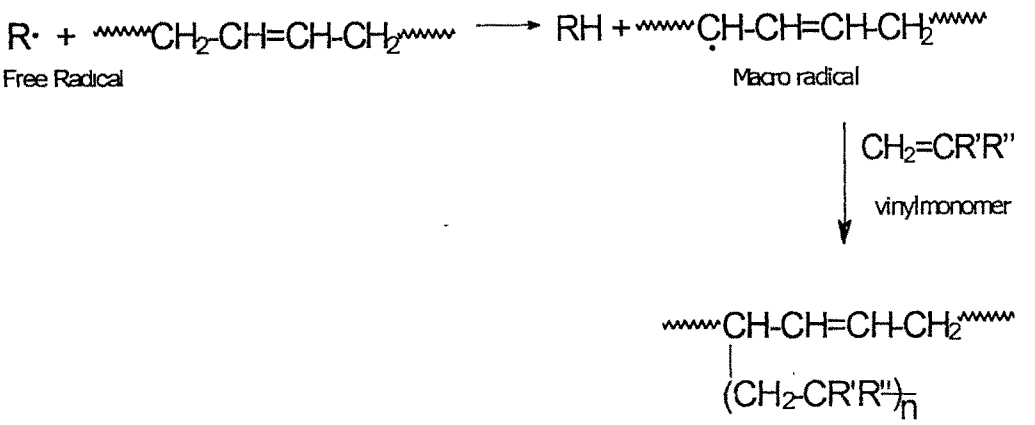

Fig.2.4a Grafting on polydiene through hydrogen abstraction

Unfortunately free radical grafting methods produce materials that are difficult to characterise and contain varying amounts of homopolymers and cross linked mass known as gel fraction[15]. However, this is the most common industrially explored method for the modification of polymers.

Free radical grafting is further subdivided according to the method used for the generation of free radicals.

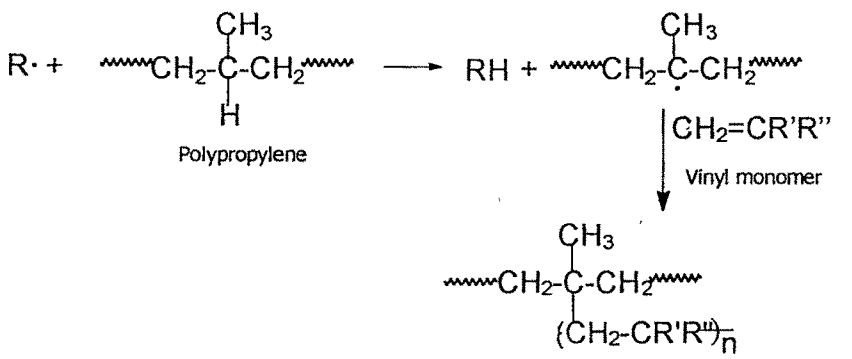

Fig. 2.4 b Grafting on polyolefin through hydrogen abstraction

The free radicals on polymer backbone (macro radicals) are generated by following methods[10].

- chemical method
- photochemical (UV radiation) method
- high energy radiation (γ rays) method
- plasma induced method

- ***Chemical method***

The free radicals can be obtained from the initiators such as benzoylperoxide (BPO), azobisisobutyronitrile (AIBN) and dicumylperoxide (DCPO) as shown below. These initiators decompose at decomposition temperature and generate free radicals, which initiate graft copolymerisation or also lead to homopolymerisation[16-18]. The sequential process of graft copolymerisation is illustrated in the **Fig. 2.5.**

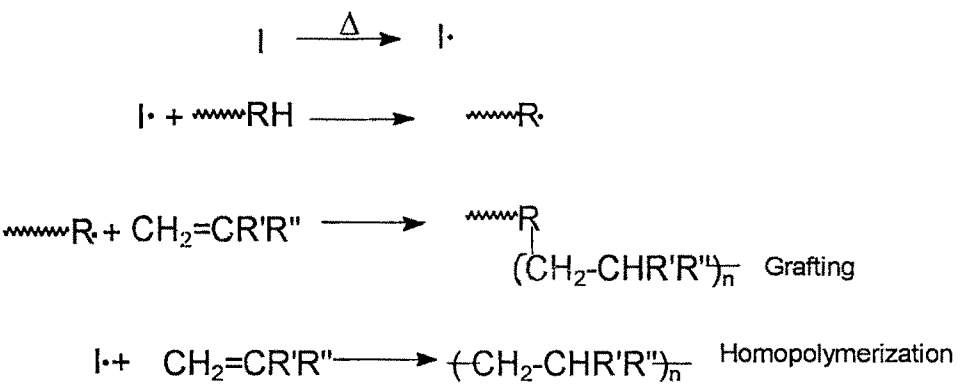

Fig. 2.5 Sequencial process of grafting

- ***Photo chemical method***

The radicals on polymer backbone can also be generated through photochemical reactions. In this method polymers containing chromophoric groups absorb electromagnetic radiation in the visible or ultraviolet region, resulting into bond breaking and subsequent generation of free radicals on the polymer backbone, which leads to initiation of grafting. If the polymer does not have chromophoric group,indirect photolysis is initiated by using photosensitive compound such as benzophenon and benzoin ethylether, which absorb the radiation and then transfer this energy to the polymer, generating free radical on the polymer backbone. The limitation of this method is that it leads to the surface modification and not the bulk modification[10].

- ***High energy radiation method***[10]

In this method graft copolymerisation occurs at radical sites generated along the polymer backbone due to high energy radiation (γ - rays). Though the method leads to high degree of grafting, it suffers due to the cross linking, homopolymerisation and degradation of the parent polymer.

Hence to overcome these disadvantages, pre irradiation technique has been used, where free radicals are trapped when the polymer is irradiated in the absence of air. There after monomer is introduced into the system, which is to be grafted onto the polymer backbone.

- ***Plasma method*** [10]

The grafting of polymers by glow discharge is known 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 copolymerisation. 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 up to 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.

2.2.2. Grafting through ionic polymerization

Through this technique lowly polydispersed graft copolymers with, high tacticity are formed. Ionic grafting can be accomplished through anionic and cationic process as

- ***Anionic process of grafting***

Anionic polymerisation also known as 'Living polymerization' is an excellent route for the synthesis of block and graft copolymers[20, 21]. Polymer backbones with more acidic protons react with base to generate anions that can be used to initiate graft copolymerisation with more reactive polar monomers.

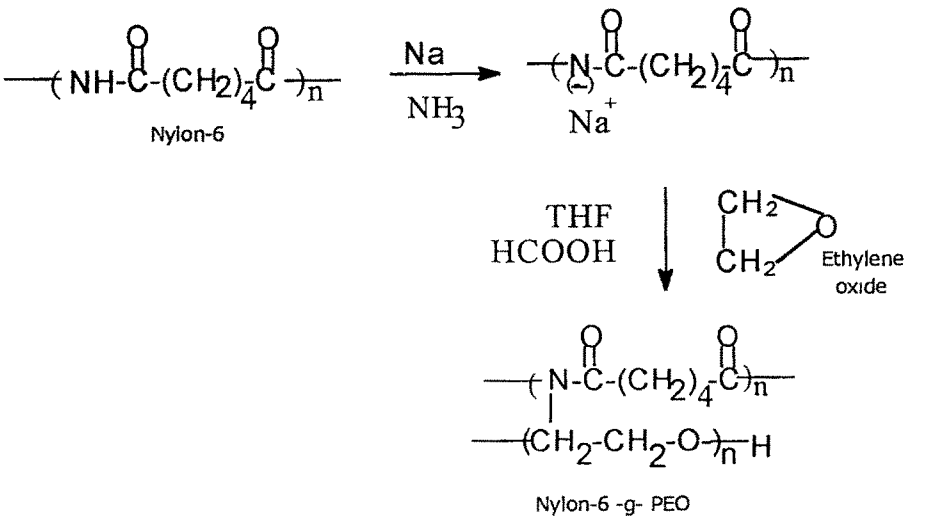

Fig.2.6 Grafting through anionic copolymerisation

Polyamides[22] and polyurethanes[23] can be metalated with sodium, sodium napthalene, or sodium hydride in liquid ammonia and then made to react with monomers such as ethylene oxide, ethylene sulfide or acrylonitrile. The mechanism of typical anionic graft copolymerisation is illustrated in **Fig. 2.6.**

- ***Cationic grafting***

Cationic grafting is limited by the types of cationically polymerizable monomers and by chain transfer reactions. Initiation reactions between labile alkyl halides and various Lewis acids have been utilized for cationic grafting of polymers with halogenated backbone such as polychloroprene, chlorinated – styrene – butadienerubber (C-SBR), chlorinated EPDM, chlorinated PP and PE etc. **Fig.2.7** shows the typical graft copolymerisation occurring through cationic polymerization[24 – 28].

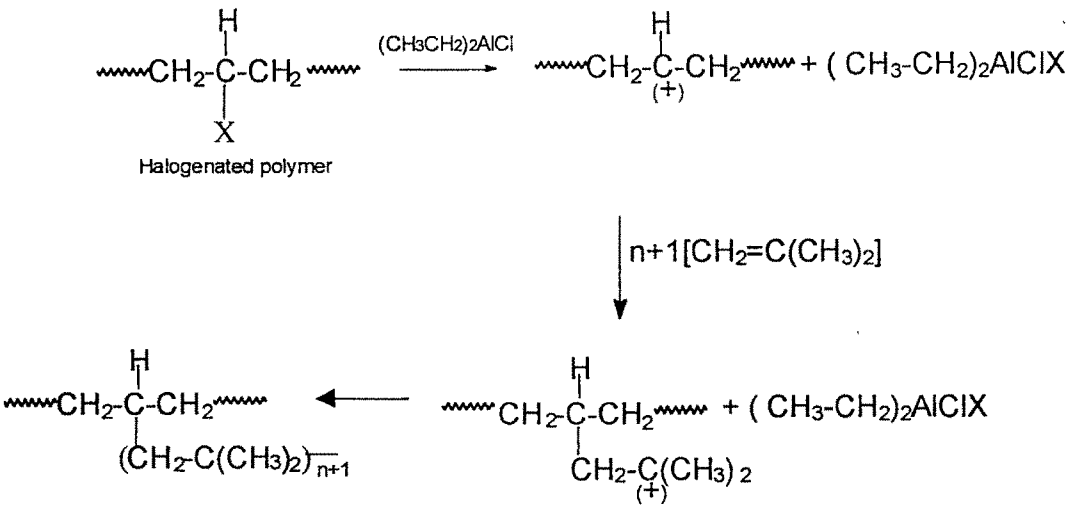

Fig.2.7 Grafting through cationic copolymerization

2.2.3. Grafting through co-ordination coupling

Grafting of olefenic monomers can also be done using Ziegler- Natta catalyst. Stereo specific initiator can give well-defined block or graft copolymer, which contains isotactic or heterotactic sequences. Greeber[29] grafted olefin onto poly(styrene-co-butadiene) using a Ziegler-Natta initiator system where diethyl aluminium hydride reacted with pendant groups to form macromolecular compound.

However, among these methods free radical grafting is widely used for the synthesis of graft copolymers.

2.3 Grafting onto Polypropylene

In recent years great interest is observed in the functionalisation of polyolefins, due to their commercial potential. Among other polyolefins PP

has important position, because of its low-cost, versatile properties and growing commercial applications. However, due to its low surface energy, lack of chemical functionalities, difficulty in dyeing, sensitivity to photo - or thermal oxidation, extremely poor hygroscopicity, low impact strength, low melting and sticking temperature, inadequate compatibility with other synthetic polymers and no adhesion to metals and glasses, it has limitations for several technologically important applications[10].

Graft copolymerisation offers an effective approach for functionalization of PP, which introduces desirable properties into the polymers and thus expands the application range of PP without affecting the architecture of the main backbone. Grafting improves adhesion, tensile strength, dyeing and dye retention capacity and also thermal and photochemical stabilities. Graft copolymerisation also promotes the compatibility of PP with other polymers and fillers[11].

The history of grafting onto PP goes back to Natta et.al's.[30] attempt of grafting MMA onto PP in 1959.

Grafting of PP can be bulk as well as surface. For bulk grafting of PP, free radical graft copolymerisation method is most widely used and grafting can be achieved mainly through two ways

(1) chain transfer/ addition method of PP grafting and,

(2) grafting on functionalised PP.

2.3.1. Grafting of PP by chain transfer

This involves chain transfer initiation, which is partially responsible for branching in polymer molecules, and is carried out via free radical polymerisation. The extent of grafting increases with increasing monomer / polymer ratio and conversion. Various factors such as temperature, nature of solvent, type of monomer and initiator have pronounced effect on grafting. The efficiency of an initiator is an important factor. An ideal initiator for a grafting process must be non-oxidative with high hydrogen abstraction ability, and a suitable half-life under grafting conditions[1]. Benzoyl peroxide, dicumyl peroxide, ditert-butyl peroxide, tert-butyl peroxypivalate, 2,5-bis (tert-butyl peroxy)-2,5-dimethyl hexane, diisopropyl peroxydicarbonate and lauryl peroxide have been successfully used as initiators for the graft copolymerisation of PP[10]. Natta et.al.[31] have grafted methyl acrylate onto atactic PP in the presence of various above mentioned initiators. GuhaniYogi et.al.[32] studied the graft copolymerisation of ethylacrylate onto an atactic PP at 80^0 C in xylene containing benzoylperoxide. They have reported increased % grafting with increasing BPO concentration up to 5 hrs. It was observed that at lower conversion the homopolymerisation was more whereas at higher conversion Mn was higher.

The efficiency and rate of grafting also depend on the nature of the monomer. The success of chain transfer grafting depends on the relative reactivity ratios of the monomers for graft copolymerisation and the

homopolymerisation. e.g. grafting efficiency of atactic PP was low with MMA than with styrene[32], whereas grafting efficiency of vinyl ester CH_2= CH_2OAc / styrene block copolymer on PP was found to be higher than that of polystyrene alone[33].

The grafting efficiency and % grafting were reported to increase with increasing temperature by Moriya et.al.[33] while grafting vinyl acetate on oxidized PP at various temperatures for 24 h. Grafting temperature and solvent were reported to be important factors affecting extent of grafting.

Lazar et.al.[34] studied the effect of solvents on grafting of styrene and / or MMA onto atactic PP using BPO and DCPO initiators. The extent of grafting of MMA was reported to be 20 % more in benzene than in n-heptane. The higher solubility of polymethylmethacrylate macro radicals in benzene was attributed to result into increased grafting efficiency. Deut and Berlin[35] grafted vinyl pyridine, acrylamide and vinyl caprolactum onto PP fibre in toluene medium. The increase of grafting efficiency was attributed to swelling of the fiber in toluene.

When grafting is carried out without dissolving a polymer in solvent, it is called a solid phase grafting method. To enhance the graft level in solid phase grafting of various vinyl monomers onto a PP surface, an interfacial agent or catalyst is required. Rangrajan et.al.[36] reported that the addition of an interfacial agent such as toluene enhanced the graft level in grafting maleic anhydride onto PP surface. Interfacial agents enhanced the graft level significantly at higher initiator concentration. Kastrea et.al.[37] carried

out the solid phase graft copolymerisation of acrylonitrile onto PP fibre, without previous activation of the polymer. It was observed that the addition of ferrous sulfate improves the graft level and suppresses acrylonitrile homopolymerisation. Perego et. al.[38] claimed grafting of syndiotactic PP with α, β-unsaturated carboxylic acids or acrylic acids by heating at 120^0 C in xylene containing BPO. The process resulted into 13.8 % grafting of maleic anhydride onto syndiotactic PP.

2.3.2. Grafting onto functionalised PP

More efficient way for the introduction of active sites on PP backbone for graft copolymerisation is reported to be[10, 11]

- hydroperoxidation, and
- halogenation of PP

- **Hydroperoxidation**

The creation of active species onto PP backbone through oxidation can have commercial potential as it leads to higher % of grafting and grafting efficiency[39]. The oxidation of polypropylene is an autocatalytic process, and controlled oxidation results in the formation of hydroperoxides at tertiary carbon of PP. The hydrogen of the tertiary carbon atom being labile acts as the site for reaction with oxygen to form the hydroperoxide linkage, which upon decomposition, results in the formation of the free radicals from where grafting takes place. However, chain scissioning is quite common in the oxidation of polypropylene and it has been reported that the tertiary peroxy radicals act as the intermediate precursors for scissioning[10, 11, 19].

Generally the hydroperoxidation of PP has been carried out by heating the polymer in an oxygen/ozone current at 70 - 80^0 C or by initiating oxidation with initiators such as tert-butyl peroxide, benzoyl peroxide and dicumyl peroxide in the presence of air or using a cationic surfactant / potassium persulfate in an aqueous slurry[19]. To attain the desired extent of peroxides, adequate for an intended graft level, the variables temperature, time, oxygen / O_3 / air concentration and concentration of initiator and surfactant were reported to be important[40]. Number of monomers such as MMA, vinyl chloride, vinyl acetate, 2-vinyl pyridine and methylacrylate, C_{1-5} alkyl methacrylate, styrene, glycidylmethacrylate and 2-hydroxyethyl methacrylate have been grafted onto PP films or fibres by this technique[10].

Ferrous sulfate is added to the reaction medium to suppress the homopolymerisation because it decomposes the peroxidized species and scavenges the free radicals. The concentration of ferrous ions was reported to be most significant variable for grafting effeciency[35]. Narebska and Bukowski[40] and Citovicky et. al.[41] prepared graft copolymers of PP and acrylic acid by immersing PP film in an aqueous solution of acrylic acid containing ferrous sulfate as activator. Benzoin and ferric stearate or ferric acetylacetonate have also been used as redox agents in the grafting of various monomers such as N, N´ dimethyl amino ethyl methacrylate and butylacrylate on hydroperoxidized PP[42]. The oxidized PP powder was also grafted at 30^0 C in an aqueous emulsion of water soluble vinyl monomer by Citovicky et.al.[43]. The grafting of water soluble monomer such as acrylic

acid onto pre-activated PP film was reported to be governed by concentration of monomer and ferrous ions, polymerisation time, and temperature. Interestingly in the case of acrylic acid, the use of nonpolar solvents such as n-hexane or heptane was observed to be desirable[44].

Ozonolysis has also been proved to be a more effective means to produce active sites on PP backbone than aerial oxidation and it also facilitates easy graft copolymerisation of various monomers onto a PP surface with higher grafting efficiency and grafting rate due to the formation of active peroxides and hydroperoxide sites[11]. Yamauchi et.al.[45] have grafted methyl methacrylate onto PP, which was oxidized with O_3. The active species, determined by ESR spectroscopy were observed to be peroxyl radicals, which were further converted to the hydroperoxide and were further decomposed to produce alkoxyl and hydroxyl radicals, which initiated graft copolymerisation[46]. Natta et.al.[47] carried out hydroperoxidation of polypropylene without substantial degradation by heating in air or oxygen current at 70 - 80^0 C. The hydroperoxidation was reported to be restricted to the surface or intercrystalline amorphous regions. Wu et.al.[48] were able to graft vinyl acetate onto hydroperoxidzed polypropylene obtained by thermal oxidation in air. Miniskar et.al.[49] carried out the oxidation of polypropylene at 70^0 C and used it for graft copolymerisation of methylmethacrylate.

Jabloner and Mumma[42] have reported hydroperoxidation of polypropylene in aqueous slurry containing surfactant. A cationic surfactant and

potassium persulfate were used to achieve wetting and to initiate oxidation respectively. Oxygen was purged into solution and slurry was heated to 100^0 C to get hydroperoxidized PP.

The surfactant has been shown to have remarkable effect on hydroperoxide formation. Successful oxidation of PP has been attributed to the formation of persulfate salt of the quaternary ammonium surfactant on the surface of the polypropylene. The subsequent thermal decomposition of this hydrophobic salt yields radicals, which are soluble and react with the base polymer and generate free radicals on backbone[50-52].

- **Halogenation**

Halogenation provides another method to introduce functional groups into the polymer[10]. Nonpolar PP has been tuned into a polar polymer by the introduction of a chlorine atom and this polarity has been reported to be directly proportional to the chlorine content in PP by Howard[53]. The increased polarity of PP also improves its surface properties useful for dyeing and adhesion[54]. Moreover, grafting of various monomers can be achieved by activating the chlorinated PP with different initiators such as BPO, DCPO and tert-butyl peroxide etc. The most commonly used method for chlorination is to heat a polymer up to 60^0 C in a chlorinated hydrocarbon generally carbon tetrachloride, in the presence of tert-butyl hydroperoxide and titanium tetrachloride as catalysts. Chlorination of PP occurred not only at tertiary carbon atoms but also occasionally at primary and secondary ones depending on the extent of chlorination. Chlorination

in carbon tetrachloride was also reported in the presence of UV, sunlight and far IR radiation[55]. Shiono and Soga[56] succeeded in preparing a series of terminally halogenated PP in fairly good yields (84 % chlorination) by halogenolysis of aluminium terminated PP in the presence of pyridine and carbon tetrachloride.

Ohshika[57] reported grafting of various monomers such as MMA, ethyl acrylate, maleicanhydride, isobutylmethacrylate and other vinyl monomers onto chlorinated PP (cPP) through various initiating systems such as benzoyl peroxide, tert-butylperoxy 2-ethyl-hexanoate and ultraviolet light.

2.4. A Consolidated Report on the Work Done on PP Grafting with Various Monomers

- **Grafting of maleicanhydride on PP**

Steinkamp and Grail[58] have described a detailed procedure for the synthesis of PP-g-MAH using DCPO as initiator and single screw extruder operated at 225 to 240^0 C. The graft copolymer was reported to contain about 0.3 % of MAH in PP. Hendewerk[59] had used variety of peroxides for the free radical grafting of MAH onto PP in a molten state. Significant difference in the efficiency of grafting was correlated to various peroxides used for grafting. It was also reported that peroxides which decompose to form free radicals having a low energy for hydrogen abstraction from PP were less prone to chain scissioning and lowering of the M_W of PP. This observation lead to the conclusion that peroxides which form the least

reactive radicals towards hydrogen abstraction give rise to the higher M_W of MAH grafted onto PP[10]. Sathe et.al.[60] have grafted MAH on PP through solution polymerization. They achieved 5.3% of grafting using BPO as an initiator. Perego et.al.[38] claimed 13.8 % grafting of MAH onto sPP at 120^0 C in xylene containintg BPO.

Inagaki and Saitoh[61] have grafted MAH onto PP, which was further used as a soluble compatibilizer for adhering of polyurethane or polyepoxy paint to PP surface. They could achieve up to 1 % grafting on PP. Hasenbein et.al.[62] have reported 0.1 % or lower grafting of MAH in single screw extruder without use of peroxide. Bratawidjaja et.al.[63] have synthesised PP-g-MAH using benzoylperoxide as a free radical initiator in a single screw extruder at 200^0 C. They could achieve upto 0.54 % MAH in graft copolymer.

Nagatoshi et.al.[64] carried out the grafting of butadiene and maleic anhydride onto PP. They have reported increased % of maleic anhydride in graft copolymer when grafting was carried out in the presence of butadiene. The reason was not stated but was probably similar to the effect when styrene was used as a comonomer in the grafting of MAH, where styrene-maleic anhydride ion structure is formed. Kawaki et.al.[65] have used free radical method for solution grafting of MAH on PP by dissolving PP in chlorobenzene. The reaction was carried out at 130^0 C for 3 h. The maximum % of grafting achieved by this technique was 11.5 %.

Maleic anhydride can be easily grafted in the presence of styrene onto PP as demonstrated by Wong[66] and Li and Xie[67]. The graft copolymers were reported to contain more MAH and suffered less degradation in M_w than when styrene was not used as a second monomer. The role of styrene is to intercept the tertiary free radical form on PP and slowing down chain scissioning and loss of Mw and the facile formation of copolymer of styrene and MAH compared to the formation of poly(MAH). They achieved 0.8 % MAH in graft copolymer with 17.3 MFI when styrene was used as comonomer. Suehiro et.al.[68] have carried out solution grafting of PP with MAH in chlorobenzene at 125^0 C, in the presence of DCPO. The graft copolymer was reported to contain 11.8 % of MAH. Mulhaupt et.al.[69] prepared block polymers of PP and PA-6 through reaction of functional polymers, such as PP with terminal unsaturation, which was further reacted with MAH to have PP with anhydride end groups. Further reaction with terminal amine groups of the PA-6 resulted into a compatibilizer PA-6-g-PP useful for PP and PA-6 blends.

- **Grafting of carboxylic acids on PP**

Steinkamp and Grail[58] and Rahma and Fellahi[70] have described synthesis of PP-g-acrylic acid, initiated by peroxide in a single screw extruder at 225 to 240^0 C. The resultant graft copolymers were reported to contain 6 - 9 % acrylic acid. Narebska and Bukowski[40] and Citovicky et. al.[41, 43] reported grafting of acrylic acid onto hydroperoxidized PP.

Morita et.al.[71] have synthesized PP-g-itaconic acid by melt grafting using tert-butyl peroxy benzoate initiator in single screw extruder at 200^0 C. The concentration of itaconic acid in a graft copolymer was reported to be 0.18 % and graft copolymer was further used for blending of PP / Nylon-6.

Ide and Hasegawa[72] have carried out melt grafting of methacrylic acid and anhydride onto PP using peroxide initiator in extruder. The extent of methacrylic acid in graft copolymer was reported to be 0.4 % using I.R. spectroscopy.

- **Grafting of acrylates on PP**

The credit of first report of grafting of MMA on PP has been awarded to Natta et.al.[30] with their attempt to modify tackiness of atactic PP. Grafting of various acrylates such as MMA, BMA, EMA, HMA etc. on PP was reported by Klosiewicz[73] in 1987 through free radical catalysed reaction. The % of grafting was reported to be 15% for BMA, 14 % for EMA where as for HMA and MMA it was 13 and 14 %. Ilenda et. al.[74] reported 12 to 25 % of MMA grafted on PP using BPO as initiator in decalin solvent. Grigo et. al.[75] have shown synthesis of PP-g-BA and PP-g-MA using BPO as initiator in emulsion medium at 60^0 C. The grafting was reported to be 4.5 % for BA and 3.5 % for MA. Yamauchi et. al.[45] have grafted MMA on PP through ozonolysis of PP. The presence of active species, peroxy radical on PP was detected through ESR spectroscopy.

- **Grafting of silanes on PP**

Solution grafting of various vinyl silanes on PP was reported by Preston and Davis[76] using benzoyl peroxide as an initiator. Grafting of methacryloyloxy propyltrimethoxy silane and vinyl trimethoxy silane onto PP was carried out using dipropionyl peroxide at 200^0 C by Nojiri et.al.[77]. They could obtain 3.2 % of grafting with methacryloyloxy propyltrimethoxy silane. Melt grafting of vinyl trimethoxy silane on PP was carried out at 210^0 C using BPO in single screw extruder by Deguchi and Inoue[78]. Surface grafting of vinyltrimethyl silane on PP was patented by Wyman[78] in 1991.

- **Grafting of styrene and other monomers on PP**

Yokoyama et.al.[80, 81] synthesised PP-g-styrene-divinylbenzene, where reactivity of the pendant styrenic double bond of DVB was further used to polymerise other monomers. Only limited amount of DVB was needed to copolymerise, in order to obtain adequate number of sites for the grafting reaction. This process accomplished 97.5% of styrene in grafting, Mn of graft copolymer was observed to be 73,700. The grafting was reported to be 39 %.

Moriya et.al.[82] have synthesised PP-g-styrene by suspension polymerisation. Free radical catalysed grafting was carried out in two stages using various peroxides, which decompose at different temperatures. The second peroxide, which decomposed at higher temperature, contained easily polymerizable acrylate or styrenic functionality for further grafting. This technique was further used for grafting of styrene and isoprene. The graft

copolymer was reported to contain 14.8 % polyisoprene and 18.1 % of polystyrene.

Wong and Baker[83] and Chen et.al.[84] grafted GMA on PP using two different initiators, which have different decomposition temperatures. Togo et.al.[85] grafted GMA onto PP in the form of a copolymer with styrene using dicumylperoxide and twin screw extruder operated at 180 - 220^0 C. Graft copolymer was reported to contain 6.2 % styrene and 1.3 % GMA through I.R. analysis. They also grafted 2-hydroxyethyl acrylate in the form of copolymer of styrene on PP, which contained 6.2 % styrene and 3.5 % of 2-hydroxyethyl acrylate. PP-g-St-AN copolymer was synthesised by Moriya et.al.[86] through suspension polymerisation technique. Grafting was executed in two stages. Each stage was separately initiated using different peroxides. The % grafting was reported to be 8.1 % with 53 % grafting efficiency.

Klosiewicz[87] has reported 15 % grafting of butyl methacrylate onto PP at 135^0 C in the presence of benzoyl peroxide. Whereas high cross linking was reported by Borsig et.al.[88] in the grafting of butyl acrylate on PP when tert-butyl peroxy-2-ethylhexanoate was used as initiator. Gelling was reported to increase with increasing monomer content. Ilenda et.al.[74] reported 15 % grafting of PP with MMA through free radical process in decalin using BPO as an initiator.

- **Grafting of vinyl acetate on PP**

Moriya et.al.[33,86] synthesised PP-g-VAc through suspension polymerisation. The grafting was free radical catalysed and was conducted in two stages. Each stage was separately initiated by different peroxides, which decompose at different temperatures. During the synthesis, PP was finely divided and suspended in water followed by addition of BPO and VAc, and butylperoxymethacryloyloxethyl carbonate as radical polymerizable monomer at 60 - 64^0 C. In second stage, the polymerisation was conducted by extruding the product using twin screw extruder at 140 - 260^0 C, which resulted in 62 % grafting efficiency.

Overall it can be said that solution grafting of PP suffers from the drawbacks such as requirement of high temperature, less percentage of grafting and more homopolymerisation. To overcome this problem we have adopted new technique in which grafting has been performed using insitu chlorinated PP[98]. This approach has not been used for grafting of PP earlier. This leads to increased % grafting. Then another technique which was adopted to reduce the homopolymersation and to increase the grafting efficiency, was in which polymer itself contained initiating species such as hydroperoxide group, which on decomposition generates free radicals only on polymer backbone. Which can further be used for grafting of various monomers with higher grafting efficiency and minimum homopolymerisation.

2.5. Experimental

2.5.1. Materials

- Isotactic polypropylene (IPP) of M0030 grade and melt flow index 10 g / 10 min at 230^0 C and 2 kg load and molecular weight 190 K in the form of 375 - 500 μm size powder was supplied by Indian Petrochemical Corporation Limited, Baroda, India. It was washed several times with acetone and dried under vacuum at 60^0 C prior to use.
- 2-Hydroxy ethyl methacrylate (2-HEMA) from Fluka, Switzerland was used after vacuum distillation. Styrene from National Chemicals, Vadodara, India was made free from inhibitor by washing with 2 % w/v sodium hydroxide solution and then dried over anhydrous calcium chloride. It was further purified by vacuum distillation and was stored at 4^0 C. Acrylonitrile (AN) from SRL, Mumbai, India, methylmethacrylate (MMA) from National Chemicals, Vadodara, India and ethyl methacrylate (EMA) from E-Merck, India were purified by vacuum distillation and stored at 4°C.
- 2,2'-Azobisisobutyronitrile (AIBN) was received from Trizma Chemicals, Baroda, India and was used after recrystallisation from methanol. Benzoyl peroxide (BPO) was received from Fluka, Switzerland and was used after recrystallisation from Chloroform. Dicumyl peroxide (DCPO) from National chemicals, Baroda, India was used after recrystallisation from toluene.

- Nitrogen gas of high purity grade was used after passing through sulphuric acid traps.

  Chlorine gas was generated in our laboratory by the reaction between potassium permanganate and concentrated hydrochloric acid. The gas was dried over concentrated sulphuric acid, silica gel and finally over anhydrous calcium chloride.

- Xylene, toluene, decalin and chlorobenzene were received from Qualigens, Mumbai, India and were dried over sodium metal in vertical distillation column. Benzene, dichloroethane, 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.

2.5.2. Synthesis

Solid phase hydroperoxidation of PP

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 ± 1^0 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 orifice 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 4^0 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.[89], which showed 3.2 meq of hydroperoxide in PP.

Graft copolymerisation onto HPP

Grafting of various monomers on HPP was carried out in a 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 mixtures in various reaction media of different polarity. The grafting was carried out at 70 ± 1^0 C for 7 hours. The product in the powder form was taken in methanol, filtered and dried at 60^0 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.

Solution grafting of 2-HEMA onto PP

Another route followed for grafting of PP was solution grafting method. In a typical procedure PP (2 % w/v) was dissolved in toluene at 110 ± 1^0 C in a five neck reaction kettle, equipped with mechanical stirrer, air condenser, nitrogen inlet, dropping funnel and thermometer. The initiator (BPO, 8.26 mM) was dissolved in 50 ml of toluene and was added dropwise to the reaction mixture. This was followed by dropwise addition of 2-HEMA (0.153 M) in 50 ml toluene. The reaction was continued for 3 h at 110^0 C. After completion of the reaction, the reaction mixture was added slowly to the nonsolvent methanol. The precipitates were collected and Soxhlet extracted to remove homopolymer. The final product was dried in vacuum oven at 60^0 C and % grafting was calculated using equation 1.

$$\% \text{ Grafting(G)} = \frac{W_1 - W_0}{W_1} \qquad (1)$$

Where W_0 is the weight of original PP, W_1 is the weight of grafted PP after complete removal of homopolymer.

Grafting of 2-HEMA onto *insitu* chlorinated PP

In solution grafting of 2-HEMA on PP lower grafting efficiency was observed due to hydrophobic nature of PP and thus less interaction of monomers with PP, this can be overcome by introduction of some polar functionality in PP. Hence in this technique to achieve higher % of grafting, simultaneous chlorination of PP was carried out during grafting. In a typical

procedure grafting was carried out by dissolving 2 % w/v PP in toluene at 110 ± 1^0 C in five-neck reaction kettle under nitrogen atmosphere. To this 8.26 mM benzoyl peroxide in 50 ml toluene was added drop wise. Purified chlorine gas was passed along with nitrogen in the reaction mixture. To this 0.153 M 2-HEMA was added and the reaction was continued for five hours under chlorine-nitrogen atmosphere. After completion of the reaction the reaction mixture was added slowly to the nonsolvent methanol. The precipitates were collected and Soxhlet extracted to remove homopolymer and then dried in vacuum oven at 60^0 C. % Grafting was calculated following equation 1.

Synthesis of PP-g-acrylic acid

Another monomer acrylic acid was solution grafted on PP through free radical method. The grafting was carried out in a five neck reaction kettle equipped with mechanical stirrer, condenser, thermometer, and nitrogen gas inlet and dropping funnels. The temperature was maintained at 110 ± 1^0 C. 5 % w/v solution of PP was prepared by dissolving PP in toluene at 110^0 C. The reaction mixture was deoxygenated by purging nitrogen before addition of initiator and monomer. To this homogenised solution benzoyl peroxide (10.3 mM in 50 ml toluene), and 5 % w/v acrylic acid dissolved in toluene were added simultaneously over a period of 1 hr. The reaction was continued for 5 hr. The reaction mixture was poured into 3 to 4-fold excess of methanol under vigorous stirring. The precipitated graft copolymer was isolated and washed several times with water and digested with hot water for 2 hrs to remove homopolymer of acrylic acid.

Finally, the products were dried under reduced pressure at 80^0C to constant weight. The % grafting was determined by acid titration method[90] and gravimetrically.

The % grafting (G) and grafting efficiency (G.E) were determined gravimetrically by using equations 1 and 2 respectively.

$$\% \text{ Grafting Efficiency} = \frac{W_1 - W_0}{(W_1 - W_0) + W_2} \times 100 \qquad (2)$$

Where, W_2 is the weight of homopolymer formed during reaction.

It should be noted that the % grafting determined gravimetrically is an 'apparent' value as the weight of grafted PP also consists ungrafted PP. However our aim of synthesis of graft copolymers is for their utility as compatibilizers in PP / ABS blends this aspect is not very critical. Hence various grafting conditions were optimised. However, we could not measure the molecular weight of graft chains. Though attempts are made to identify the fraction of each monomer in graft copolymers using ^{13}C NMR analysis.

2.5.3. Optimisation of reaction conditions for grafting

Following conditions were optimised to achieve maximum percentage of grafting through different routes.

- **Effect of reaction medium**

To study the effect of polarity of reaction medium on % grafting, reactions were carried out in various solvents with different polarity. The solvent in which maximum % grafting and grafting efficiency was observed was used for the further studies.

- **Effect of Reaction Temperature**

Grafting onto HPP: Effect of reaction temperature on solid phase grafting onto HPP was studied by varying the temperature from 60 - 80^0 C for 5 h reaction time using 1 w % monomer concentration.

Grafting onto PP: Effect of reaction temperature on grafting onto PP through solution polymerization was studied by varying the reaction temperature from 90 - 110^0 C The reaction was carried out at 0.2 w / v, 8.26 mM of BPO concentration, 1 w / w monomer concentration and 3 h reaction time. Further studies were carried out at the optimised reaction temperature.

- **Effect of type of initiator and concentration**

Grafting onto PP: Various types of initiators such as benzoyl peroxide, azobisisobutyronitrile and dicumyl peroxide were used for grafting onto PP at 110^0C using toluene as solvent. The initiator giving optimised % grafting was used for further studies. The concentration of initiators was varied from 0.025 to 0.3 % w/v (1.07 mM - 12.93 mM). The initiator concentration resulting into higher % grafting was further used for grafting.

- **Effect of monomer concentration**

Grafting onto HPP: The effect of monomer to polymer ratio on grafting was studied by varying the w/w ratios from 0.5 to 4.0 w / w for grafting of various monomers on HPP. The reaction was carried out at 70 ± 1^0C using water as reaction medium for 7 h reaction time.

Grafting onto PP: For Grafting of 2-HEMA on PP and on insitu chlorinated PP through solution polymerisation, the monomer: polymer concentration was varied from 0.5 to 2 w / w of PP. The reaction time was also varied from at 1 - 7 h, the reaction was carried out in toluene at 110 ± 1^0 C temperature using 10.75 mM BPO concentration.

The optimised monomer concentration was used for further studies.

- **The effect of reaction time**

The reaction time was varied from 1 h to 16 h when grafting was carried out at 110 ± 1^0C temperature, using 0.2 w/v, 8.62 mM BPO concentration and 1 w / w monomer concentration. Effect of reaction atmosphere on grafting was also studied, using oxygen and nitrogen atmosphere.

2.5.4. Characterisation

- **FTIR** spectra of selected samples of graft copolymers were recorded on Perkin Elmer 16PC FT I R spectrophotometer using KBr pellets.
- **^{13}C NMR** spectra of selected graft copolymers were recorded on JEOL JNM FX-100FT-NMR (25 MHz) spectrometer using 10 - 15 % solution in trichloro- benzene at 110^0 C using hexamethyldisiloxane (HMDS) as an internal reference. The spectral measurements were carried out under complete decoupling mode under following conditions: PW_1 was 13 μs, PR was 5 second and number of pulses accumulated were 1000.
- **Scanning Electron Microscopy (SEM)** To study the surface morphology the selected graft copolymers and hydroperoxidized PP beads were gold coated using Poloran, USA, automatic gold sputter and were analysed using JEOL JSM 35C scanning electron microscope.
- **Contact θ angle measurements** of the films were done on contact θ meter developed at the Leeds University, England, using various solvents of different surface tensions. Measurements were carried out at 5 different positions on 1 cm^2 area and mean of those values were recorded.
- **Thermo gravimetric analysis (TGA)** of the graft copolymers was carried out on Shimadzu DT30 thermal analyser at 20^0 C / min heating rate in an air atmosphere.
- **Differential scanning calorimetric (DSC)** studies were conducted using Perkin Elmer - DSC - 7 thermal analyser. The analysis was carried out at a constant heating and cooling rate of 10^0 C / min under nitrogen

atmosphere. The percentage crystallinity of IPP and grafted PP was calculated from the thermograms considering the heat of fusion of 100% crystalline PP (ΔH^0_f) to be 207 J / mole [91]

$$\% \text{ Crystallinity } (\chi) = 100 \times \frac{\Delta H^*_f}{\Delta H^0_f} \qquad (3)$$

where ΔH^*_f is heat of fusion of graft copolymer obtained from DSC thermogram.

- **The % gelling** in the graft copolymers was determined by Soxhlet extracting the accurately weighed samples of graft copolymer in boiling xylene for two hours. The undissolved part was washed with xylene and then with acetone and dried till the constant weight. Blank experiments were carried out using PP and HPP powder. The % gelling was determined as per the procedure given by Naffosa et. al.[92]

$$\% \text{ Gelling} = 100 \times \frac{We}{Wg} \qquad (4)$$

where We is weight of the sample after extraction and Wg is weight of sample before extraction.

2.6.Synthesis of PP-g-2-HEMA

2.6.1 Results and Discussion

Shukla and Athalye[93] and Fang and Shi.[94] have reported grafting of 2-HEMA onto PP through U.V. and γ-radiation polymerisation. However, radiation grafting has inherent drawback of cross-linking, which develops difficulties in processing. This can be overcome by solution grafting technique. Moreover radiation grafting only alters the surface properties. There are no reports on solution grafting of 2-hydroxyethylmethacrylate (2-HEMA) onto PP. Hence we are reporting the solution grafting of 2-HEMA onto iPP, and insitu chlorinated PP (cPP). Further these graft copolymers can be used as compatibilizers for proposed PP / ABS blends. Various parameters have been optimised for grafting of 2-HEMA on PP.

(a) Effect of initiator type

Using various initiators such as AIBN, DCPO and BPO the grafting of 2-HEMA onto iPP was carried out through solution method. The results are given in **Table-2.1.** The lower % of grafting achieved with AIBN may be due to the steric hindrance generated at the free radicals causing decreased ability to abstract hydrogen atom from tertiary carbon of PP. The energy required for the decomposition of DCPO (159 kJ $mole^{-1}$) is much higher than that for BPO (124 kJ $mole^{-1}$) [95]. As a result at 110^0 C temperature the extent of decomposition of DCPO will be much lower than

that of BPO. Hence lower % of grafting was observed when DCPO was used. Therefore further work was carried out using BPO initiator.

TABLE 2. 1 Effect of initiator type on % grafting

Type	Grafting W%	Activation energy of initiator kJ mol $^{-1}$
A1BN	0.7	-
BPO	3.6	124
DCPO	2.2	159

(b) Effect of initiator concentration

The results obtained in the study of effect of initiator concentration on % grafting of PP are given in **Fig 2.8**. It was observed that with increasing concentration of benzoyl peroxide % grafting initially increases and then decreases. Similar observation was made by Nagata[93] in their study. This is a typical behaviour observed in grafting processes occurring via chain transfer mechanism. Initially % grafting increases due to increased availability of free radicals for grafting of monomers, but when concentration of initiator exceeds certain limit, increased free radical concentration in the solution increases homopolymerisation and hence decreases % grafting. In addition mutual termination is also favoured resulting into decreased % grafting.

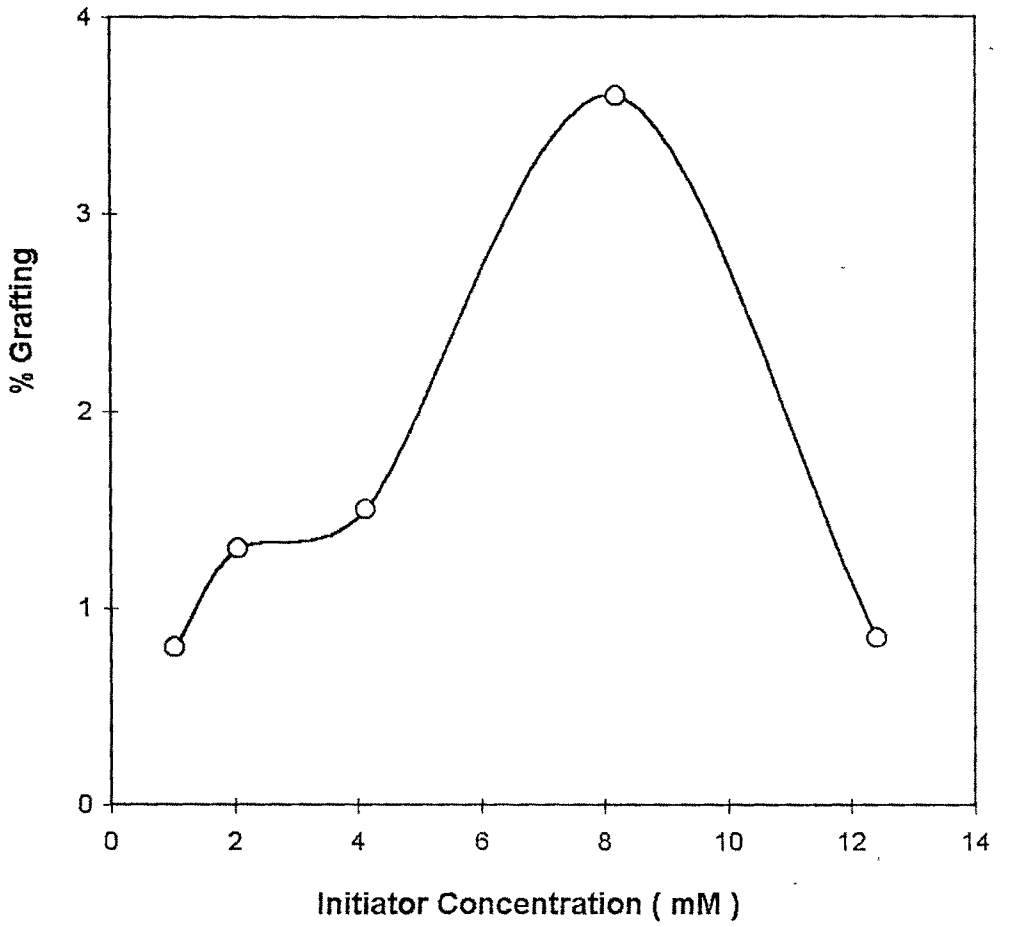

Fig.2.8 Effect of initiator concentration on % grafting of 2-HEMA on iPP

polymer / monomer ratio : 1 w / w; reaction temperature : 110 ± 1^0C; reaction volume: 100 cm^3 ; reaction medium toluene ; reaction time 3 h

(c) Effect of reaction time

The results obtained in the study of effect of reaction time on % grafting are illustrated in **Fig. 2.9.** It was observed that % grafting increases initially with time upto three hours, but further increases in reaction time might cause the β-chain scissioning of the side chains from PP backbone resulting into decrease in % grafting. Similar observation was reported by Sathe et. al.[60] in the grafting of butyl acrylate on PP.

(d) Effect of temperature

Grafting of PP with 2-HEMA was carried out at 90, 100 and 110 ^{0}C for three hours using 0.2 % (w/v) BPO and (1:1 w/w) PP: 2-HEMA concentration. It was observed that as the temperature increases % grafting increases (**Table-2.2**).

Table. 2.2 Effect of reaction temperature on % grafting

Reaction temperature ^{0}C	Grafting W %	Critical surface tension γ_c
90	0.4	27.5
100	0.7	24.9
110	3.6	24.0

This can be attributed to the increased number of free radicals generated and increased mobility of the free radicals at higher temperatures.

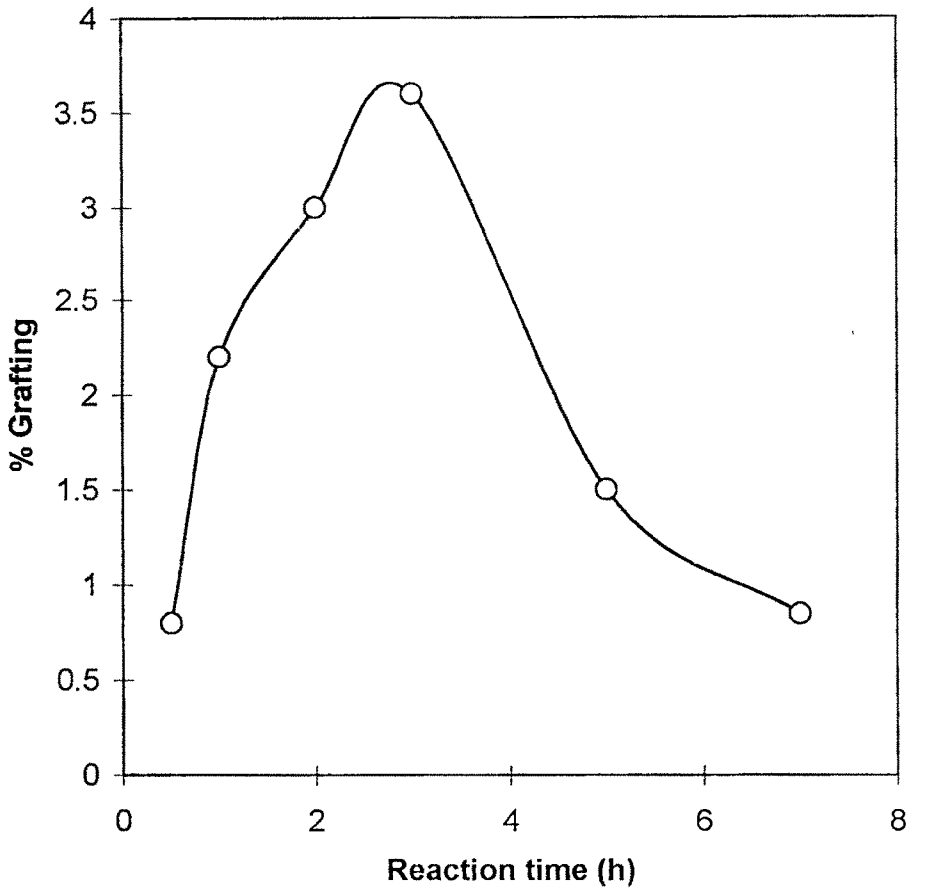

Fig. 2.9 Effect of reaction time on % grafting of 2-HEMA on IPP.

reaction temperature : 110±1^0 C; reaction volume: 100 cm^3 ; reaction medium: toluene; initiator concentration: 8.2 mM (BPO), monomer to polymer ratio 1 w/ w

(e) Effect of monomer concentration

The effect of monomer concentration on % grafting of 2-HEMA on PP is shown in **Fig.2.10**. It was observed that as the monomer concentration increases the % grafting increases initially and then decreases. At lower concentration of the monomer most of the monomer is quantitatively utilised for grafting by the available free radical sites on the PP backbone, and extent of homopolymerisation is very less. Whereas more homopolymerisation is taking place due to excess availability of monomer at higher concentration of monomer, leading to decrease in % grafting. As the monomer : polymer ratio goes on increasing, the time required to attain maximum % grafting decreases. However, maximum % grafting was observed when monomer: polymer ratio was 1:1 (**Fig.2.10**). Grafting reaction was also carried out in various solvents. From the results given in **Table-2.3** it is observed that maximum % grafting is achieved in toluene.

However, except for decalin % grafting was observed to decrease with increasing polarity of the reaction medium. Similarly when grafting was carried out in air and in nitrogen atmosphere, decreased % of grafting observed in air may be due to the deactivation of initiator[95] (**Table-2.3**).

(f) Grafting on *insitu* chlorinated iPP

Chlorinated PP is expected to be more reactive. Hence insitu chlorination of iPP was carried out followed by free radical graft copolymerisation of 2-HEMA. From the results presented in **Fig.2.11** for the grafting of PP with

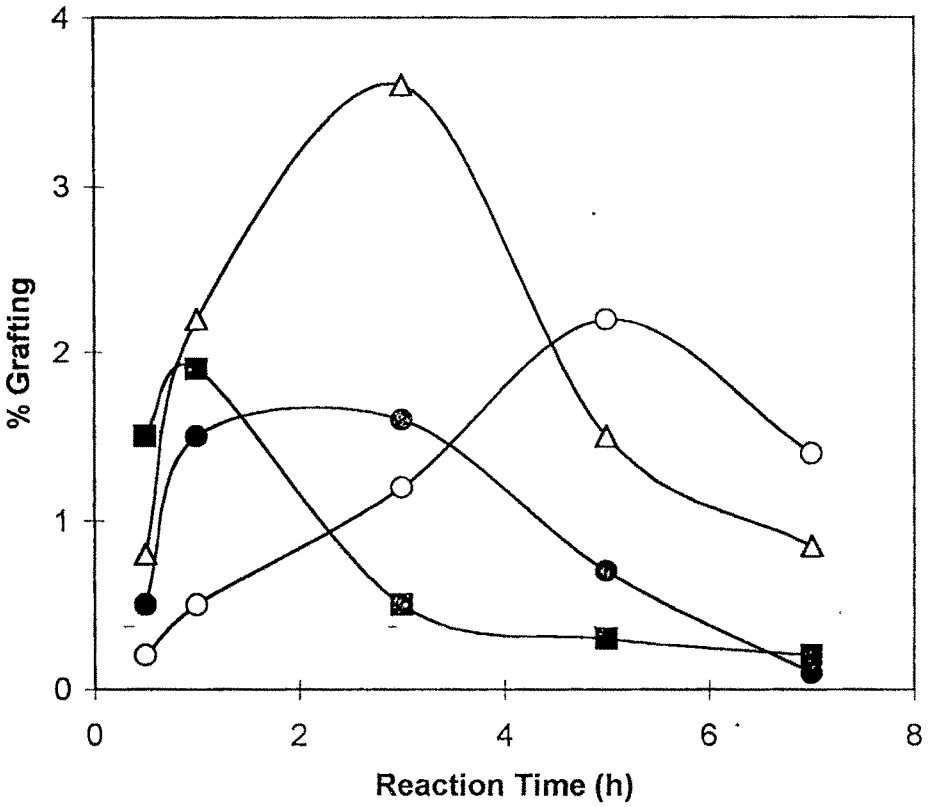

Fig. 2.10 Effect of monomer to polymer ratio on % grafting of 2-HEMA on iPP

reaction temperature : 110 ± 1^0 C; reaction volume: 100 cm^3; reaction medium : toluene; initiator concentration : 8.2 mM (BPO)

Monomer to Polymer ratio

(O) 0.5 : 1.0; (Δ) 1 : 1; (●) 1.5 : 1 and (▣) 2.0 : 1

2-HEMA in the presence and absence of chlorine, it is observed that extent of grafting increases with increased chlorination time.

Table 2.3. Effect of reaction medium and atmosphere on % grafting

Reaction Medium	Dipole moment (μ)	Grafting (w %) in	
		Nitrogen	air
Toluene	0.42	3.6	2.1
Xylene	2.57	0.8	n.d
Decalin	0.00	2.2	n.d
Chlorobenzene	1.72	0.6	n.d

The maximum grafting was obtained at 5 h reaction time. As shown in **Fig. 2.12**, % grafting results from two graft copolymerisation processes first one is directed through abstraction of hydrogen by benzoyl peroxide and second is chlorination of PP and the grafting onto chlorinated PP. The plausible reaction mechanisms is illustrated in **Fig.2.12**

The higher % of grafting of 2-HEMA on CPP can be explained by the difference in the grafting mechanism. In addition chlorinated PP being more reactive, free radicals are generated more by the removal of chlorine from chlorinated PP by BPO, as well as by hydrogen abstraction

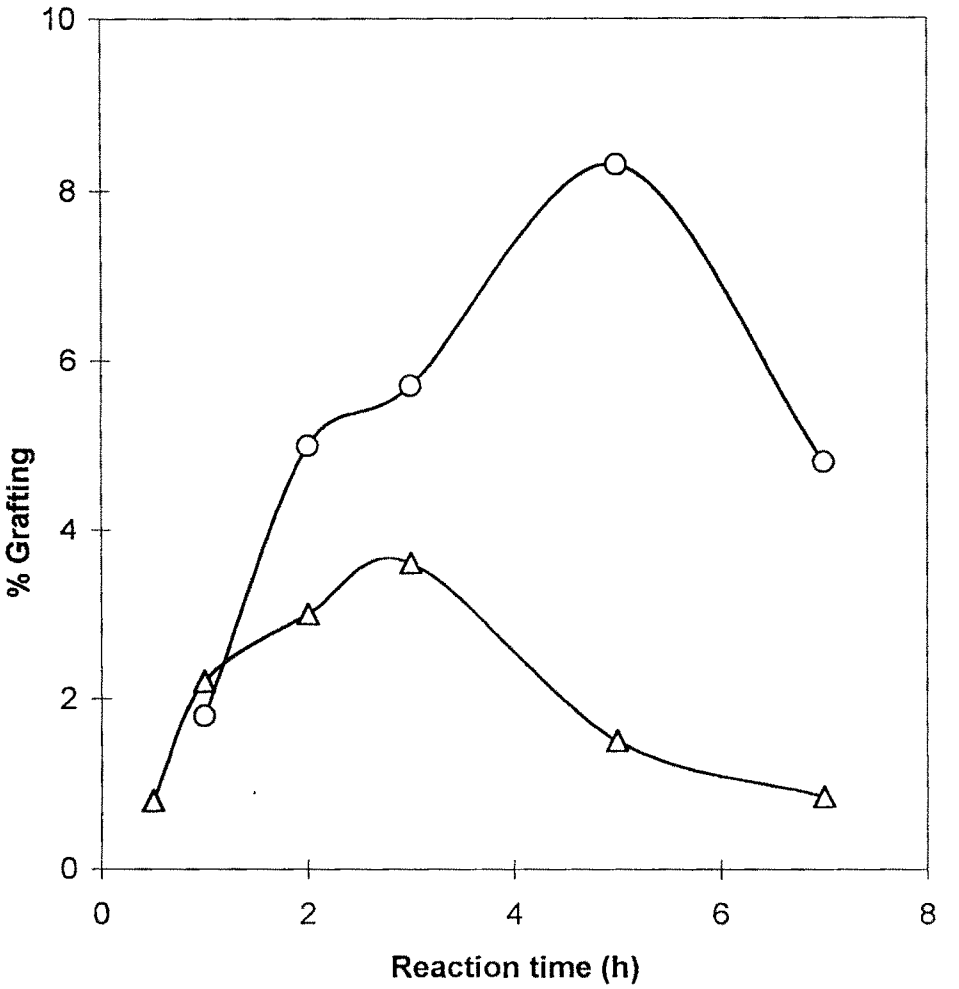

Fig.2.11 Effect of reaction time on % grafting of 2-HEMA on iPP and cPP.

polymer / monomer ratio : 1 w / w; reaction temperature : 110 ± 1^0 C; reaction volume: 100 cm^3 ; reaction medium toluene ; initiator concentration 8.2mM (BPO)
(Δ) Grafting on iPP , (O) Grafting on cPP

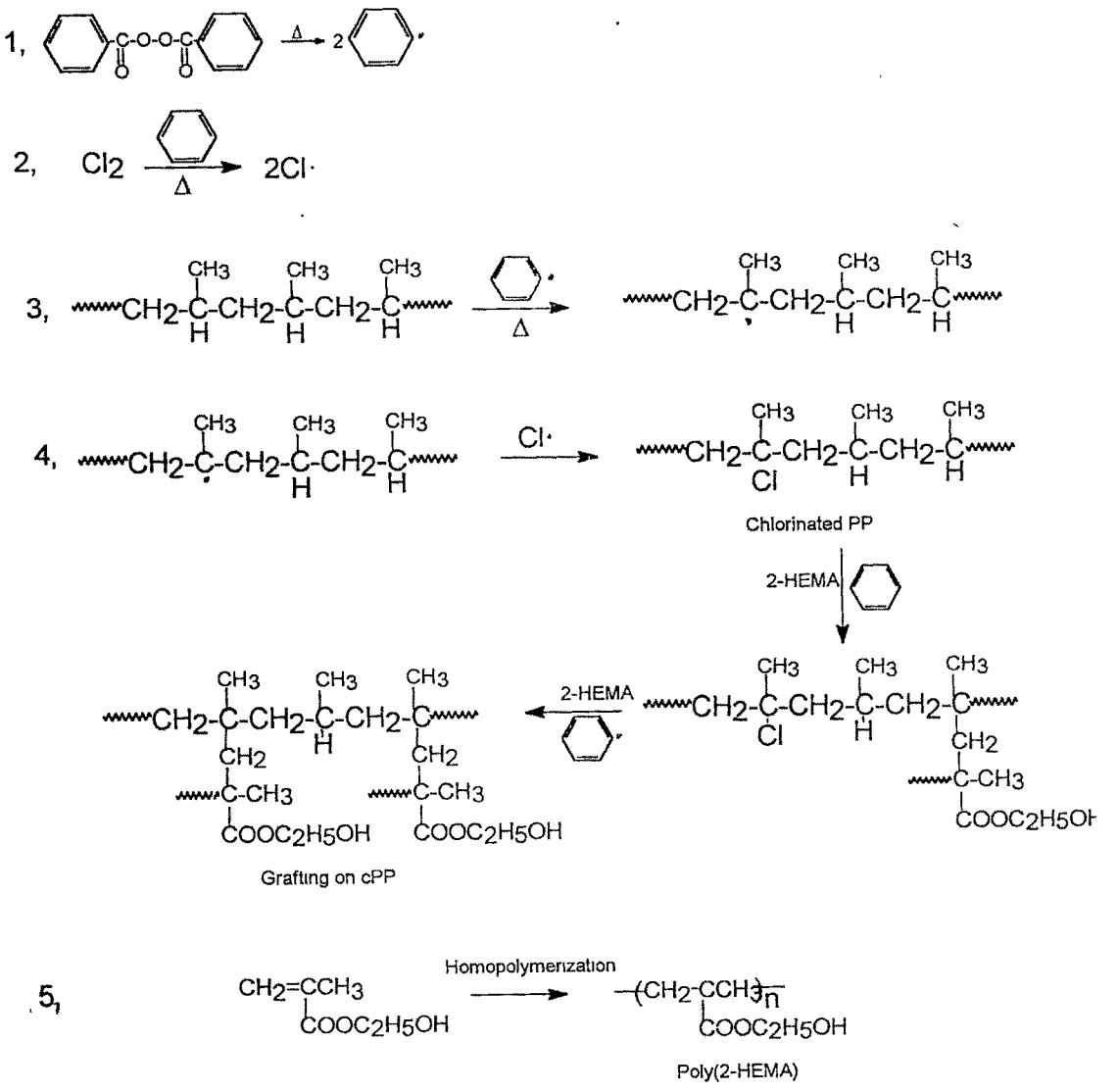

Fig.2.12 Plausible mechanism for the grafting of 2-HEMA on iPP and cPP

mechanism. Thus more number of free radicals generated lead to higher % of grafting.

2.6.2 Characterisation

The FTIR Spectra of PP showed the stretching vibrations due to –C-H from $-CH_3$ group at 2930 -3194 cm^{-1}. The bending vibrations due to –C-H from $-CH_3$ and $-CH_2$ appeared at 1359 -1470 cm^{-1}. The rocking vibrations due to $-CH_2$ were observed at 690 - 694 cm^{-1}.

Inaddition to these bands the graft copolymers showed band due to stretching vibrations of –OH group at 3525-3656 cm^{-1} and band due to stretching vibrations of >C=O group at 1714-1727 cm^{-1}. A band observed at 1219 - 1255 cm^{-1} can be assigned to bending vibrations of –C-O-C appeared at 1219 -1255 cm^{-1}. In the case of graft copolymer of insitu chlorinated PP and HEMA a bending vibrations of –C-Cl resulted into an appreance of band at 755-760 cm^{-1} **(Fig.2. 13)**.

The TGA plots for iPP, PP-g-HEMA and insitu chlorinated PP-g-2-HEMA are given in **Fig.2.14.** From these thermograms, it was observed that increase in % grafting increases the thermal stability of the PP. The T_{50} values of graft copolymers were observed to be somewhat higher than those for the virgin PP.

The contact angle (θ) for the graft copolymer films were measured by using different solvents of variable surface tensions[60]. The critical surface tension (γ_c) values of the grafted polymers were calculated from the plot of

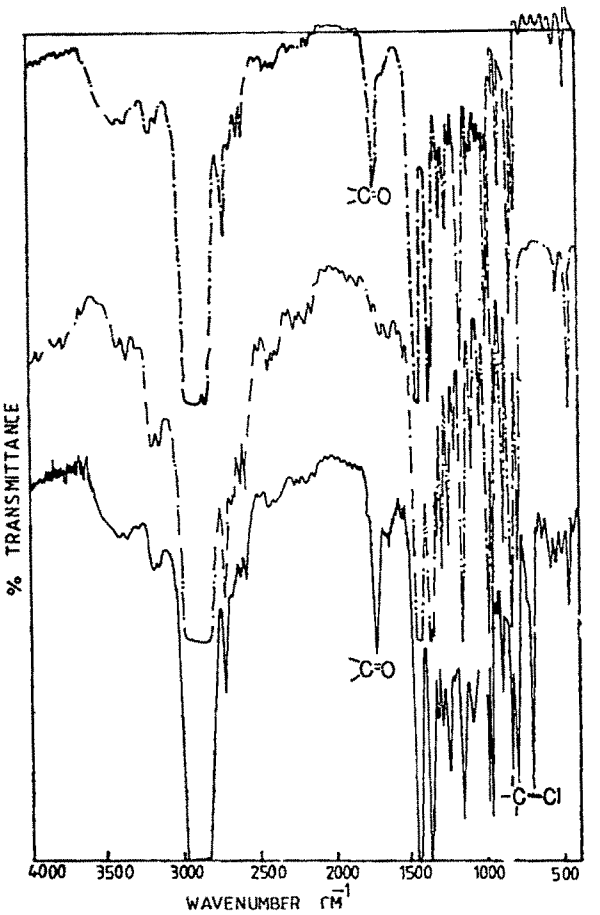

Fig. 2.13 FTIR Spectra of graft copolymers

Insitu cPP-g-2-HEMA with 8.4% grafting (—) ; iPPg-2-HEMA with 3.4 % grafting 3.4 % grafting (- - -.-) and iPP (-.....-)

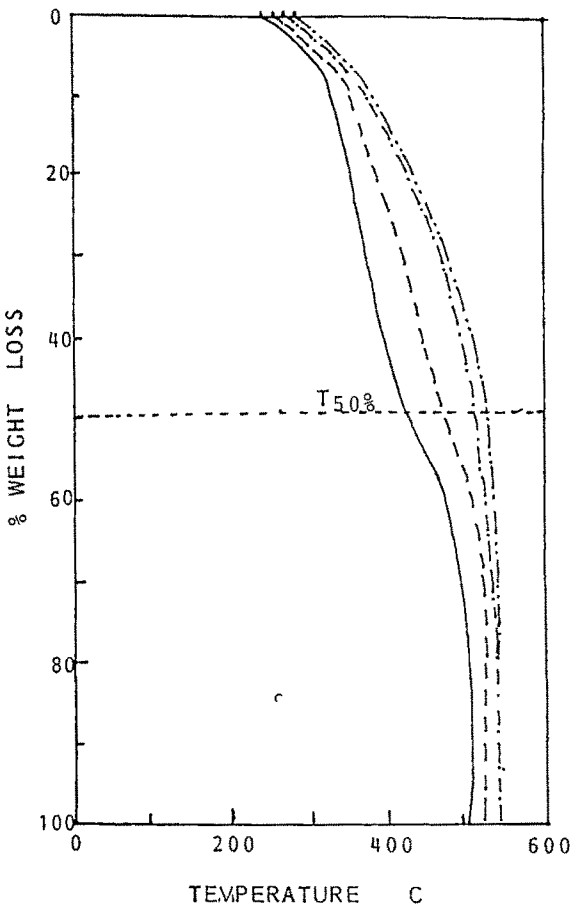

Fig. 2.14 TGA plots of graft copolymer

Insitu cPP-g-2-HEMA with 8.4% grafting (- - - -); iPPg-2-HEMA with 3.4 % grafting (- - - -); iPPg-2-HEMA with 2.4 % grafting (- - - -) and iPP (——)

surface tension vs COS θ and extrapolating this plot to COS θ = 1 which gives the critical surface tension γ_c. It was observed that γ_c decreases with increasing % grafting. All grafted samples showed 22 - 27 dynes/cm^2 critical surface tension values, whereas iPP showed 29-dynes/ cm^2. This indicates that grafting has imparted surface polarity to the samples prepared in our laboratory.

The heat of fusion (ΔH_f^*) obtained from DSC analysis and IDT and $T_{50\%}$ obtained from TGA of grafted samples are given in **Table-2.4.**

TABLE - 2. 4 Thermal analysis

Samples	% Grafting	T_m °C	ΔH^*_f cal/g	% Crystallinity	IDT	$T_{50\%}$
iPP		168.71	-	-	230	425
iPP-g-2-HEMA	2.4	166.89	20.37	40.75	240	475
cPP-g-2-HEMA	8.6	126.78	11.25	28.00	250	515

The percentage crystallinity was calculated on the assumption that the heat of fusion (ΔH_f^0) of 100 % crystalline IPP is 207 kJ / mole. As the heat of fusion is directly proportional to the amount of crystallinity in the samples, it decreases linearly with an increase in grafting percentage[60]. The thermal stability of grafted samples was increased as compared to iPP, which is shown in **Table 2.4.** The $T_{50\%}$ of grafted sample was increased as compare to iPP. The IDT of grafted samples also increased as compared to iPP which shows the incresed thermal stability of grafted samples.

2.7 Grafting on Hydroperoxidized PP

Various monofunctional and bifunctional monomers have been used for grafting of PP through different routes. Solution grafting of PP suffers from the drawbacks such as requirement of high temperature, less percentage of grafting and more homopolymerisation. In our earlier studies we could achieve higher % of grafting using insitu chlorinated PP[98]. However, grafting efficiency was observed to be poor. These drawbacks were overcome by generating initiating sites on PP backbone through controlled oxidation, which results in the hydroperoxidised PP. Reports are available for the hydroperoxidation of PP in solution and in film or fiber form using ozone / oxygen / air and γ - radiation or peroxide initiator[10] which was further used for grafting of styrene[41], methyl methacrylate[41], acrylic acid[43], 2-vinylpyridine[41] and glycidyl methacrylate[89]. Most of the reports are based on the cleavages of the hydroperoxide group using metal - chelate redox system, which is further used for grafting. However, requirement of surfactant as interfacial agent, metal salts and other ingredients makes grafting dependent on more variable parameters[19]. Grafting through thermal cleavage though is easiest and more convenient; formation of homopolymerisation is also high. This can be over come by choosing proper reaction medium for grafting. In the present work grafting of various monomers and monomer pairs on HPP using thermal cleavages of hydroperoxide group is reported[99]. The various monomers and monomer pairs used were styrene, methylmethacrylate (MMA), ethylmethacrylate (EMA), styrene - acrylonitrile (St-AN), ethylmethacrylate - acrylonitrile

(EMA-AN), methylmethacrylate - acrylonitrile (MMA-AN) and styrene - methylmethacrylate (St - MMA).

(a) Effect of reaction medium

The grafting of various monomers on HPP was carried out in the various reaction media of different polarity in which HPP was suspended. From the results given in **Table-2.5** it was observed that % grafting increases with polarity of the reaction medium, irrespective of monomer used. Highest % of grafting for all the monomers under study was obtained in acetone and water. More than 90% of grafting efficiency in all the media (**Table-2.5**) indicates lower extent of homopolymer formation. This is because on decomposition of hydroperoxide group, one free radical is generated on PP backbone and 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 solvents 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.

TABLE - 2. 5 Effect of reaction medium on % grafting

Reaction medium	% Grafting						
	Styrene	St-AN	MMA- AN	MMA	EMA- AN	EMA	St-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)	21.2 (89.6)	21.8 (92.6)	21.4 (91.5)	18.4 89.2)	19.7 (92.3)

Values in brackets indicate % grafting efficiency.

Whereas lower affinity of polar solvents 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.

(b) Effect of reaction temperature

The effect of reaction temperature on % grafting was studied by varying the reaction temperature from 60 to 80^0 C. From the results (**Fig.2.15**) it was observed that maximum % grafting was obtained at 70^0 C for all the monomers. Below 70^0 C quantitative thermolytic cleavage of the peroxide

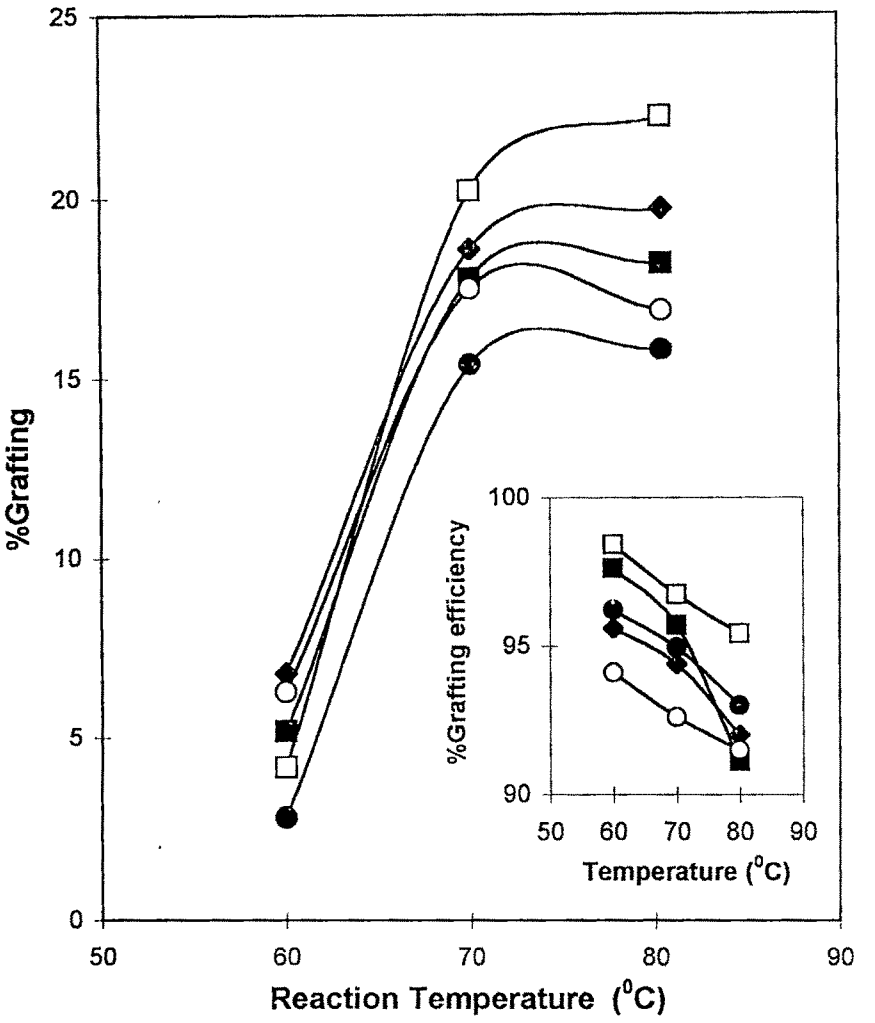

Fig. 2.15 Effect of reaction temperature on % grafting and grafting efficiency

HPP 25 % w / v; monomer : polymer 2:1; reaction medium : water ; reaction time : 7h

(□) HPP-g-Styrene, (O) HPP-g-EMA , (◆) HPP-g-St-AN, (■) HPP-g- St-MMA, (⊗) HPP-g-MMA

linkages from HPP backbone may not be taking place. As a result lower % grafting was observed. At and above 70^0 C all the peroxide linkages are cleaved leading to maximum % grafting. Increased grafting at 70^0 C can also be attributed to the increased diffusion of monomer in HPP. This can be supported from the swelling studies of HPP in monomers. Swelling of HPP in styrene at 30, 60, and 70^0 C was observed to be 9, 14 and 18% respectively. However, with increasing temperature grafting was observed to increase but grafting efficiency was observed to decrease. This may be due to the possible increase in the solubility of monomers in the reaction media at higher temperature leading to the homopolymerisation.

(c) Effect of reaction time

Percentage grafting initially increases with time and then levels off, where as opposite trend was observed for grafting efficiency (**Fig.2.16**). The extent of grafting and grafting efficiency were observed to be related to the hydrophobic character of the monomers.

The observed trend for grafting of various monomers in water was Sty > St-MMA > MMA > EMA. This can be correlated to the extent of sorption of monomers in HPP which was observed to be 40, 10.3, 8.8, 5.3, 31.2 % for styrene, MMA, EMA, AN and Sty-MMA (1:1) respectively at 25^0 C and 5 h sorption time.

Due to increased availability of monomers at active sites the % grafting was observed to increase initially with increasing monomer concentration (**Fig. 2.17**) and then levelled off. Decreased percentage grafting efficiency

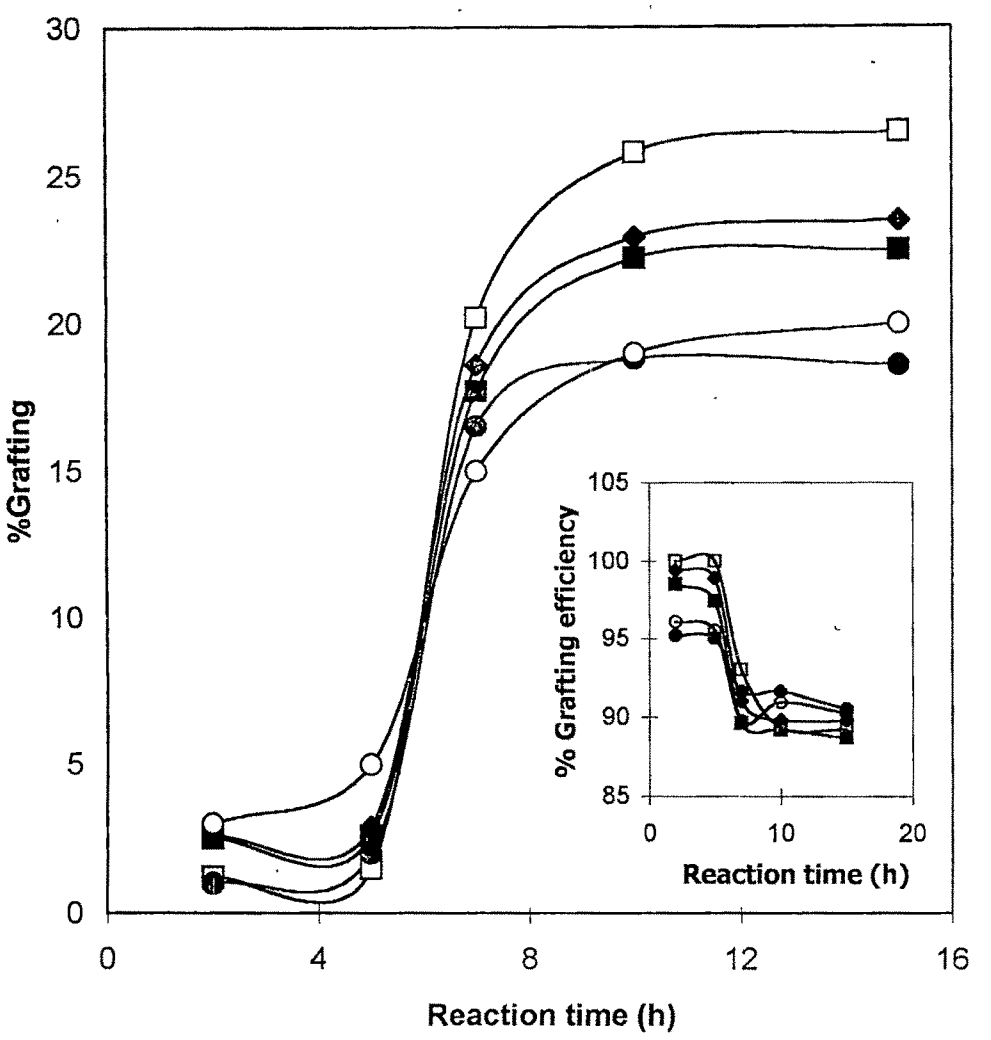

Fig. 2.16 Effect of reaction time on % grafting and grafting efficiency

HPP 25 % w / v ; monomer : polymer 2:1 ; reaction medium : water ; reaction temperature 70 ± 1^0 C

(□) HPP-g-Styrene, (O) HPP-g-EMA , (◆) HPP-g-St-AN, (■) HPP-g- St-MMA, (●) HPP-g-MMA

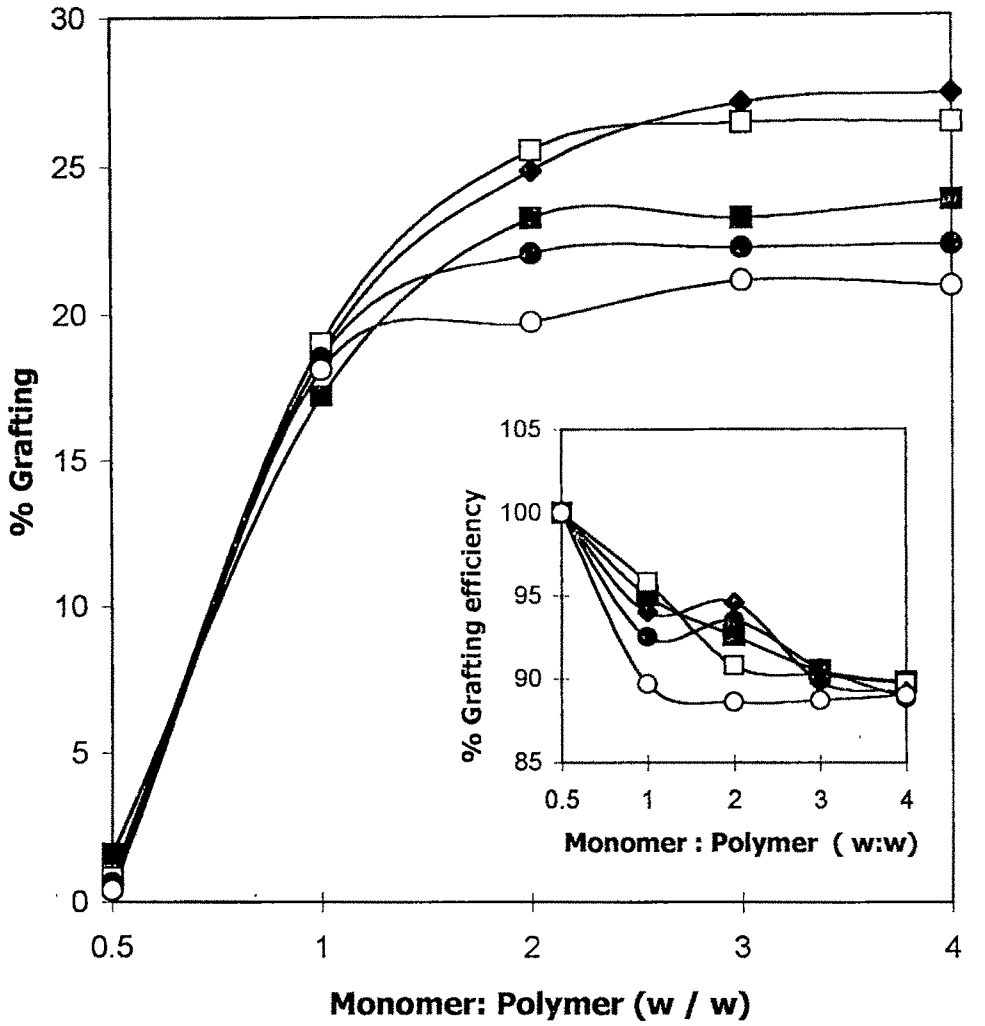

Fig. 2.17 Effect of monomer concentration on % grafting and grafting efficiency.

HPP 25 % w / v ; monomer : polymer 2:1 ; reaction medium : water ; reaction temperature : 70 ± 1^0 C ; reaction time: 7 h.

(□)HPP-g-Styrene, (O) HPP-g-EMA, (◆) HPP-g-St-AN, (■)HPP-g- St-MMA, (❂) HPP-g-MMA

with increased monomer concentration may be due to the increased homopolymerisation.

(d) Gelling studies

The observed higher % of gelling (7.2 %) in the case of styrene can be attributed to the possibility of cross linked network developed between growing graft chains and the free radicals generated on the HPP backbone (**Table - 2. 6**). Due to the lower % of grafting in MMA less number of growing graft chains lead to the decreased possibility of the crosslinking and hence decreased % of gelling. The possible mechanism of gel (crosslink) formation is shown in **Fig.2.18** and is reported earlier[99].

TABLE - 2.6 % Gelling in various graft copolymers at various levels of grafting.

Graft copolymer	Grafting (w %)	Gelling (w %)
HPP-g-St	17.7	4
	25.6	7.2
HPP-g-MMA-AN	5.2	1
	20.4	2.3
HPP-g-St-MMA	5.2	1.2
	18.6	2.6

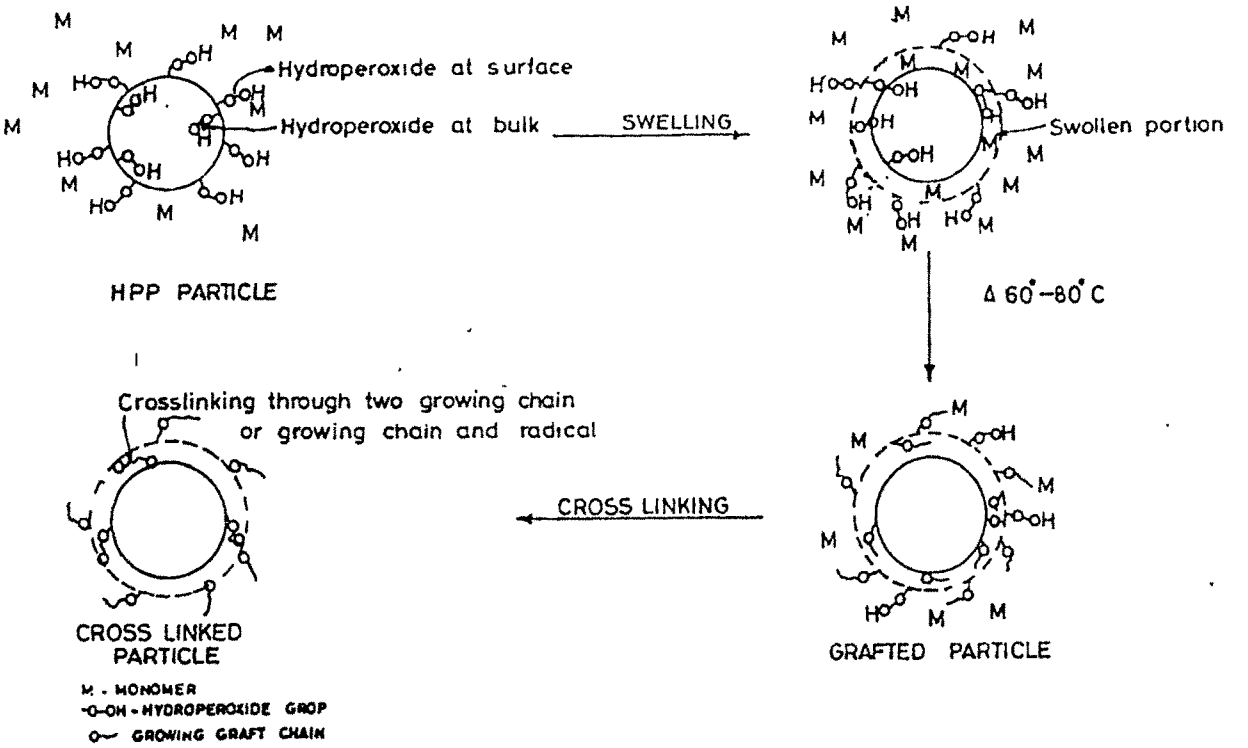

Fig. 2.18 Mechanism of crosslinking formation during grafting

2.7.2 Characterisation

It is expected that grafting occurs mainly at surface and to some extent at the peripheral bulk, which can be seen from the difference in the topography of grafted samples and of HPP particles. SE micrographs of HPP in **Fig.2.19** show relatively smooth surface whereas grafted copolymers show rough surfaces.

The FTIR Spectra of HPP showed the stretching vibrations due to –C-H from $-CH_3$ group at 2930 - 3194 cm^{-1}. The asymmetric stretching vibrations of –C-H from –CH2 appeared at 2961 cm^{-1} whereas bending vibrations due to –C-H from $-CH_3$ and $-CH_2$ resulted into appearance of band at 1359 - 1470 cm^{-1}. The band corresponding to rocking vibration from $-CH_2$ appeared at 690 - 694 cm^{-1}.

Graft copolymers of HPP and EMA, MMA and St-AN exhibited additional bands at 1715-1730 cm^{-1} corresponding to –C=O stretching vibrations and at 1270 -1282 cm^{-1} corresponds to bending vibrations of –C-O-C bonds of ester group . The skeletal vibrations due to aromatic >C=C< from styrenic group appeared at 1453-1600 cm^{-1}. The band at 2232-2236 cm^{-1} was observed for stretching vibrations of -C≡N bond from acrylonitrile of HPP-g-St-AN graft copolymer. (**Fig.2.20**)

From the DSC thermograms of selected graft copolymers the heat of fusion ΔH_f^* and % crystallinity of graft copolymers was calculated as described earlier. The results are given in **Table-2.7**. Introduction of graft chains

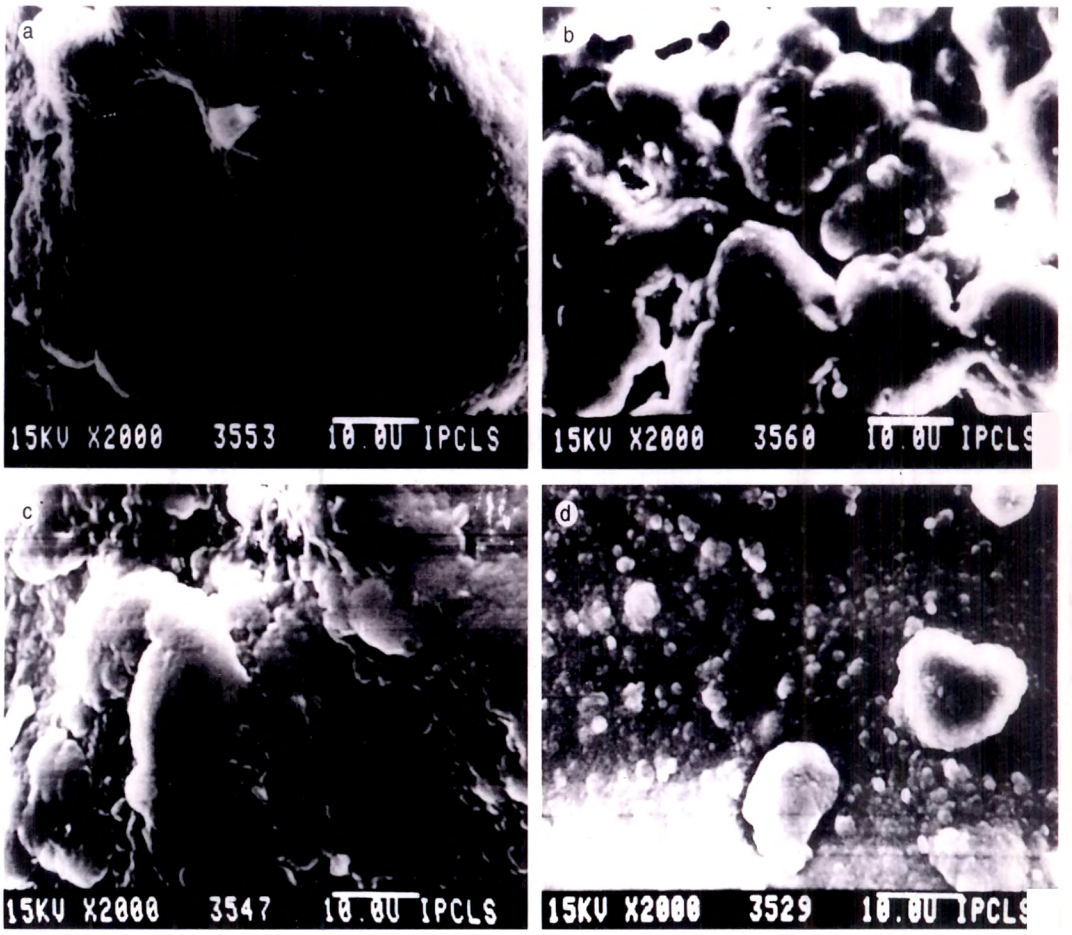

Fig. 2.19 SE micro photographs of graft copolymers

HPP particles (a); HPP-g-St-MMA (b); HPP-g-St-AN (c); HPPg-EMA (d)

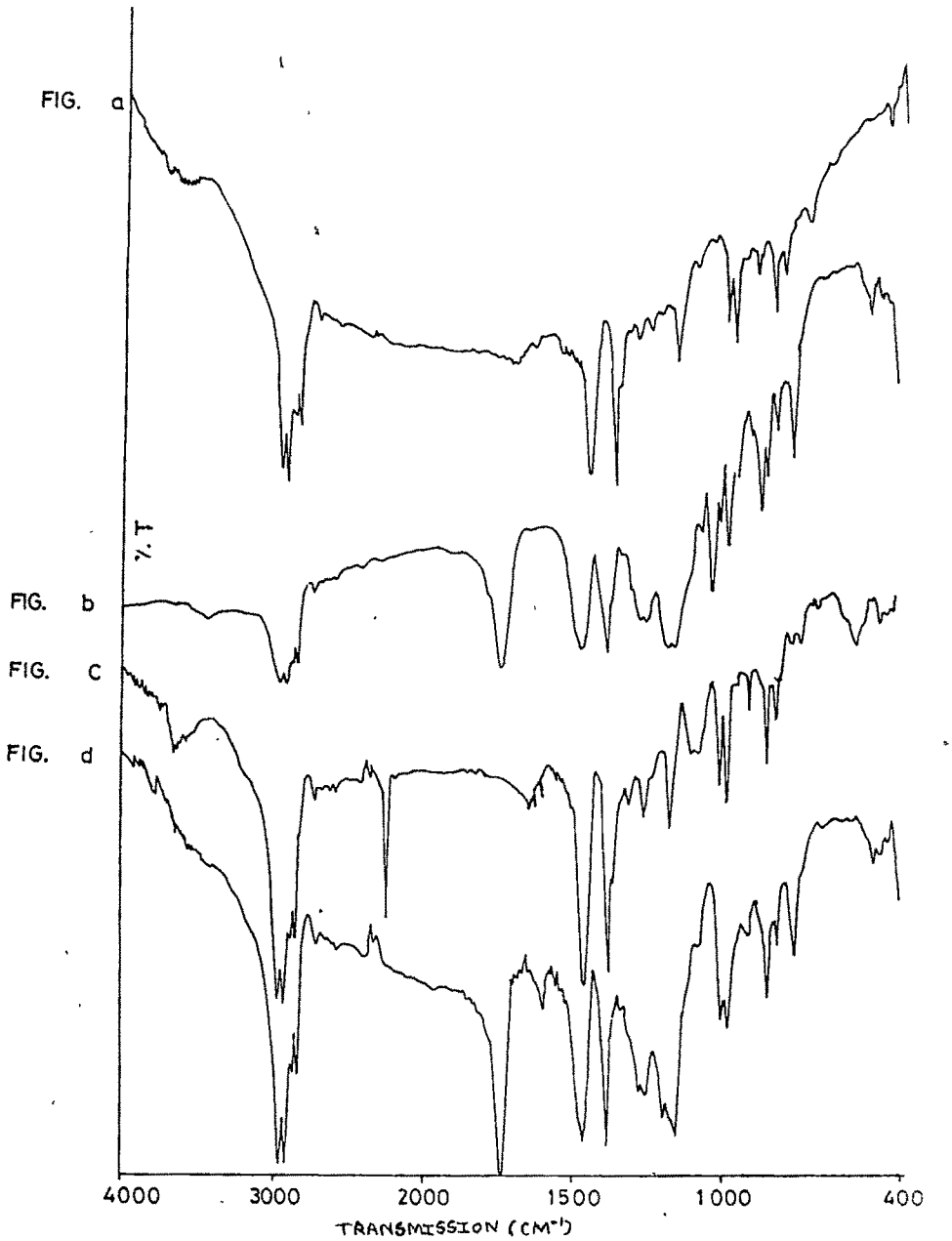

Fig. 2.20 FTIR spectra of graft copolymers

HPP particles (a); HPP-g-St-MMA (b) HPP-g-St-AN (c); HPPg-EMA (d)

hinders the crystallisation and hence crystallinity decreases with increasing % of grafting (**Table-2.7**). Similar results were obtained by Sathe et. al.[60] and Martuscelli et. al.[91]. Thermal stability of the grafted copolymers was observed to increase with increased % of grafting (**Fig.2.21**). The initial decomposition temperature (IDT), % crystallinity (χ) and melting temperature (T_m) of various graft copolymers are given in **Table-2.7.**

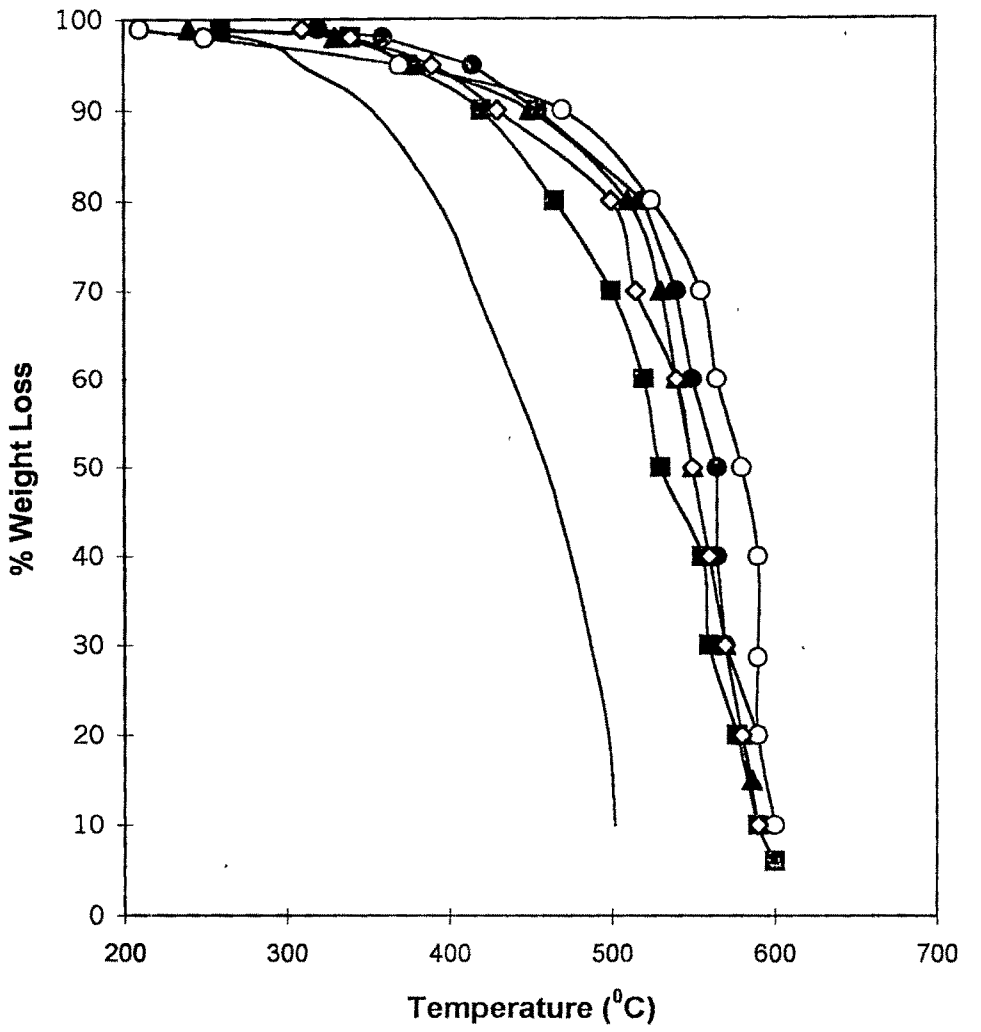

Fig. 2.21 TGA plots of graftcopolymers

(—) HPP; (■) PP ; (◎) HPP-g- St-AN with 21.4 % grafting; (O) HPP-g- St-AN with 15.6 % grafting; (◇) HPP-g-EMA-AN with 17.6 % grafting; (▲) HPP-g-MMA 19.3 % grafting

^{13}C NMR analysis

Composition of graft copolymers was estimated using ^{13}C NMR. Some of the representative spectra are illustrated in **Fig.2.22**. For the HPP-g-EMA (9.6% grafting) resonance signals of the carbonyl carbon (C_4), the aliphatic quaternary carbon (C_1) and the methylene carbon (C_2) of EMA appeared at 176, 46.15 and 13.89 ppm respectively (**Fig.2.22**). The % of EMA grafted on HPP was calculated from the relative intensities of the resonance signals. The results are given in **Table - 2. 8.**

Table 2.7 Thermal properties of graft copolymers

Sample	T_m	ΔH^*_f J /g	% χ_c	IDT	$T_{½}$
PP	167.3	-	-	240	450
HPP	157.5	146	70.5	260	530
PP-g- St-AN (15.6 %grafting)	160.8	115	55.5	290	550
PP-g-St-AN (15.6%grafting)	161.3	110	53.1	310	565
PP-g-MMA (20.6%grafting)	164.5	108	52.1	260	450
PP-g- MMA-AN (17.6%grafting)	164.0	114	55.0	320	570
PP-g- Styrene (12.8%grafting)	161.7	95	45.8	310	550

Tm: Melting temperature, ΔHf* : Heat of fusion, χ_c: % of Crystallinity

IDT: Initial decomposition temperature

Table 2.8 Composition of graft copolymers through ^{13}C NMR

Sample	% Composition through ^{13}C NMR (w%)				% Grafting by	
	EMA	St	AN	MMA	^{13}C NMR w %	Gravimetrically w %
HPP-g-EMA	8.03	-	-	-	8.03	9.6
HPP-g-MMA	-	-	-	9.0	9.0	11.2
HPP-g-St-AN	-	4.1	2.6	-	6.7	8.6
HPP-g-EMA-AN	23.2	-	6.2	-	24.6	29.4
HPP-g-St-MMA	-	6.3	-	4.1	10.4	14.7

The % of styrene and acrylonitrile grafted on HPP was calculated from relative signal intensities of aromatic carbon and nitrile carbon appearing at 146 and 121 - 123 ppm respectively, where as that of styrene and MMA grafted on HPP was calculated from the relative intensities of signals for carbonyl carbon (C_4) of MMA at 165 ppm and that of C_3 aromatic carbon of styrene at 148-145ppm (**Table - 2.8.**). In the case of HPP-g-MMA the carbonyl carbon (C_4) appeared at 161-165 and methyl carbon at 29.87 ppm .The % grafting calculated is given in **Table - 2.8.** Good correlation was observed between % of grafting obtained from ^{13}CNMR and that calculated by gravimetric method.

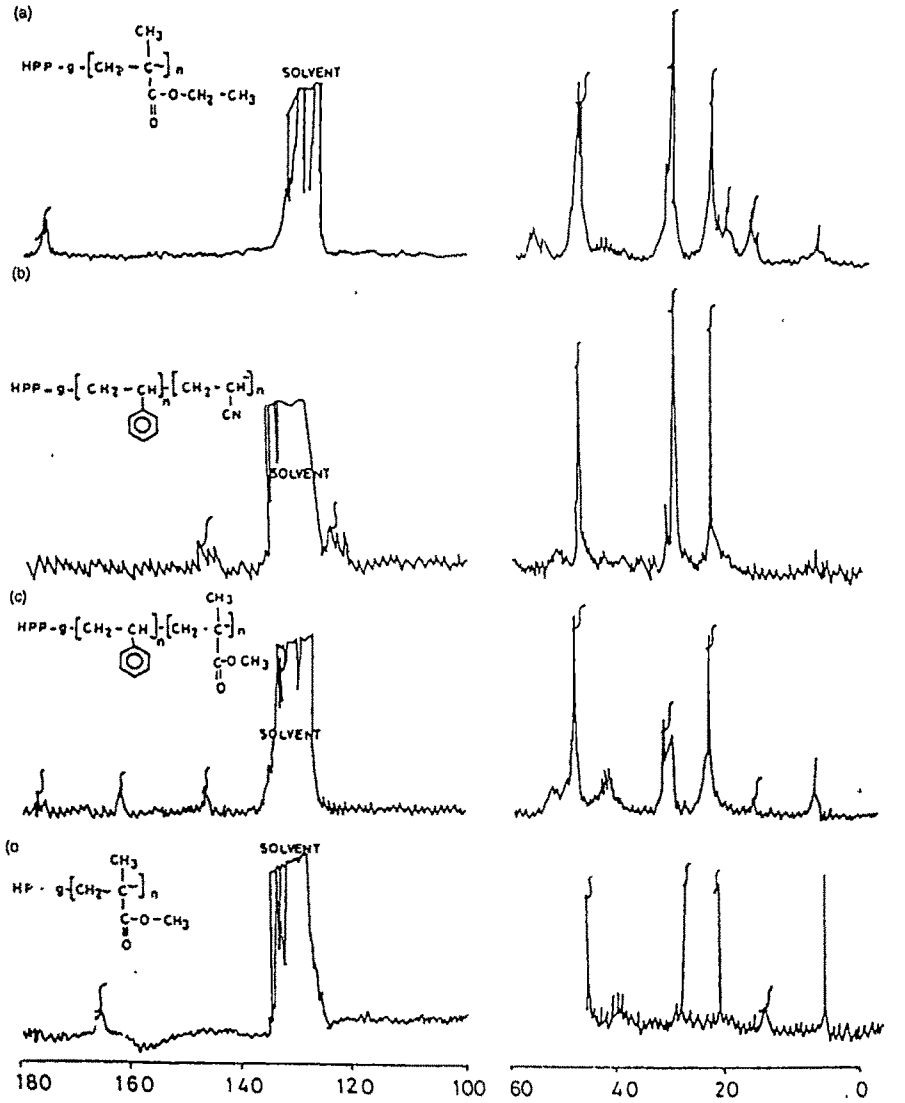

Fig. 2.22 ^{13}C NMR spectra graft copolymers

HPP-g-EMA (a); HPP-g-St-AN (b); HPP-g-St-MMA (c); HPP-g-MMA (d)

2.8 Conclusion

Grafting of 2-HEMA on PP and styrene, MMA, EMA on HPP by solution and solid phase polymerization resulted in to 3 to 22 %. Grafting of 2-HEMA on PP using BPO as initiator, 3 h reaction time at 110^0 C in toluene resulted into 3.2 % grafting. Whereas that on insitu chlorinated PP after 5h reaction time at 110^0 C using 8.26 mM BPO in toluene resulted into 8.6 % grafting. The higher % of grafting is attributed to more reactive nature of chlorinated PP, which results into more free radicals on PP backbone. Thus more number of free radicals generated lead to higher % of grafting.

The graft copolymers were characterised by FTIR, TGA and DSC. FTIR spectra of PP-g-2-HEMA showed stretching band of >C=O group at 1720 cm^{-1} confirming the incorporation of 2-HEMA 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 2-HEMA on iPP.

The higher % of grafting was achieved when HPP was used in place of iPP and cPP. This is attributed to the generation of free radicals only on PP backbone, which initiate grafting. Grafting of various monomers and monomer pairs such as styrene, MMA, EMA, St-AN, St-MMA in water at polymer to monomer ratio one and 5 h reaction time resulted into 18.6, 21.8, 18.4, 19.4 and 19.7 % grafting respectively.

FTIR spectra of grafted samples showed >C=O stretching band at 1720 cm^{-1} confirming the presence of MMA in PP-g-MMA and PP-g-St-MMA and EMA in PP-g-EMA, whereas stretching band at 2130 cm^{-1} confirmed the presence of –C≡N in PP-g-St-AN. The thermal stability of grafted samples was also observed to increase with increased % grafting. The PP-g-St and PP-g-St-AN grafted samples showed higher thermal stability as compared to PP-g-MMA and PP-g-EMA. The % composition of various grafted samples was confirmed by ^{13}C NMR analysis and the % grafting obtained through it was in good agreement with that obtained gravimetrically.

Thus it can be conclude that

- Insitu chlorinated PP leads to higher % of grafting of 2-HEMA on PP
- Hydroperoxidation of PP further increases the extent of grafting and grafting efficiency.
- The polar reaction medium gives higher % of grafting as compared to non-polar medium used for the grafting on HPP.

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