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Grafting: a versatile means to modify polymers Techniques, factors and applications

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Abstract

The modification of polymers has received much attention recently. Among the methods of modification of polymers, grafting is one of the promising methods. In principle, graft co-polymerization is an attractive method to impart a variety of functional groups to a polymer. Graft co-polymerization initiated by chemical treatment, photo-irradiation, high-energy radiation technique, etc. is documented in this review. Several prime controlling factors on grafting are discussed. In the past several years, there has been increased emphasis on applications of grafted polymers. The modified polymers through grafting have a bright future and their development is practically boundless. In this review, we have tried to cover two important applications employing grafting technique, viz. membrane separation science and conducting polymers.

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Keywords: Grafting; Free radical; Living radical; Membrane; Conducting polymer

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1. Introduction

One trend in modern civilization is to effect gradual replacement of natural materials with either all synthetic materials or modified natural materials. In the polymeric age, it is essential to modify the properties of a polymer according to tailor-made specifications designed for target applications. There are several means to modify polymers properties, viz. blending, grafting, and curing. ‘Blending’ is the physical mixture of two (or more) polymers to obtain the requisite properties. ‘Grafting’ is a method wherein monomers are covalently bonded (modified) onto the polymer chain, whereas in curing, the polymerization of an oligomer mixture forms a coating which adheres to the substrate by physical forces. Curing gives a smooth finish by filling in the valleys in the surface. This is somewhat different from the curing (or vulcanization) of rubber which produces chemical cross-links between loosely coiled polymeric chains, producing elasticity as the chains stretch under a stress, and retract on release of the stress. Actually there is no time scale for the process of grafting, which can take minutes, hours or even days, whereas curing is usually a very rapid process, occurring in a fraction of second. The schematic presentation of the polymer modification is presented in Fig. 1.

In this review, we concentrate on grafting methods. Two major types of grafting may be considered: (i) grafting with a single monomer and (ii) grafting

with a mixture of two (or more) monomers. The first type usually occurs in a single step, but the second may occur with either the simultaneous or sequential use of the two monomers. Mosaic grafting has attracted much attention for binary monomer grafting. Two different monomers are grafted side-by-side to obtain the requisite property. This is the origin of bipolar membranes. The first part of the review discusses different techniques of grafting, and the primary factors, which control the grafting. Following that, two applications are discussed, viz. membrane separation science and conducting polymers.

2. Techniques of grafting

Considerable work has been done on techniques of graft co-polymerization of different monomers on polymeric backbones. These techniques include chemical, radiation, photochemical, plasma-induced techniques and enzymatic grafting.

2.1. Grafting initiated by chemical means

Chemical means the grafting can proceed along two major paths, viz. free radical and ionic. In the chemical process, the role of initiator is very important as it determines the path of the grafting process. Apart from the general free-radical mechanism, grafting in the melt and atom transfer radical

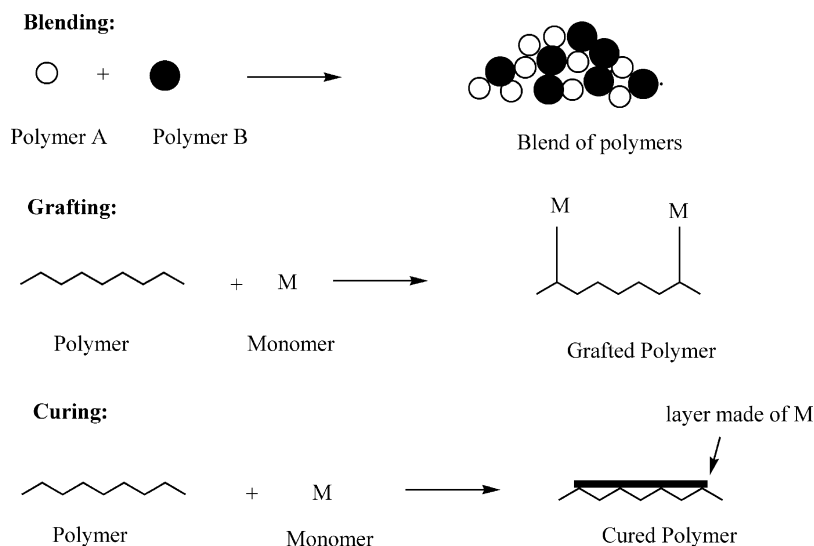


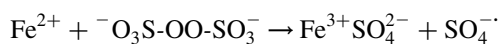
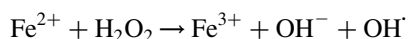
Fig. 1. Schematic representation of the methods of polymer modification.

polymerization (ATRP) are also interesting techniques to carry out grafting.

2.1.1. Free-radical grafting

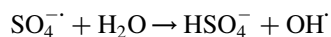
In the chemical process, free radicals are produced from the initiators and transferred to the substrate to react with monomer to form the graft co-polymers. In general, one can consider the generation of free radicals by indirect or direct methods.

An example of free radicals produced by an indirect method is the production through redox reaction, viz. M^{n+}/H_2O_2 , persulphates [1–5]:



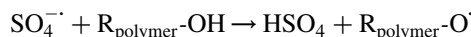
It may be observed that the active species in the decomposition of H_2O_2 and potassium-persulphate induced by Fe^{2+} are OH^\cdot and $SO_4^{\cdot-}$, respectively.

There are different views regarding the activity of $SO_4^{\cdot-}$. Some authors reported that initially formed $SO_4^{\cdot-}$ reacts with water to form OH^\cdot , subsequently producing free radicals on the polymeric backbone:



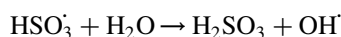
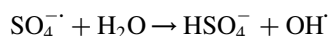
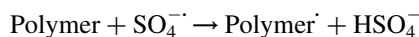
An alternate view is that $SO_4^{\cdot-}$ reacts directly with the polymeric backbone (e.g. cellulose) to produce

the requisite radicals

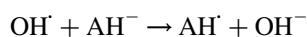
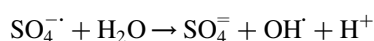
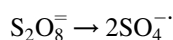


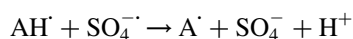
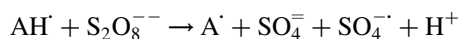
However, Misra et al. [3] established that during grafting of vinyl monomers onto wool/cellulose, OH^\cdot is more reactive than $SO_4^{\cdot-}$.

Similar electron transfer reaction may also occur when organic hydroperoxides, persulphates, Fe^{3+} , Cu^{2+} , etc. are used in place of H_2O_2 together with a reducing reagent such as sodium bisulphite, thiosulphate or Ag^+ :



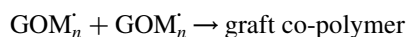
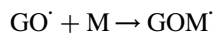
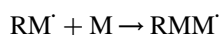
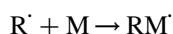
Bajpai et al. [6] reported peroxydisulphate–ascorbic acid initiated graft co-polymerization. In this case, the reaction between peroxydisulphate and ascorbic acid involves chain reaction catalyzed by Ag^+ , because of the production of sulphate ion radicals, which are well-known chain carriers



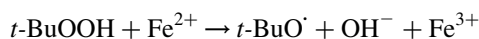


where AH refers to ascorbic acid.

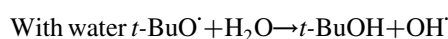
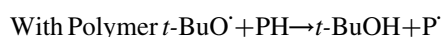
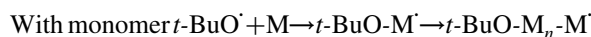
It is apparent from the above that $\text{SO}_4^{\cdot-}$ or $\text{AH} \cdot$ may initiate graft co-polymerization by hydrogen abstraction from a polymer chain, e.g. from guar gum backbone. However, for the latter, Bajpai et al. have proposed the generation of guar gum macroradical ($\text{GO} \cdot$) by reaction (a) below, since initiation of vinyl polymerization is faster than H-abstraction by primary radicals:



Hydroperoxides and Fe^{2+} comprise another important redox system, with free radicals generated by the interaction between them via thermal decomposition [7]. By analogy with Fenton's reagent ($\text{Fe}^{2+} - \text{H}_2\text{O}_2$), the activity of tertiary butyl hydroperoxides– Fe^{2+} system is attributed to the formation of *t*-butoxy radical arising from one electron transfer between *t*-butyl-hydroperoxide (TBHP) and Fe^{2+} :



The resulting *t*-BuO \cdot may participate in hydrogen abstraction reaction to generate OH \cdot and the macro-radical on polymeric backbone:

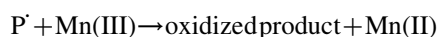
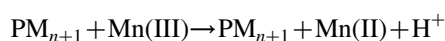
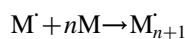
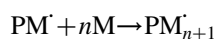
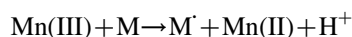
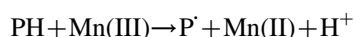


Free-radical sites may be generated on a polymeric backbone by direct oxidation of the backbone by certain transition metal ions (e.g. Ce^{4+} , Cr^{6+} , V^{5+} , Co^{3+}). The redox potential of the metal ions is the important parameter in determining the grafting

efficiency. In general, metal ions with low oxidation potential are preferred for better grafting efficiency. The proposed mechanism for such a process has been ascribed to the intermediate formation of a metal ion–polymer chelate complex, viz. ceric ion is known to form a complex with hydroxyl groups on a polymeric backbone, which can dissociate via one electron transfer to give free radicals [8–14].



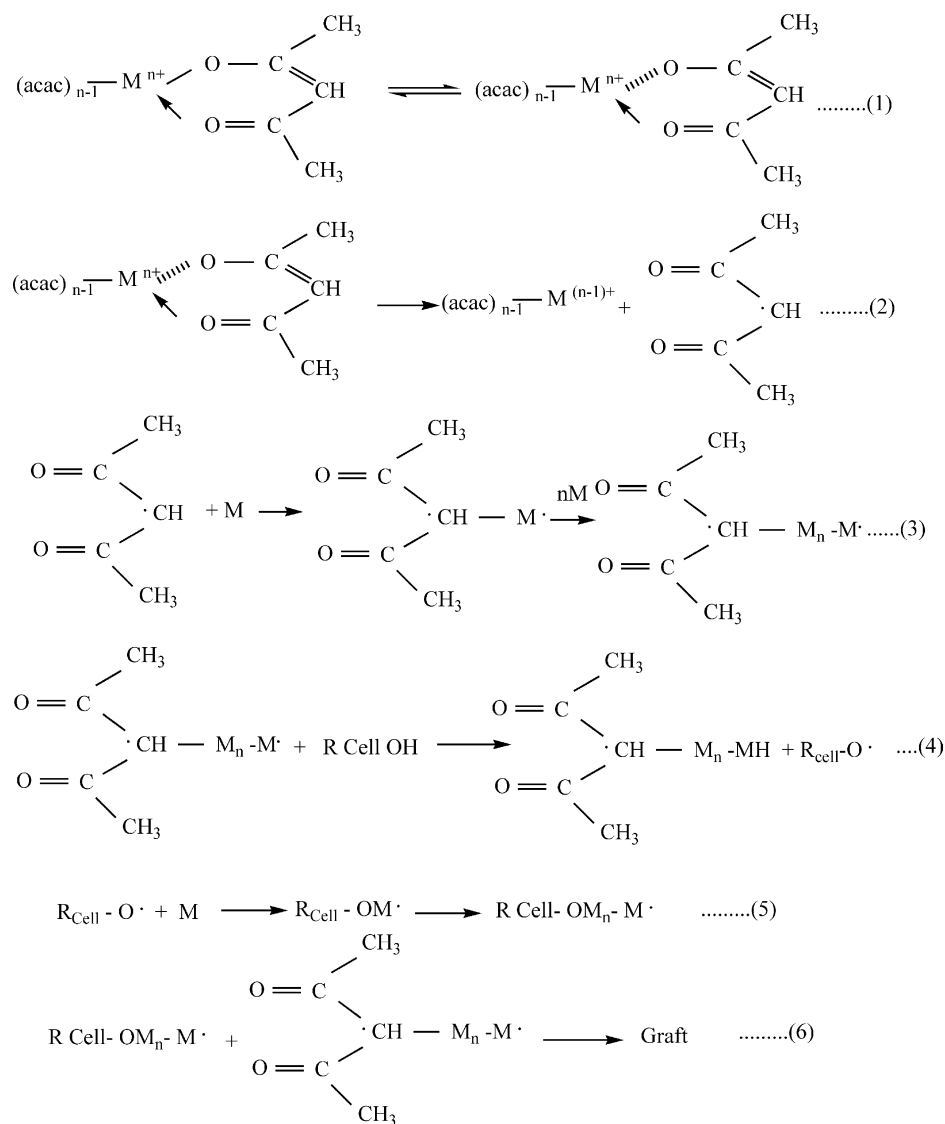
MnO_4^- dissolves in the acid medium to give rise to Mn^{3+} ions via Mn^{4+} . These highly reactive Mn^{3+} ions are responsible for initiating graft co-polymerization and homopolymerization [15]



where PH refers to polymer.

The use of metal chelates in grafting is not quite conventional, but has some advantages. If the potential of M/M_n^{z+} is high, it may react with monomer, which will lead to an increase in homopolymerization. Therefore, to avoid that outcome, it is better to select a metal ion of low oxidation potential, or metal chelates (e.g. $\text{Fe}(\text{acac})_3$, $\text{Zn}(\text{acac})_2$, $\text{Al}(\text{acac})_3$, $\text{VO}(\text{acac})_2$; acac, acetyl acetoate). The participation of metal chelates can be presented (Scheme 1) in the following manner, as suggested by Misra et al. [16,17].

In the above mechanism, it is proposed that the metal chelates first loosen the metal–oxygen bond upon heating, followed by decomposition into a free-radical species by a one-electron transfer process. The free-radical species thus formed is responsible for grafting, as well as for homopolymerization. There are some compounds (Fig. 2), which can produce free radicals on heating, which are then transferred to



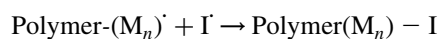
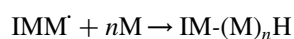
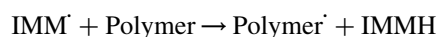
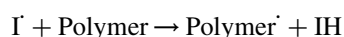
Scheme 1. Reaction scheme using metal chelates [17]. Reproduced from J Macromol Sci Chem 1980;A14(7):1061.

the chain (e.g. azo compounds, peroxides, hydroperoxides, peroxide diphosphate, etc.). In this context, the study of Tsubokawa et al. [18] is quite interesting. Organic pigments having incorporated azo groups enable to polymerize vinyl monomers through radical mechanism (Scheme 2).

Apart from the initiators discussed earlier, benzoyl peroxide (BPO) and azoisobutyronitrile (AIBN) are also effective in grafting reactions [19,20]. This is important to note that the grafting efficiency is low

with BPO and AIBN, compared with that obtained using one-electron transfer agents. For example, not all of the radical species contribute towards grafts of poly(methyl acrylate) on cellulose and vinyl acetate on starch. Moreover, between the two, BPO is more reactive than AIBN, since the effects of resonance stabilization reduce the efficiency of the primary radical (I) from AIBN in generating active sites on the backbone (Fig. 2) [19–21]. A plausible mechanism of grafting in the presence of a radical initiator is as

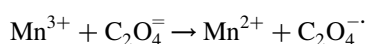
follows



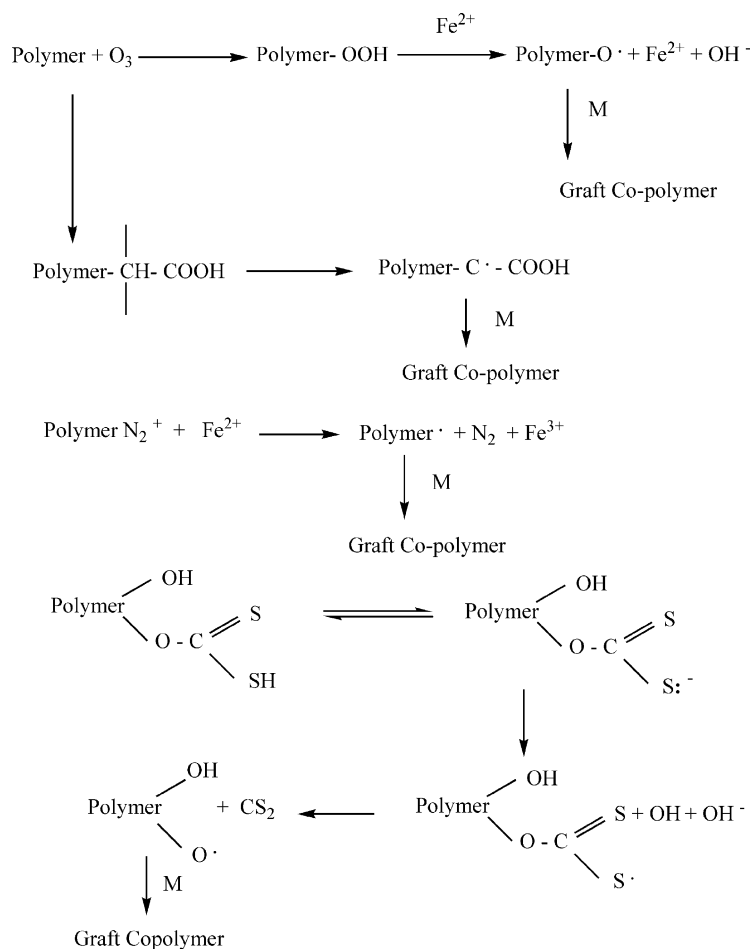
Chemical pre-treatment (e.g. ozonation, diazotization, xanthation) of the polymer backbone may also

generate free-radical sites (Scheme 3), which can provide sites for grafting [22–32].

Aside from the formation of free-radical sites through complex formation with metal ions, the generation of secondary free radicals is reported in systems, which may ultimately generate the free-radical sites required for grafting [33], e.g. secondary free radicals such as $CO_2\cdot^-$, $C_2O_4\cdot^-$ may be formed in the system with Mn^{4+} ion as the initiator in the presence of oxalic acid and sulfuric acid as follows:



In this connection, it is relevant to mention free-radical grafting in the melt [34]. In this case, backbone



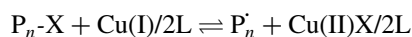
Scheme 3. Chemical pre-treatment methods [157]. Reproduced from Prog Polym Sci 1983;10:171.

polymer, monomer and initiators comprise a mixture at high temperature, so that grafting occurs in the melt. One interesting application of the melt free-radical grafting technique is to change the chemically reactive properties of the polymer, but not its mechanical properties. For example, functional monomers widely used in the modification of PP mainly include maleic anhydride [35–38], glycidyl methacrylate [39–42], methacrylic acid and their derivatives [43,44], oxazoline and silanes [45–47], conjugated chain monomers, e.g. oleic acid and undecylenic acid. Mixtures of monomers, e.g. mixtures of maleic anhydride and styrene, styrene and acrylic acid and vinyl acetate and vinyl chloride are also reported [48].

2.1.2. Grafting through living polymerization

In recent years, methods of ‘Living Polymerization’ have developed to provide a potential for grafting reactions. In the view of Szwarc et al. [49], the most plausible definition of a ‘living polymer’ is ‘that retains their ability to propagate for a long time and grow to a desired maximum size while their degree of termination or chain transfer is still negligible’. Controlled free-radical polymerizations combine features of conventional free-radical and ionic polymerizations. Conventional free-radical polymerization requires continuous initiation, with termination of the growing chain radicals in coupling or disproportionation reactions, and as a result leads to unreactive (‘dead’) polymers and essentially time invariant degrees of polymerization and broad molecular weight distribution. In case of a living polymerization, it provides living polymers with regulated molecular weights and low polydispersities [50–57].

Controlled free-radical polymerization may be effective through ATRP. ATRP of styrene and various methacrylates has been reported, using various catalytic systems [58,59]. In that method, dormant chains are capped by halogen atoms, which are reversibly transferred to metal complexes in the lower oxidation state. This generates the transient growing radicals and complexes in the higher oxidation state. The key reaction of ATRP is the activation–deactivation dynamic equilibrium process



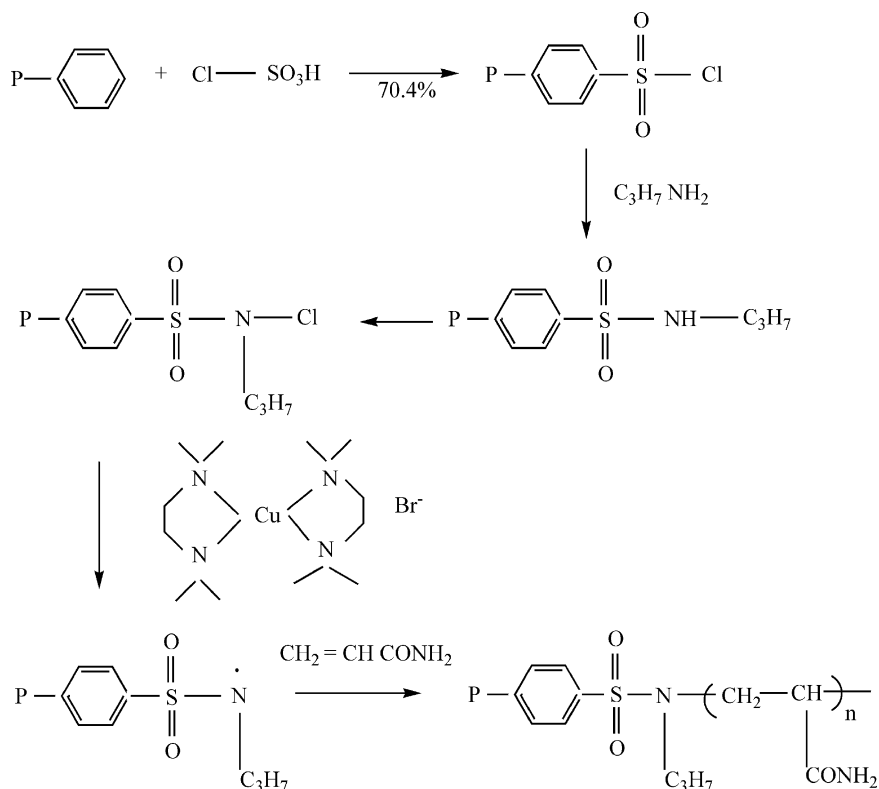
$P_n\text{-X}$ is the polymeric halide and copper (I) complex $\text{CuX}/2\text{L}$ ($\text{X} = \text{Cl}/\text{Br}$ and $\text{L} = 2, 2'$ bipyridine or a 4,4' disubstituted 2,2' bipyridine).

The copper (I) complex acts as a reversible halogen atom transfer reagent between the active and dormant polymer chains. The kinetically optimum ratio of ligand to copper (I) halide for these polymerization is found to be 2:1, which tentatively indicates that the coordination sphere of the active copper (I) center contains two bipyridine ligands [59]. Contrary to redox radical telomerization, the molecular weight increases linearly with increasing monomer conversion in ATRP.

Multidentate amine based ligands (e.g. tetramethylene diamine (TMEDA), N,N,N',N'' -pentamethyldiethylenetriamine (PMDETA), (tris-2-aminoethyl)amine (TREN) are also used in the copper mediated ATRP of styrene, methyl acrylate and methyl methacrylate [60,61]. It is observed that compared to bi-pyridine based ligands, PMDETA and 1,1,4,7,10,10-hexamethyl triethylene tetramine (HMTETA) resulted in faster polymerization rates for styrene and methacrylate. This is attributed to the lower redox potential of coordination complexes between copper and the simple amines in comparison with that for the copper–bipyridine complex, resulting in higher rates of activation of the dormant halides.

Grafting from polymers including poly(vinyl chloride) (PVC), polyisobutene, polyethylene, and ethylene-*co*-vinyl acetate co-polymer has also reported through ATRP [62–66]. Sonmez et al. [67] reported acrylamide grafting by ATRP; the initiation appears to take place via radical formation in a redox reaction of *N*-chlorosulfonamide groups with CuBr , as shown in Scheme 4. Sakaguchi and Shimada [68] reported the grafting of polystyrene on a polypropylene backbone with 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO). In that work, γ -irradiation in air was used to form a PP macromolecular initiators, after which TEMPO was used to control the grafting polymerization. The reaction scheme is as follows (Scheme 5).

Janata et al. [69] reported the preparation of a multifunctional ATRP macroinitiator for the synthesis of graft co-polymer. A polystyrene macroinitiator substituted with 1-(2-bromopropionyl oxy)ethyl or 1-(2-bromoisobutyryl oxy)ethyl groups was prepared from polystyrene using a three step functionalization procedure consisting of Friedel Craft's acylation



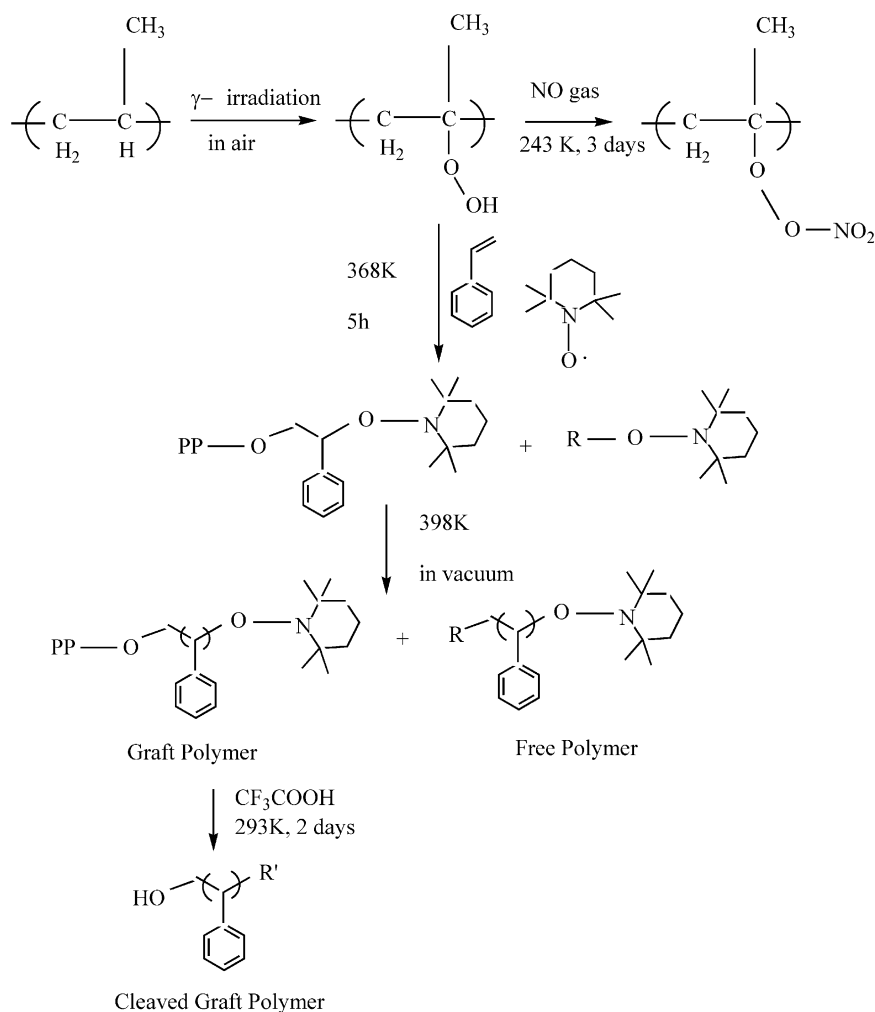
Scheme 4. Proposed mechanism for ATRP grafting of polyacrylamide onto functional PS-DVB resin [67]. Reproduced from React Funct Polym 2003;55(1):1.

reduction of carbonyls to secondary hydroxyl groups with LiAlH_4 and esterification with 2-bromopropionyl bromide or 2-bromo isobutyryl bromide or 2-bromoisobutyryl bromide to introduce 2-bromopropionyloxy or 2-bromoisobutyryloxy groups on polystyrene (Fig. 3). The ATRP macroinitiators thus obtained contain hydrolyzable ester linkages, useful for determination of the molecular weight distributions of the grafted chains following the ATRP treatment.

As controlled radical polymerization involves (essentially) simultaneous initiation of individual growing polymer chains with negligible transfer or termination and simultaneous growth (or fast exchange of the active growing species) between all polymer chains, it is the most suitable technique for the synthesis of gradient co-polymers. The technique has also proved its potential for the preparation of molecular brushes, i.e. high grafting density polymer, using a 'grafting from' approach. It has been used successfully to prepare molecular brushes with either

methacrylate or polystyrene backbones and various polyacrylates, polymethacrylates and polyethylene side chains [71–74]. In the high grafting density polymer preparation, two major steps are involved (1) macroinitiator preparation and (2) brush synthesis from macroinitiator. The subsequent synthesis of the macroinitiator p(MMA-grad-BPEM) (poly(methyl methacrylate-gradient-hydroxy methyl acrylate-2-(2-bromopropionyl-oxy)ethyl methacrylate) and macromolecular brush co-polymer poly[(MMA-grad-BPEM)-*graft-n*-BuA] is sketched in the scheme (Scheme 6) [72].

The ATRP/controlled living radical polymerization technique would provide an excellent means of expanding the versatility of macromonomer method, as it increases the number of monomers available for making macromonomers and the ease with which they can be made. Grafting through using macromonomers from PVE, PMMA, PDMS, PLA, PE and PS has been reported [75–81]. A reaction scheme using



Scheme 5. Reaction scheme of graft polymerization of styrene to PP. The most likely end structures R are groups generated through Diels Alder Reaction of ST and hydroxy group generated by decomposition of the PP peroxide. The most likely end group R' of the cleaved PS graft is a hydroxy and/or TEMPO moiety [68]. Reproduced from *Macromolecules* 2001;34:2089.

polystyrene is presented in [Scheme 7](#): a vinyl acetate–polystyrene macromonomer is prepared via ATRP and then co-polymerized with NVP by a conventional free-radical polymerization. Both steps can be performed by the combination of two living polymerization steps for poly(*n*-butyl acrylate)-*graft*-branched polyethylene [81].

Surface grafting by controlled radical polymerization has been reported from polymeric substrates, colloidal particles and inorganic materials [82–91]. For example, Carlmark and Malmstrom [90] immobilized 2-bromoisobutryl bromide by reaction

with the hydroxyl groups on the filter paper. Then, grafting is accomplished by immersing the modified paper into a reaction mixture containing methyl acrylate, Cu(I)Br, tris 2-(dimethyl amino)ethyl amine (Me₆-TREN), sacrificial initiator and ethyl acetate ([Scheme 8](#)).

In another example, Pyun et al. [87] report the functionalization of hybrid nanoparticles of an inorganic colloidal core and chain end immobilized organic co-polymers, allowing their subsequent application as initiators for the ATRP of styrene and meth(acrylate) monomers ([Scheme 9](#)).

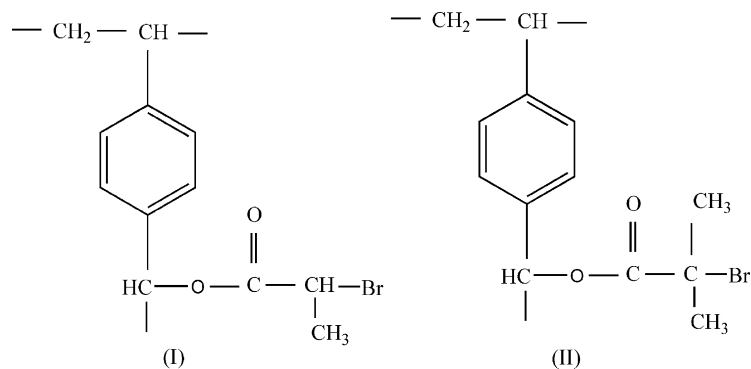
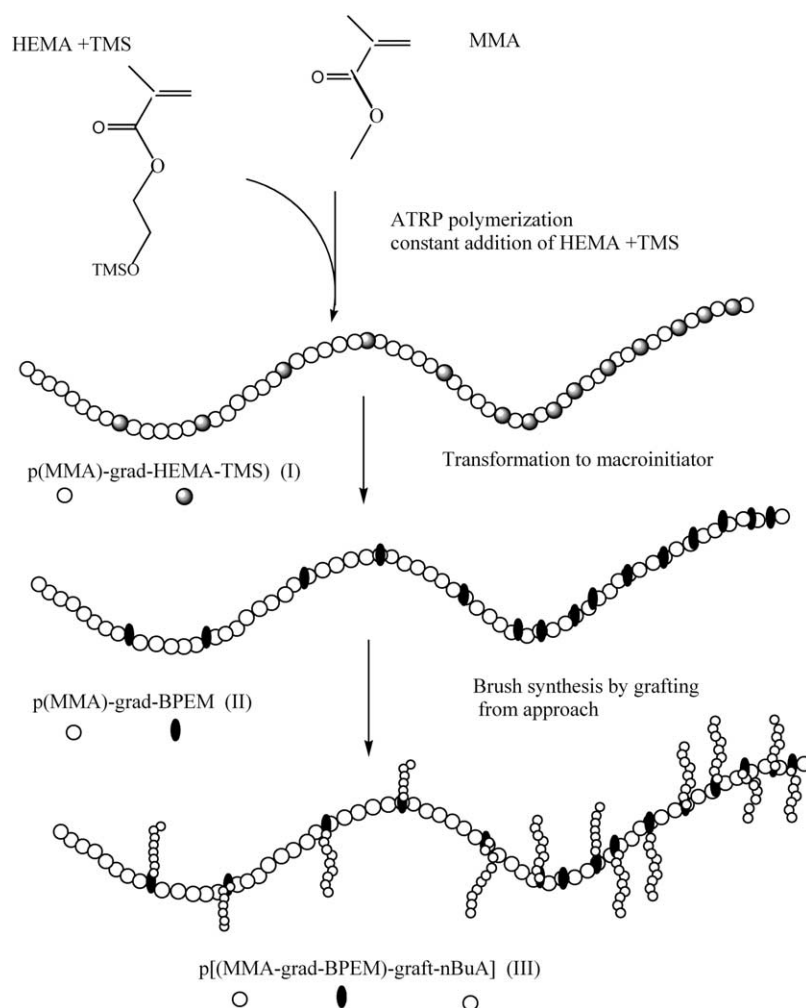
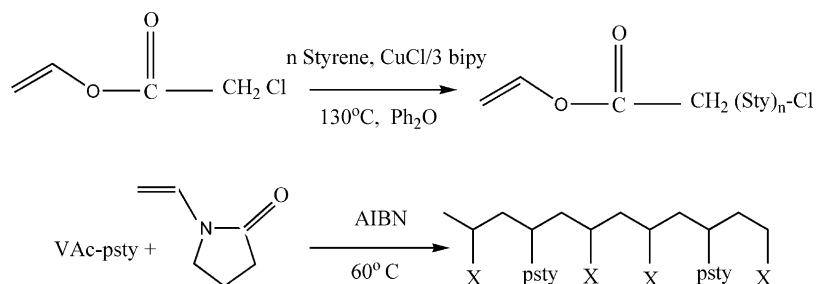


Fig. 3. Structure of the 2-bromopropionyl bromide and 2-bromoisobutyryl bromide [69]. Reproduced from React Funct Polym 2001;50:67.



Scheme 6. Subsequent synthesis of the macroinitiator precursor(I), the macroinitiator(II) and macromolecular brush co-polymers (III) [72]. Reproduced from Macromolecules 2002;35:3387.



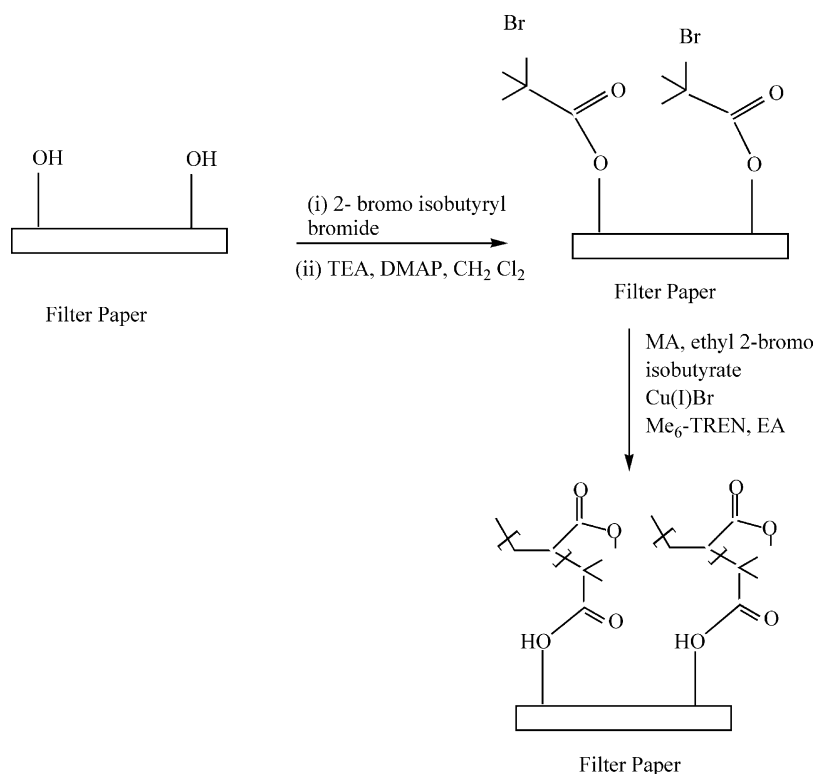
Scheme 7. Preparation of the VAc-psty macromonomer via ATRP and free-radical co-polymerization of VAc-psty with NVP [81]. Reproduced from J Polym Sci, Part A: Polym Chem 1998;36:823.

Living free-radical polymerization has been widely investigated using different initiators, called inferfers (derived from initiator-transfer agent terminator). Peng and Cheng [92] used a photoinferfer for the sequential grafting of PNIPAAm and PMAA on porous PE membranes. Here, it is proposed that under UV-irradiation xanthone is excited and turns into xanthone ketyl radical after abstracting hydrogen atom. The

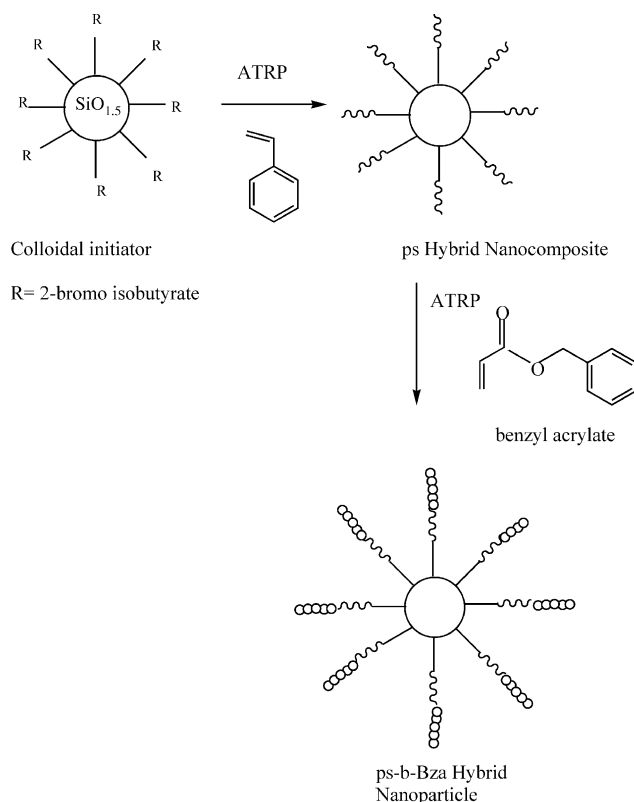
radical participates mainly in a termination process, resulting in grafted PMAA chains with terminal xanthone ketyl groups that can decompose to form free radicals, leading to additional PMAA grafting.

2.1.3. Ionic grafting

Grafting can also proceed through an ionic mode. Alkali metal suspensions in a Lewis base liquid,

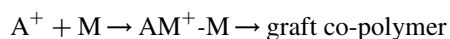
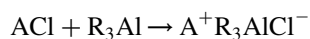


Scheme 8. Schematic presentation of surface grafting on cellulose via controlled living radical polymerization [90]. Reproduced from J Am Chem Soc 2002;124:900.



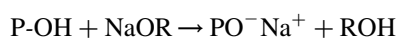
Scheme 9. Synthesis of 2-bromo isobutyrate functional nanoparticles and ps-b-p-BzA hybrid particles using microemulsion and ATRP process [87]. Reproduced from *Macromolecules* 2003;36:5094.

organometallic compounds and sodium naphthalene are useful initiators in this purpose. Alkyl aluminum (R_3Al) and the backbone polymer in the halide form (ACl) interact to form carbonium ions along the polymer chain, which leads to copolymerization. The reaction proceeds through cationic mechanism



Cationic catalyst BF_3 can also be used.

Grafting can also proceed through an anionic mechanism. Sodium–ammonia or the methoxide of alkali metals form the alkoxide of polymer (PO^-Na^+), which reacts with monomer to form the graft co-polymer



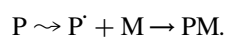
2.2. Grafting initiated by radiation technique

2.2.1. Free-radical grafting

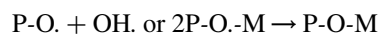
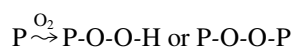
The irradiation of macromolecules can cause homolytic fission and thus forms free radicals on the polymer. In the radiation technique, the presence of an initiator is not essential. The medium is important in this case, e.g. if irradiation is carried out in air, peroxides may be formed on the polymer. The lifetime of the free radical depends upon the nature of the backbone polymer. Grafting proceeds in three different ways: (a) pre-irradiation (b) peroxidation and (c) mutual irradiation technique. In the pre-irradiation technique [93–97], the polymer backbone is first irradiated in vacuum or in the presence of an inert gas to form free radicals. The irradiated polymer substrate is then treated with the monomer, in liquid or vapor state or as a solution in a suitable solvent. In the peroxidation grafting method, the trunk polymer is subjected to high-energy radiation in the presence of air or oxygen

to form hydroperoxides or diperoxides, depending on the nature of the polymeric backbone and the irradiation conditions. The stable peroxy products are then treated with the monomer at higher temperature, whence the peroxides undergo decomposition to radicals, which then initiate grafting. The advantage of this technique is that the intermediate peroxy products can be stored for long periods before performing the grafting step. On the other hand, with the mutual irradiation technique, the polymer and the monomers are irradiated simultaneously, to form free radicals and subsequent addition [98–104]. Since the monomers are not exposed to radiation in the pre-irradiation technique, the obvious advantage is that the method is relatively free from homopolymer formation, which occurs with the simultaneous technique. However, the decided disadvantage of the pre-irradiation technique is scission of the base polymer due to its direct irradiation, which can result in the formation of block co-polymers. These processes are represented through simple mechanisms described below.

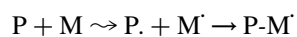
(a) Grafting (pre-irradiation)



(b) Grafting (peroxidation)



(c) Grafting (mutual irradiation)



2.2.2. Ionic grafting

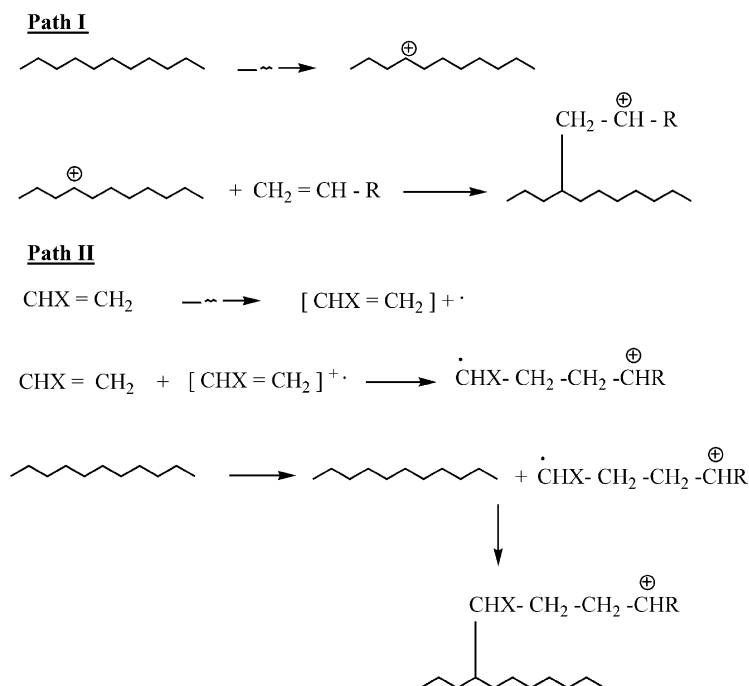
Radiation grafting can also proceed through an ionic mode, with the ions formed through high-energy irradiation. Ionic grafting may be of two different types: cationic or anionic. The polymer is irradiated to form the polymeric ion, and then reacted with the monomer to form the grafted co-polymer. The potential advantage of the ionic grafting is high reaction rate.

Thus, small radiation doses are sufficient to bring about the requisite grafting. The cationic grafting initiated from the backbone is shown in Scheme 10 (Path I). An alternate cationic grafting mechanism can proceed through monomer radical cation, which subsequently forms a dimer. Charge localization in the dimer occurs in such a way that the dimer radical cation then reacts with the radical produced by the irradiation of the polymer, e.g. see Scheme 10 (Path II).

Analogous mechanisms involving an anion as the initiator operates in the case of anionic grafting.

Thus, MeV proton beams (Scheme 11) have been successfully applied as ionizing radiation to induce graft polymerization of acrylonitrile to prepare amidoxime type adsorbents on PE film substrates [105, 106]. The H-molecules liberated in a polymer film irradiated with an ion beam leave chemically active tracks in the substrate. A variety of carbon radicals, C=C bonds, C-C bonds and cross-linking form in the chemically active track. One unique advantage of high linear energy transfer (LET) with short stopping ranges irradiation, is the possibility to develop a radical distribution with a spatial variation of the order of nm, whereas for low LET (e.g. γ -rays, e-beams), relatively uniform formation of the radical is expected for a specimen with a thickness of the order of mm.

Radiation induced grafting differs from chemical initiation in many aspects. In a mechanistic way, as in a radiation technique the initiator is not required, free-radical formation is on the backbone polymer/monomer whereas in a chemical method, a free radical forms first on to the initiator and then it is transferred to the monomer/polymer backbone. Unlike the chemical initiation method, the radiation-induced process is free from contamination, so that the purity of the processed products may be maintained. Chemical initiation is limited by the concentration of the initiator, and it may be difficult to determine an accurate concentration of the initiator in pure form. Chemical initiation often brings about problems arising from local heating of the initiator, an effect that is absent in the formation of free-radical sites by radiation, which is only dependent upon the absorption of high-energy radiation. Due to large penetrating power of higher energy radiation, methods using radiation initiation provide the opportunity to carry out grafting at different depths of the base polymer matrix. Moreover, the molecular weight of the products can be better



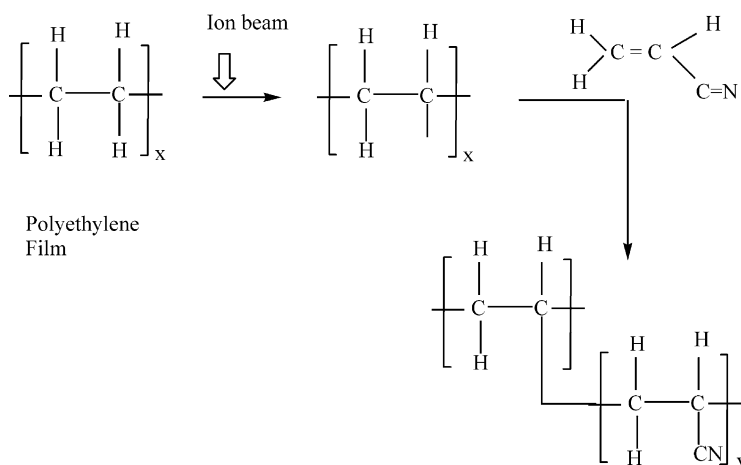
Scheme 10. Path I. Reaction mechanism of cationic grafting initiated from the backbone. Path II. Reaction mechanism of cationic grafting initiated through monomer [157]. Reproduced from Prog Polym Sci 1983;10:171.

regulated in radiation techniques, and these are also capable of initiation in solid substrates. Regarding its limitation, nuclear radiation energy is usually expensive in comparison with chemical reactions. The length of irradiation time and setting up the optimum conditions present limitations of the radiation

technique. Moreover, it should be well known whether the polymer is stable in the radiation range of interest.

2.3. Photochemical grafting

When a chromophore on a macromolecule absorbs light, it goes to an excited state, which may dissociate

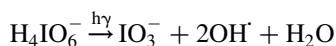


Scheme 11. Reaction scheme of grafting of acrylonitrile onto polyethylene film employing MeV proton beams [105]. Reproduced from Radiat Phys Chem 2004;69:171.

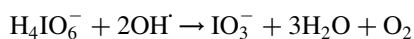
into reactive free-radicals, whence the grafting process is initiated. If the absorption of light does not lead to the formation of free-radical sites through bond rupture, this process can be promoted by the addition of photosensitizers, e.g. benzoin ethyl ether, dyes, such as Na-2,7 anthraquinone sulphonate or acrylated azo dye, aromatic ketones (such as benzophenone, xanthone) or metal ions UO_2^{2+} . That means the grafting process by a photochemical technique can proceed in two ways: with or without a sensitizer [92,107,108]. The mechanism without sensitizer involves the generation of free radicals on the backbone, which react with the monomer free radical to form the grafted co-polymer. On the other hand, in the mechanism 'with sensitizer', the sensitizer forms free radicals, which can undergo diffusion so that they abstract hydrogen atoms from the base polymer, producing the radical sites required for grafting (see Scheme 12).

Uchida et al. [109] reported a novel method in which oxygen removal from polymerization mixture was not required, for the graft polymerization of acrylamide (AM) on the surface of poly(ethylene

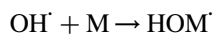
terephthalate) (PET) film, with simultaneous UV-irradiation without a photosensitizer. In that method, the addition of NaIO_4 plays a crucial role in the removal of any oxygen present in the aerated monomer solution, as oxygen is the strong inhibitor of radical polymerization. The periodate ion present in an aqueous solution containing NaIO_4 generally exists in the hydrated forms H_4IO_6^- and H_2IO_5^- , and H_4IO_6^- may produce OH^\cdot and IO_3^- :



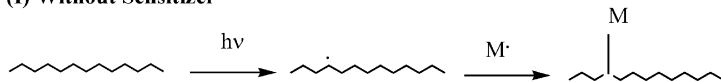
In the absence of a reaction with a monomer, the following reaction seems to take place, resulting in the generation of O_2 :



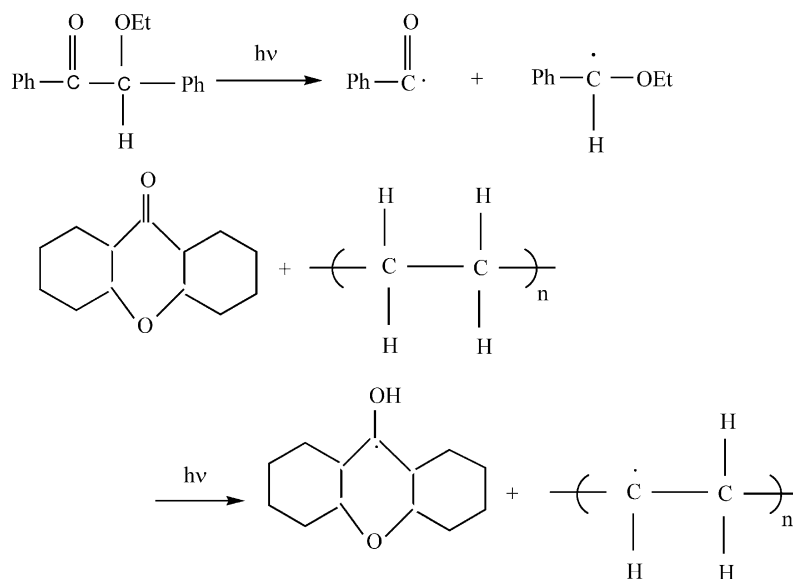
If a monomer (M) is added to the periodate solution, O_2 must be consumed as a result of polymerization initiated by OH^\cdot as shown by the following reactions:



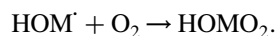
(I) Without Sensitizer



(II) With sensitizer



Scheme 12. Mechanism for photochemical grafting method [157]. Reproduced from Prog Polym Sci 1983;10:171.



If NaIO_4 is present in very small quantity, neither O_2 formation nor OH^{\cdot} generation are significant, with little effect on the graft polymerization. When the NaIO_4 quantity is large enough, the O_2 concentration may increase in the beginning of the photochemical reaction as then O_2 formation should exceed O_2 consumption. After that however, O_2 generation should decline, as all of the ions decompose to form IO_3^- , as demonstrated in the O_2 generation reaction above.

2.4. Plasma radiation induced grafting

In recent years, the plasma polymerization technique has received increasing interest. Plasma conditions attained through slow discharge offer about the same possibilities as with ionizing radiation [110,111]. The main processes in plasmas are electron-induced excitation, ionization and dissociation. Thus, the accelerated electrons from the plasma have sufficient energy to induce cleavage of the chemical bonds in the polymeric structure, to form macromolecule radicals, which subsequently initiate graft co-polymerization.

2.5. Enzymatic grafting

The enzymatic grafting method is quite new. The principle involved is that an enzyme initiates the chemical/electrochemical grafting reaction [112]. For example, tyrosinase is capable of converting phenol into reactive *o*-quinone, which undergoes subsequent non-enzymatic reaction with chitosan.

Enzymatic grafting on a poly(dicarbazole-*N*-hydroxysuccinimide) film was reported by Cosnier et al. [113], thionine and toluidine blue have been irreversibly bound to the poly(dicarbazole) backbone and the grafting of polyphenol oxidase (PPO) on polydicarbazole has been reported.

3. Controlling factors of grafting

In the following sections, several of the many variables that control grafting will be discussed, including the nature of the backbone, monomer, solvent, initiator, additives, temperature, etc.

3.1. Nature of the backbone

As grafting involves covalent attachment of a monomer to a pre-formed polymeric backbone, the nature of the backbone (viz. physical nature, chemical composition) plays an important role in the process. Ng et al. [114] concluded that whereas cellulose is resistant to grafting reactions in water owing to its insolubility, due to the immense size of the polymeric chain bonding between the amino residues, the cystine linkages and intramolecular H-bonding in wool are responsible for shaping and setting characteristics. In the presence of UV light, oxidative reactions are initiated and free radicals are formed, leading ultimately to grafting if monomers are present.



CeO-H refers to cellulose.

Even though the backbone of cellulose is highly structured and bulky, swelling of the backbone may take place in the presence of an appropriate solvent, which enhance the mobility of radicals generated in the monomer (e.g. by irradiation) to active sites on the substrate backbone to effect grafting. A similar situation is observed for the wool. As wool absorbs UV light effectively, degradation occurs at the disulphide bonds, where the formation of the oxidized SO_3 and then reduced -SH species from cystine are generated. The photochemical cleavage of cystine cross-links near the fiber surface results in soluble proteins being released from the irradiated fibers and at the same time increases the number of bonding sites in wool structure where grafting may occur.

Ibrahim and Nada [115] reported that crystallinity decreases with increasing degree of substitution, affecting the grafting of acrylamide on acetylated wood pulp. As the crystallinity decreases, it is less ordered and facilitating the grafting reaction. The amorphous fraction and solvent can also play role. In the case of styrene grafting to polyethylene, the addition of MeOH or MeOH- H_2SO_4 along with the monomer increases the viscosity in the amorphous region, thus increasing the grafting rate [116]. Clark et al. [117] reported the effect of the microstructural characteristics of the backbone on the course of both

grafting and cross-linking reactions. Both cross-linking and grafting events were enhanced for polyethylene containing high levels of terminal unsaturation reacted in the presence of peroxide or maleic anhydride. Cross-linking was still observed for PE containing a high concentration of terminal unsaturation when styrene was added as co-monomer to eliminate undesirable side reactions. The result was attributed to low reactivity between styrene and the allylic radical generated on the PE backbone, believed to be responsible for increased cross-linking.

There are various reports regarding the role of chemical composition on grafting. For example, the presence of lignin (phenolic -OH) in straw affected the grafting of 2-methyl vinyl pyridine, since lignin is a good scavenger of radicals [118]. This phenomenon has also been observed in ethyl acrylate grafted to a sisal fiber system; sisal fiber contains 8% lignin. The grafting rate is higher when NaOH is used as a lignin remover, but the reverse is also been reported, i.e. the presence of lignin increases the grafting yield if the backbone is ozonized and grafted using $\text{Fe}^{2+}-\text{H}_2\text{O}_2$ as the initiator. In that case, lignin is oxidized with ozone, as a result of which the carboxylic group is formed in the lignin structure, favoring the free-radical formation influences grafting [26]. This phenomenon has also been observed if acrylonitrile grafted on pulp by xanthation method. In cases in which lignin is present in the cellulose structure, chain transfer may occur to lignin from the OH radical, giving rise to less reactive lignin radical [31].

The presence of functional groups in the backbone also influences the grafting. Styrene is grafted relatively with high efficiency on cellulose acetate-*p*-nitrobenzoate. This result indicates that the pendant aromatic nitro group is more effective in obtaining a graft co-polymer [119]. Replacement of -OH by -SH groups in a cellulose substrate increases the level of grafting as initiation by Ce^{4+} ion occurs by H-abstraction from C-atoms having -OH groups. But in case of MMA grafting on holocellulose (comprising a mixture of α -cellulose plus the hemicelluloses), H-abstraction is not the mode of initiation, and -SH group is associated with a marked decrease in the level of grafting [120]. The vicinal -OH groups in PVA influences

head-to-head monomer incorporation in case of vinylidene chloride grafting on PVA [121]. Rao and Rao [122] studied the rates of grafting of acrylic acid on different backbones and explained the trends observed on the basis of chain transfer of the growing polymer chain, in the order nylon-6 > polyester \cong PP fiber. Treatment with chemical agents also influences the grafting. Ghosh et al. [123,124] observed good grafting percentage and efficiency in the case of diethylene triamine modified oxycellulose. This may be due to complex formation, which initiates grafting. Annealing of backbone also influences grafting, e.g. annealed PVA gave higher degree of grafting than untreated backbone with vinyl monomers [125].

3.2. Effect of monomer

As with the nature of backbone, the reactivity of the monomer is also important in grafting. The reactivity of monomers depends upon the various factors, viz. polar and steric nature, swellability of backbone in the presence of the monomers and concentration of monomers.

Recently Naguib et al. [126] calculated the reactivity ratio of vinyl imidazole and acrylic acid by different techniques [127–130], with results given in Table 1. It was found that maximum grafting on polypropylene films by γ -irradiation was achieved for a monomer composition with 60% vinyl imidazole and 40% acrylic acid. However, it is also reported that the monomer reactivity ratios for the grafting process are completely different from values observed for conventional solution polymerization, e.g. for mixtures of monomers acrylonitrile/styrene, acrylamide/styrene [131]. In addition, the graft co-polymerization

Table 1
Reactivity ratios of vinyl imidazole and acrylic acid [126].
Reproduced from Polym Test 2003;22(7):825

Fineman–Ross		Kelen–Tudos		Non-linear least square	
r_1	r_2	r_1	r_2	r_1	r_2
0.121	1.1258	0.1215	1.126	0.122	1.126

r_1 , reactivity ratio of vinyl imidazole and r_2 , reactivity ratio of acrylic acid.

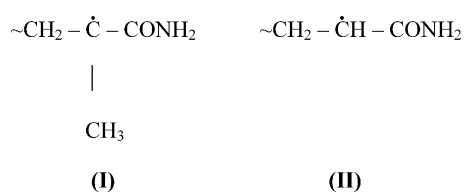
of mixed monomers is a more complex process than the grafting of individual monomers owing to synergistic effects resulting from the differences in monomer reactivity ratios. Nurkeeva et al. [132] studied the grafting of vinyl ether of monoethanolamine (VEMEA) in the presence of the more active monomer, vinyl ether of ethylene glycol (VEEG). Monomer reactivity ratios (r_1 and r_2) for the conventional solution co-polymerization of VEMEA and VEEG are found to be equal to 0.7 and 1.2, respectively. The addition of the more active VEEG to the binary mixture enhances the grafting of both monomers due to an increase in the co-polymerization rate.

The difference in grafting of vinyl acetate (2.6%) and ethyl acrylate (60.8%) on wool can be explained on these monomers. Since vinyl acetate acts as electron donating monomer, it is extremely susceptible to monomer concentration, whereas ethyl acrylate is highly reactive to free radicals [133].

Thus, the percentage of grafting of ethyl acrylate is higher because the loss of ethyl acrylate in side reaction is minimal. On the other hand, being less reactive to radicals, vinyl acetate is reduced in side reactions. Nagaty et al. [134] also observed differences in grafting acrylonitrile, ethyl acrylate and methyl methacrylate on insoluble starch. In this case, the reactivity order $AN > EA \approx MMA$ is observed. In this case, grafted polyethylacrylate forms gel over the starch granules, acting as a barrier to monomer diffusion to the vicinity of starch.

The order of the monomers on wool in terms of grafting is $MA > EA > MMA > VAc > AAc$ [135]. The reactivity of first three monomers is explained by steric considerations. Thus, MMA, being a highly crowded monomer, forms complex with Ce^{4+} less readily and affords minimum grafting. By contrast, VAc is susceptible to monomer transfer reaction and tends to terminate the growing grafted chain by that process, and resulting in poor grafting efficiency. Since AAc and its polymer are soluble in water, AAc tends to undergo homopolymerization preferentially, resulting in poor grafting efficiency. Bhattacharya et al. [94] have compared grafting for substituted acrylamides, showing that the grafting order on cellulose acetate is acrylamide $>$ methylacrylamide $>$ *N,N* dimethylacrylamide. The methyl group in methylacrylamide may reduce

the mobility of the monomer, thus suppressing grafting. The low grafting with methylacrylamide may also be due to the stability of the polymer radical, which is tertiary (I) whereas polymer radical from acrylamide is secondary (II). The secondary radicals are more reactive than the tertiary.



With *N,N* dimethyl acrylamide, two methyl groups play a key role on the extent of grafting. Due to the steric effect of the two-methyl groups, the easy approach of the monomer to the backbone is maximally hindered, and thus the extent of grafting is the least. Earlier workers also observed this phenomenon in case of substituted acrylates [136, 137]. The grafting order on cellulose by means of a Ce^{4+} initiation is methyl acrylate $>$ ethyl acrylate $>$ butyl acrylate $>$ methyl methacrylate. They offered an explanation of reactivity in terms of steric and polar effects. It was also proposed that grafting depends upon the stability of the radical. The polymer radical that is formed in case of methyl methacrylate is relatively stable, whereas in case of methyl methacrylate, which is the most reactive, the corresponding polymer radical is probably stable. It has also been reported by Dworjanyn and Garnett [138] that during radiation grafting certain substituents activate monomers, whereas others deactivate, e.g. relative to styrene, 2-vinyl pyridine is strongly deactivated whereas *o*-methyl styrene is strongly activated to cellulose.

In general, the grafting efficiency will depend on the monomer concentration. For example, in comparing the grafting efficiency observed for 4-vinyl pyridine and methyl acrylate monomers, Kaur et al. [139] explained the phenomena in terms of the monomer solubility and the polymerizability ($k_p/k_t^{1/2}$) values 213×10^{-3} and 7×10^{-3} for MA and 4-vinyl pyridine, respectively. The higher value for MA is responsible for more homopolymer formation than for grafting as compared to 4-vinyl pyridine, and in addition, 4-vinyl pyridine, being more

soluble than MA in an aqueous medium, produces higher grafting in an aqueous environment owing to its greater accessibility to the active sites. It is often reported that the grafting efficiency increases with monomer concentration up to a certain limit and then decreases with further increase in the monomer concentration [140]. This behavior may reflect an initial increase of the monomer concentration in close proximity to the backbone. After a certain limit, the increase in monomer concentration accelerates the homopolymerization reaction rather than grafting.

3.3. Effects of solvent

In grafting mechanisms, the solvent is the carrier by which monomers are transported to the vicinity of the backbone. The choice of the solvent depends upon several parameters, including the solubility of monomer in solvent, the swelling properties of the backbone; the miscibility of the solvents if more than one is used, the generation of free radical in the presence of the solvent, etc.

The solubility of the monomer depends on the nature of the solvent and the polymer, e.g. alcohols are useful solvents for grafting styrene [141–143]. This is because alcohols can swell the backbone effectively and can dissolve the styrene so that the monomer can easily diffuse in the cellulosic structure. The extent of grafting, however, decreases progressively when the alcohol is changed from methanol to ethanol to isopropanol and to *t*-butanol, this decrease in grafting is due to the gradually decreased swelling properties of the alcohol, known to be corroborated by the bulkiness of the alcohol molecules. Lenka [144] also observed similar trend for the alcohols, i.e. methanol > ethanol > propanol > butanol > pentanol in case of grafting of methyl methacrylate on nylon-6. Similar observation was also reported for styrene grafting on PVC by the irradiation technique [138]. In this case, radiolysis fragments of methanol, particular H-atoms would also assist the grafting by creating grafting sites in the backbone polymer by H-abstraction reactions.

It is observed that unlike styrene, acrylamide is not grafted at all from pure alcohol media. This may be explained as due to the following reactions. The effect of solvent would primarily, loosening the network of the polymer, so that grafting reaction can occur [145]. The efficiency of grafting in a solution will depend

upon the relative reactivity of monomer and solvent in competing for the radicals induced on the base polymer



where C' represents the peroxy radical of the base polymer, formed under the conditions of the experiment and X denotes the monomer styrene or acrylamide. The H-abstraction rate constant follows the order isopropanol > ethanol > methanol > *t*-butanol. When reaction (a) is operative, one will obtain the desired graft co-polymer, whereas in case of reaction (b) polymer backbone radical abstracts H-atom from alcohol and produces $\cdot CH_2OH$, leading to the formation of a homopolymer rather than a graft. For example, it appears that in grafting onto cellulose acetate, reaction (a) is faster when styrene is the monomer, but that the reverse is probably true, with reaction (b) faster if acrylamide is the monomer. Thus, alcohols are suitable solvents for grafting styrene, but not acrylamide, on cellulose acetate. However, when water is added gradually, grafting begins to be noticeable. On increasing water, the extent of grafting increases for the acrylamide in alcohol system. The limiting fraction f of water in the alcohol–water mixture when grafting is just initiated varies from 30 to 70% as the alcohol is changed from *t*-butanol to isopropanol. In fact, these observed f values are in conformity with those expected from the known rate constants of H-abstraction reactions from such alcohols as given above.

The grafting of styrene is suppressed by the addition of water to alcohol in the grafting medium. Incidentally, although cellulose acetate has a greater affinity for water than for MeOH, grafting from the alcohol–water mixture is affected by the decreased solubility of styrene in the solvent [143]. Nevertheless, the grafting process is characterized by a detrimental effect up to a certain limit when water is slowly added to alcohol. Beyond these limits, however, the extent of grafting increases with the gradual increase of water content, attaining a maximum and then decreasing again. The appearance of such maxima can be explained by means of Trommsdorff type effect. Since water is a poorer solvent for polystyrene, the growing homopolymer chains become sufficiently immobilized, as a result of

which their rates of collisions with the growing graft chains are decreased and consequently termination is inhibited. Such decrease in termination rate unaccompanied by change in initiation rate leads to a higher steady concentration of radicals and hence to a higher overall rate of graft co-polymerization. Subsequent decrease in grafting on further addition of water is associated with the decreasing solubility of styrene in the solvent mixture.

Diffusion of the monomer controls chain growth and chain termination in the internal structures of the polymer [146]. The solubility parameters δ of the solvents should be close to the polymeric backbone so that the necessary chemical energy to disrupt intermolecular cohesive forces between polymer chains and permit chain mobility. In general, the chemical nature of polyethylene terephthalate suppresses the formation of radicals that can initiate grafting, and in addition, the high crystallinity and ordering of the amorphous regions retard monomer diffusion. Considering PET, an $(AB)_x$ alternating co-polymer, where A is the semirigid aromatic segment $-\text{CO}-\text{C}_6\text{H}_4-$ with a δ value of 9.8 and B is a flexible aliphatic ester $-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-$ with a value of 12.1, where solubility parameters are close to those of PET, e.g. DMSO (12.93), Py (10.61), DCE (9.0). These solvents promote diffusion and incorporation of the monomer and subsequently grafting takes place. The inclusion of the solvents in the films increased with treatment time and temperature in the medium.

As wetting of the polymer by the solvents is important criteria, the surface tension data gives the useful information regarding the key role in grafting. The high graft yield in the presence of tetrahydrofuran and alcohol can be attributed to the low surface tensions of those solvents, which may significantly improve the wetting of monomer towards PTFE [147, 148]. Grafting of methacrylic acid on polypropylene fibers was reported to be same in toluene and benzene because of similar equilibrium swelling of polypropylene fiber in both solvents [149]. The homopolymer yields are also almost similar in both solvents. The significant feature of methacrylic acid grafting on polypropylene fiber is that chlorobenzene gives a higher grafting yield compared to other solvents like benzene or toluene. This is because of comparatively higher degree of swelling of polypropylene fiber by chlorobenzene. Swelling behavior of polypropylene

(PP) fibers in benzene–methanol mixture decreases continuously and almost linearly with increasing methanol content in the solvent mixture. In methanol, no swelling is observed. In this system, polymethyl methacrylate precipitates out from the reaction mixture, so that the viscosity of the reaction medium is not affected. Hence, the graft levels should be more regulated by the swelling of PP fibers in the reaction medium.

The presence of water is essential for the grafting on to collagen as onto other protenious materials. It seems that initially the water adsorbs on the surface of collagen and then grafting sites are formed directly between Bu_3B and hydrated collagen most likely via the complex [150] (Fig. 4).

For grafting mechanism, the generation of free radical of solvent is very important, besides the free-radical formation on backbone and monomer. That is why proper choice of solvent is important. The graft co-polymer (i.e. AN on starch) had more grafted chains when prepared in aqueous organic solvent systems than preparation in water alone [151]. The more frequent grafting in the presence of CH_3OH could have resulted from chain transfer to starch via free radical derived from CH_3OH has approximate same effect as water in grafting concentration of polystyrene on starch but ethyl alcohol was clearly less effective as a promoter of homograft copolymers. Methyl alcohol permeates starch structure effectively and as a result free radicals derived from methanol can easily disrupt H-bonds in starch.

In the presence of water, $\text{PP}-\text{OOH}$ may undergo swelling that facilitates the accessibility of the monomer to the active sites in case of acrylonitrile grafting on isotactic polypropylene [152]. As water has zero chain transfer constant, the side reaction involving chain transfer is minimal in water. Thus, water is an excellent medium for grafting. Grafting in

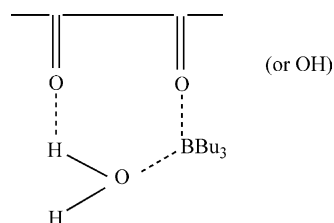


Fig. 4. Structure of the complex between collagen and Bu_3B [150]. Reproduced from J Appl Polym Sci 1983;28:87.

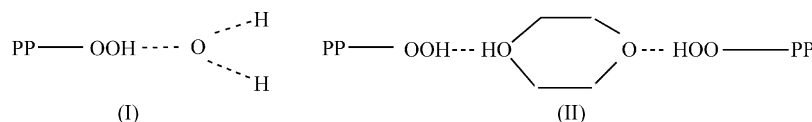


Fig. 5. H-bonded complex of polypropylene with water and dioxane [152]. Reproduced from J Polym Sci Polym Chem 1985;23:1749.

water medium is more than grafting in dioxane. This can be explained in terms of H-bonding. PP-OOH is capable of forming H-bonded complexes I and II with water and dioxane, respectively (see Fig. 5). (II) being fairly stable blocks some -OOH groups of PPOOH resulting in decrease of grafting. In the presence of methanol grafting occurs without accelerating effect. This is explained by the fact that in the presence of methanol, various chain transfer and H-abstractions are accelerated leading to decrease in grafting. The reactivity order for different solvents is water > bulk > dioxane > methanol.

3.4. Effect of initiator

Apart from the radiation technique, all chemical grafting reactions require an initiator, and its nature, concentration, solubility as well as function need to be considered. There are various kinds of initiators: ($\text{Fe}^{2+} - \text{H}_2\text{O}_2$), AIBN, $\text{K}_2\text{S}_2\text{O}_8$, etc. The nature of the initiator has a profound effect on grafting. For example, as described above, AIBN exhibits resonance stabilization. No such resonance stabilization exists with conventional peroxide initiators, and higher grafting yield should be obtained with peroxide initiators than with AIBN [153]. In another example, in the grafting of HEMA on cellulose, AIBN gives poor grafting and $\text{K}_2\text{S}_2\text{O}_8$ is unsuitable as an initiator, since it degrades the cellulose chain.

The rate of grafting is dependent upon the initiator concentration as well as the monomer and the backbone polymer [154,155]. There are various empirical relationships regarding the dependence of the grafting efficiency on the initiator concentration [156,157]. It is apparent from the observations that once a certain initiator concentration is reached, higher levels of initiator do not increase the conversion of grafted monomer [158,159]. Sanli and Pulet [146] explained the behavior in the case of acrylamide grafting on PET using Bz_2O_2 . The enhancement of grafting by increasing the Bz_2O_2 concentration to a certain limit implies that the primary free-radical

species ($\text{C}_6\text{H}_5\text{COO}\cdot$), and/or the secondary free-radical species ($\text{C}_6\text{H}_5\cdot$) formed by the dissociation of Bz_2O_2 in the polymer system, participate directly in the initiation of grafting. Above a certain limit, the abundance of these radicals leads to their participation in the termination of the growing polymer, as well as to the combination of phenoxo and phenyl radicals, thereby giving rise to decreased grafting [159]. However, it is observed that maximum graft efficiency occurs at particular initiator concentration that depends on the grafting system [160,161]. At higher concentration, Ce^{4+} participates in the termination of growing grafted chains as follows, base on an example for grafting onto wool [160]:



where WH refers to wool; M_1 and M_2 are the two monomers.

The solubility of the initiator in the grafting medium is another prime factor. Ideally, the initiator should be fully soluble so that it can initiate the grafting reaction through monomers. Nakamura et al. [162] reported an interesting observation regarding styrene, vinyl acetate, methyl methacrylate and methacrylic acid grafting on sericin (obtained by scouring silk fiber). It has been shown that water-soluble initiators were superior to water-insoluble initiators in obtaining graft co-polymers having homogeneous molecular weight distribution for the grafting of water-soluble monomers (e.g. methacrylic acid) to the sericin.

3.5. Role of additives on grafting

Grafting yield or the extent of graft co-polymerization depends on the presence of additives such as metal ions, acids, and inorganic salts. Thus, the reaction between the monomer and the backbone must compete with any reactions between the monomer and additives. Although some additives may enhance

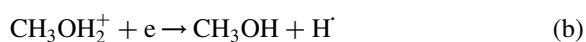
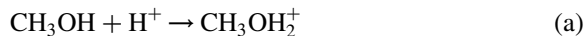
the monomer/backbone reaction to augment the grafting efficiency, the reverse will be true if the reaction between the monomer and the additive is dominant.

The role of acid additives is important in some grafting processes [116,163,164]. However, the nature of the acids is important. Among the mineral acids, only sulfuric acid is effective, dependent, of course, on the nature of the polymer backbone. The use of nitric acid is limited, for example, by the tendency to degrade cellulose during irradiation. Hydrochloric acid has been found to exert negative effect in grafting efficiency, as chlorine is incorporated in the polymer [165]. The mechanism of the acid enhancement of the grafting efficiency has been the subject of considerable work. In the case of radiation grafting, the acid enhancement is attributed to two predominant factors: the radiolytic yield of H-atoms, and the extent to which the grafting monomer is soluble in the bulk solution. Enhanced grafting (e.g. of styrene to polyolefins) due to the effects of thermalized electron captures reaction leads to increased G(H), the number of molecules formed per 100 eV of absorbed energy, and hence more sites for grafting are available by H-atom abstraction reactions. In any grafting system, there is an equilibrium concentration of monomer absorbed within the region of the backbone polymer, where grafting takes place. As the grafting proceeds, the grafting region may continually change owing to the changed composition of the grafted polymer. Thus, in grafting styrene to cellulose, during the initial part of the reactions, the grafting region is cellulosic in nature, however as the reaction proceeds, the grafting region contains an increased polystyrene component. The degree to which monomer is absorbed by the grafting region will therefore depend on the chemical structure of the region at the specific time of grafting.

The addition of acids and alkali can affect the nature of the backbone, solvent as well as the initiator, so that it can influence the grafting. Zaharan and Zhody [166] showed that when ethyl acrylate and styrene are co-grafted on sisal fiber, the presence of sulfuric acid or alkali controls the grafting yield. The increase in crystallinity due to the alkali treatment will result in reduction in the sorption capacity of the fiber. As a result, the amount of monomer solution sorbed in the fiber during the grafting process will be reduced. This accounts for the decrease in the grafting

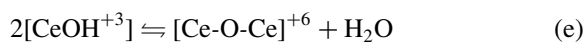
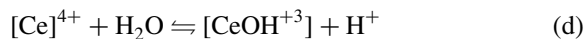
efficiency for sisal fibers subjected to alkali treatment. By contrast, when the fibers are subjected to the combined treatment, fibrillation due to the intracrystallite swelling by the acid facilitates the subsequent penetration of NaOH solution, resulting in better grafting onto cellulose. Moreover, the combined treatment may result in increase in ordering of the fibers in addition to an increase in the crystalline regions. These effects are reflected in the slight decrease in the grafting yield of fibers subjected to the combined treatment, compared to that of the fibers subjected to the alkali treatment alone.

Solvent structure is considered to be important and the lower molecular weight alcohols are efficient reagents for grafting [147]. In the presence of an acid, the radiolytically produced H-atoms (reactions (a) and (b)) abstracted H-atoms from the base polymer (PH) (reaction (c)), yielding additional grafting sites [148]



where PH refers to polymer.

Misra et al. [167,168] studied the effect of sulfuric acid in the mechanism for the grafting of methyl acrylate onto cellulose in the presence of Ce^{4+} as initiator. Maximum grafting takes place in the presence of sulfuric acid. In aqueous medium, initiator Ce^{4+} is believed to combine with water in the following manner



Thus, Ce^{4+} exists as $[\text{Ce}^{4+}]$, $[\text{CeOH}^{+3}]$ and $[\text{Ce-O-Ce}]^{+6}$ in aqueous solution. The concentration of these species varies with the acid concentration in the manner described.

From reaction (d)

$$[\text{CeOH}]^{3+} = k_1[\text{Ce}]^{4+}/[\text{H}^+]$$

where $[\text{Ce}^{4+}]$ = total concentration of ceric ion.

From the above, it is clear that $[\text{Ce}^{4+}]$ facilitates the formation of complex with the base polymer with increasing $[\text{H}_2\text{SO}_4]$, as the equilibrium shifts towards formation of more and more of $[\text{CeOH}]^{3+}$ and $[\text{Ce}]^{4+}$.

Having smaller size, these species facilitate the formation of a complex between Ce^{4+} ion and the polymer (e.g. cellulose), resulting in an increase in percentage of grafting. Beyond an optimum $[\text{H}_2\text{SO}_4]$, considerable $[\text{Ce}^{4+}]$ and $[\text{CeOH}]^{+3}$ are formed, accelerating the termination of growing grafted chains, and resulting in a decrease in grafting efficiency. The same behavior was seen for the grafting of poly(methyl methacrylate) on to wool in the presence of nitric acid [160,169].

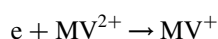
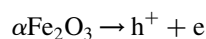
The enhancement of grafting is also been established by partitioning phenomena in the presence of an inorganic salt (e.g. LiClO_4 or LiNO_3) [170,171]. Metal salts such as LiClO_4 are more efficient than acids in enhancing photografting due to the overall monomer partitioning effect. This partitioning behavior may be interpreted as an example of the ‘salting out’ technique employed in solvent extraction, except that here one phase is a solid. The monomer solubility decreases with the addition of salts, inducing increased partitioning of monomer into the substrate. The net result of this driving force is higher rates of monomer diffusion and equilibrium monomer concentrations within the substrate. It has also been shown that LiClO_4 is more efficient than LiNO_3 in promoting UV photochemical grafting [172]. Synergistic effects in the simultaneous use of these additives have been reported [171,173].

Generally, the presence of a metal ion (e.g. Fe^{2+} , Cu^{2+}) and Mohr’s salt preferentially reduces homopolymer formation, and thus enhances grafting efficiency. The efficiency of this process also appears to be controlled by the partitioning phenomena, which can be followed visually in the grafting system when copper salts are used in the case of polypropylene [174]. When a natural polymer (e.g. cellulose) is used as the backbone, a high proportion of Cu^{2+} ions are partitioned from the bulk solution to the vicinity of the backbone. The relatively high concentration of Cu^{2+} near the backbone polymer reduces grafting because the depletion of Cu^{2+} in the bulk solution reduces scavenging of monomer radicals in the monomer solution, and thus homo-polymerization is increased. In the case of styrene grafting onto cellulose, though initially it behaves in its pure form, but as grafting proceeds, cellulose is progressively enriched with polystyrene, causing the grafting process to resemble that for polypropylene. Kubota and Hata [174]

reported that hydroquinone influences the distribution of MAA grafted chains in polyethylene film, though it has no effect on the graft efficiency in the system.

The addition of NaNO_3 or NaCl in the grafting of vinyl acetate and methyl acrylate on cellulose acetate has also been studied. The presence of NaNO_3 or NaCl affected the graft co-polymerization by enhancing the oxidation of cellulose by the transition metal ions (viz. Ce^{4+}) initiates the formation of free radicals for grafting), but it left the homopolymerization almost unaffected [175]. A comparison of different inorganic salts was studied by Lenka et al. [144,176,177], showing that grafting of methyl methacrylate onto nylon-6 was affected in the order $\text{CuSO}_4 > \text{KCl} > \text{NaCl} > \text{NaBr} > \text{LiNO}_3 > \text{NaF} > \text{MnSO}_4$. The addition of either Na-lauryl sulfate surfactant or CuSO_4 separately suppressed the formation of homopolymer, and thus increased the efficiency of grafting in the case of methyl methacrylate grafting on nylon-6. Apart from the acid enhancement and the inorganic salt effects, organic inclusion compounds like urea [178] and multifunctional acrylates [179–181] also may increase the grafting efficiency, probably by partitioning phenomena [182].

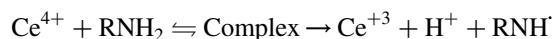
The role of semiconductor (e.g. colloidal Fe_2O_3) on grafting has also been studied [183]. Colloidal Fe_2O_3 acts as photosensitizer, which absorbs photons of bandgap energy, promoting the electrons to the conduction band, which are then scavenged by methyl viologen. The valence band holes can abstract H-atoms from the backbone (e.g. of cellulose acetate), thus creating active sites onto which acrylamide was grafted. The grafting mechanism is as follows:



The effects of complexing agents, such as ascorbic acid, potassium fluoride and EDTA, on the grafting efficiency of PEA onto cellulose have been studied [2]. All of these additives reduced the grafting of poly(ethyl acrylate) on cellulose. With KF as a complexing agent, however, the decrease in percentage of grafting was much less, and grafting occurred without homopolymer formation. With Fenton’s

reagent initiated grafting, the primary radical OH[•] responsible for the generation of active sites on cellulose is destroyed by reaction with Fe³⁺ formed during the reaction of H₂O₂ and Fe²⁺. Consequently, grafting may be favored by complexation of Fe³⁺ by a suitable agents (e.g. ascorbic acid, KF or EDTA). It is also observed, however, that further increase in the concentration of KF considerably reduces grafting of ethyl acrylate, and similar behavior was seen in the grafting of vinyl acetate in the presence of Fenton's reagent. This may indicate that whereas at a lower concentration KF reduces Fe³⁺ by complex formation, promoting grafting, at higher concentration of KF, oxidized KF to elemental fluorine derived by the oxidation of KF by H₂O₂ may add to a vinyl monomer, with a consequent decrease in percent grafting. Thus, the addition of KF did not improve the percentage of grafting of VAc to cellulose.

The effect of amines upon ceric ion initiated grafting of poly(methyl acrylate) onto wool [184] has been explained by assuming a complex formation between wool and the ceric ion. Amines are known to form complexes with ceric ion in the following manner:



The ceric amine complex decomposes to give free-radical species, which at lower concentration generate more active sites on wool by H-abstraction. However, there exists a critical concentration of amines that promotes grafting. With a further increase in concentration, the percentage of grafting decreases owing to termination of growing grafted chain-by-chain transfer with the amine:



The complex formation between the amine and Ce⁴⁺ will be determined primarily by three factors:

the basicity, the nucleophilicity and steric requirements of the amine [185]. In the case of grafting poly(methyl acrylate), the reactivity of amines followed the order: triethylamine > diethylamine > *n*-butylamine > triethanolamine > *N,N* dimethylaniline. The grafting percentage increases linearly with an increase in the basicity of the amines. This would be expected the complexation of amines with ceric ion should be enhanced by increased basicity of the amine. The exceptional behavior in case of triethylamine is due to the fact that with triethylamine both the nucleophilic reactivity of the amine to form a complex with Ce⁴⁺, and the stability of the complex between Ce⁴⁺ and the amines is dependent on the ability of various substituents in the amines to increase electron density at nitrogen. Because of its three ethyl groups, triethyl amine is more nucleophilic than diethylamine, which will facilitate the formation of a complex with Ce⁴⁺. Because of increased crowding, the triethylamine Ce⁴⁺ complex readily undergoes decomposition to yield free-radical species, which by abstracting H-atom create more active sites on wool to initiate grafting. The grafting efficiency generally increases as the size of the amines increases. This indicates that because of their large size, tertiary amines will form complexes with Ce⁴⁺ only at a higher concentration of the ion. The oxygen atom at the β-position in triethanolamine reduces the electron density in nitrogen, and hence does not aid in the formation of a complex. Complex formation between Ce⁴⁺ and dimethylaniline is not favored because of the electron delocalisation in the amine, which will reduce and may completely suppress grafting (see Fig. 6).

In the case of grafting poly(vinyl acetate) onto wool, the effect of amines has been studied for triethyl and triethanolamines [7]. Since complex formation

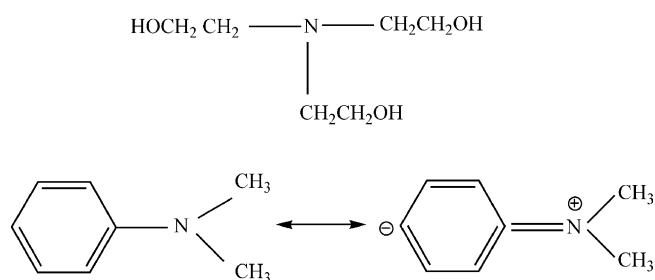
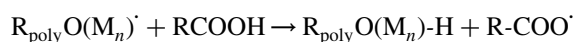
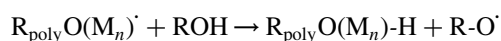
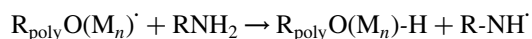


Fig. 6. Structure of ethanolamine and dimethylaniline [186]. Reproduced from J Polym Sci Polym Chem 1980;18:1911.

between Ce^{4+} and triethylamine is inhibited in the presence of vinyl acetate, hence no acceleration in grafting occurs on addition of the amine. As mentioned earlier, with triethanolamine the oxygen reduces the electron density on the nitrogen, and complex formation between Ce^{4+} and triethanolamine is not favored. In addition, the size factor also inhibits the complex formation between triethanolamine and Ce^{4+} . Thus, neither grafting nor homopolymerization are favored in the presence of triethanolamine.

The reactivity of various amines toward graft copolymerization onto wool [186] followed the order diethylamine > dipropylamine > ammonia > triethylamine > triethanolamine > pyridine. Though diethylamine is as nucleophilic as dipropylamine, only DEA enhances grafting rate tremendously, while in the presence of DPA no accelerating effect upon grafting efficiency is observed. This is explained by the steric factor, such that DEA, having a smaller steric requirement than DPA, easily forms a complex with Ce^{4+} . The substantial difference in behavior between DEA and DPA is also explained by the steric factor. Ammonia, having a smaller steric requirement than TEA, forms a complex with Ce^{4+} more easily than does TEA. With triethanolamine and pyridine, all three factors (basicity, nucleophilicity and steric size) are responsible for giving a low efficiency of grafting.

L-Threonine possess -OH, $-NH_2$ and $-COOH$ groups capable of forming complexes with Ce^{4+} [169]. In general, the efficiency of grafting of methyl acrylate on cellulose was found to increase with increasing L-threonine concentration, but at higher concentration of L-threonine, the complex formation is reduced through competition by an enhanced rate of abstraction of H-atom from L-threonine by the growing grafted chains:



Grafting of methyl acrylate on cellulose was suppressed by 5-hydroxytryptophane and 5-hydroxytryptamine additives. Apparently, the phenolic -OH groups present in these additives inhibit both polymerization and grafting. This may indicate that

radio-protecting agents involve a free-radical mechanism in their mode of action.

3.6. Effects of temperature

The temperature is one of the important factors that control the kinetics of graft copolymerization. In general, grafting yield increases with increasing temperature, until a limit is attained. One factor in this can be faster monomeric diffusion processes in the backbone increases with increasing temperature, facilitating grafting, as observed by Dilli et al. [140]. In the case of grafting MMA on silk, the graft yield increases significantly with increasing temperature due to greater swelling of silk, and a corresponding enhanced rate of diffusion of the monomers in the vicinity of silk [188]. However, Sun et al. [140] explained this behavior as increased thermal decomposition rate of initiator and the initiator efficiency in producing free-radicals on base polymer with increasing temperature, resulting in increased polymer macroradicals concentration, and thus enhanced the graft polymerization. Increasing temperature, initially enhancing the grafting yield, facilitates the decomposition of peroxide. However, as reported by Maldas [189], the grafting yields subsequently decreases with an increase in temperature in case of acrylamide grafting on cellulose acetate. The initial increase in grafting is due to the decomposition of peroxides formed as a result of irradiation of the base polymer in air, making the requisite radicals available for grafting, and the subsequent decrease is due to the increased molecular motion with increased temperature, resulting in increased radical decay. One interesting observation is that the maximum graft yield occurs for a temperature near the glass transition temperature [146,190]. For temperatures below the glass transition temperature T_g , the radicals formed in the polymer chains cannot react, owing to the reduced diffusion of the monomer, whereas for T above T_g , the number of radicals available for grafting will decrease with increasing temperature; with increasing temperature, the combination of monomer radicals results in lower graft yield [191].

4. Applications

Modified polymers can be very useful as they can be tailored to the requirements of particular applications. There are, in fact, many applications of grafted polymers, a number of which were discussed in a previous paper in this journal by one of the authors [192]. Here, discussion is limited to two different applications for grafting materials, viz. membranes for separation technology and conducting polymers.

4.1. Membrane separation science

For use in separation technologies, a membrane may be considered to be a phase that acts as a barrier to prevent mass movement in general, but allows restricted and/or regulated passage of one or more species through it, i.e. it controls the selective transfer of molecules or ions. This specificity is almost always due to some kind of heterogeneity in the membrane [193]. In general, homogeneous films are not suitable in separation science. Separation process through membranes started after the discovery of osmosis by Abbe Nolet in 1748. Fick first developed the first synthetic membrane, made apparently of nitrocellulose in 1855. Bechhold, around the year 1907 developed methods for controlling the pore size of the collodion membranes. He is generally credited with introducing the term ultrafiltration [194].

Different conventional techniques are available in separation science, but separation through membranes is advantageous, and is often preferred due to advantages including low cost of the technique,

energy savings and no requirement for a change of phase or state of the solvent. Thus, membrane based separation science is a part of the Green Mega drive, i.e. it is a technique with reduced energy consumption, and hence less environmental pollution.

There are a number of membrane based separation techniques, varying in the driving forces employed, including concentration, pressure and electric potential. For example, osmosis and dialysis, useful in the separation of solutes involving large molecules, are concentration driven. Microfiltration, ultrafiltration, nanofiltration, and reverse osmosis are pressure driven techniques, by which solutes of different sizes may be separated, as shown in Table 2. Pervaporation especially suitable for separation of azeotropic mixture is a vacuum driven technique, in which volatile small molecules pass through the membrane. Thus, a non-volatile solute can be separated from the volatile solvent. Electrodialysis is an electric potential driven separation technique useful to separate ionized molecules.

Polymeric substances are often the material of choice in the development of membranes with desirable separation properties, as well as chemical and environmental stability. Unfortunately, though polymeric membranes exhibit general separation ability, they may not possess the specific separation ability needed or have the necessary mechanical properties. Consequently, serious efforts have been devoted for the development of the polymeric membranes, and in this context, 'grafting' is a popular method to modify the polymeric membranes. It is a simple method to obtain 'tailor-made' membranes with specific properties, and is conveniently

Table 2
Membrane based separation techniques

Process	Driving force	Retentate	Permeate
Osmosis	Concentration difference	Solutes, water	Water
Dialysis		Large molecules, water	Small molecules, water
Microfiltration	Pressure	Suspended particles, water	Dissolved solutes, water
Ultrafiltration		Large molecules, water	Small molecules, water
Nanofiltration		Small molecules, divalent salts, dissociated acids, water	Monovalent ions, undissociated acids, water
Reverse osmosis		All solutes, water	Water
Pervaporation	Vacuum	Non-volatile molecules, water	Volatile small molecules, water
Electrodialysis	Electrical potential	Non-ionic solutes, water	Ionized solutes, water

implemented by grafting polar monomers onto tough hydrocarbon polymers.

Separations involving polymeric membranes have gained enormous popularity, and a membrane separation technique is the method of choice in the desalination of sea-water. Here, we are interested in membranes prepared through the modification of a parent polymer. For convenience, the existing membranes obtained through a graft co-polymerization processes are divided in two major categories, depending on whether they operate on aqueous or non-aqueous media. Apart from these, some other membranes that can be used in gas separation will also be considered.

4.1.1. Separation from the aqueous systems

The separation of water–ethanol mixtures is a useful aqueous industrial application. There are a number of reports on the preparation of membranes suitable for this separation by grafting [195,196]. Chowdhury et al. [197] reported a polystyrene grafted cellulose acetate membrane. The separation performance of the membrane increased with grafting percentage up to an optimum level, the separation efficiency decreased with further graft content due to decreasing preferential solubility in water, as the formation of homopolystyrene in the membrane increased. Ihm and Ihm [198] reported the use of membranes prepared by grafting polystyrene (PS) onto a porous polyvinylidene difluoride (PVDF) to address this problem in the separation of water–ethanol mixtures by pervaporation. Membranes were prepared of the graft co-polymer, PVDF-*g*-PS, its sulfonated derivative, PVDF-*g*-PSS, and the sodium salt of the latter, PVDF-*g*-PSS[−]Na⁺. The permeation rate followed the order: PVDF-*g*-PSS[−]Na⁺ > PVDF-*g*-PSS > PVDF-*g*-PS. The separation factor depended on the weight fraction of ethanol in the feed: of the PVDF-*g*-PSS[−]Na⁺ membrane was higher than that of PVDF-*g*-PSS for ethanol content greater than 60 wt%, but the reverse was found for lower ethanol content. The so-called swelling or salting out effect can explain this [199]. The swelling of the PVDF-*g*-PSS[−]Na⁺ membrane was dominant with excess water in the feed mixture, but the salting out effect (exclusive effective for ethanol) was dominant in the presence of an ionized group in the feed mixture. Niemolter et al. [200] classified different

types of interactions with the grafted membrane. In this respect, the behavior of membranes is related to the polar, basic, acidic or ionic functional groups grafted to the backbone (e.g. neutral: *N*-vinyl pyrrolidone, *N*-vinyl methylacetamide, vinyl acetate; basic: 4-vinyl pyridine, *N*-vinyl imidazole; acidic: acrylic acid, methacrylic acid). The nature of intermolecular interactions then varies with the functional group type: neutral functionality, dipole–dipole interaction; basic/acidic functionality, H-bond interaction; and ionic functionality, ion–dipole. Non-ionic membranes exhibit moderate separation factors, e.g. $\alpha_{\text{H}_2\text{O}} = 2\text{--}15$, where $\alpha = Y_{\text{w/E}}/X_{\text{w/E}}$ with $Y_{\text{w/E}}$ and $X_{\text{w/E}}$ the concentration ratio of water(w) and ethanol(E) in the permeate and in the feed, while ionic grafted chains lead to very low ethanol concentration in the permeate, corresponding to $\alpha_{\text{H}_2\text{O}}$ up to 1000 for 80% ethanol in the mixture.

Ionized porous membranes of PP-*g*-poly(acrylic acid) show good pervaporation performance (for EtOH–H₂O mixture) [201,202], with that performance dependent upon the grafting degree of poly(acrylic acid) and with a water permselectivity dependent upon the poly(acrylic acid) content. The separation factor increased with increasing graft PAA content in the range of 30–70 wt%. It has been reported that PAA grafted membranes with both high selectivity and high permeation flux to water can be obtained when counter ions such as Li⁺, Na⁺ and K⁺ are incorporated into the membrane [203]. Incorporating different metallic counter ions as well as multifunctional co-monomer into the grafted chains could improve the selectivity, but sacrificed the permeation flux. The separation factor of the counter ion containing membrane decreased according to the order Al³⁺ > K⁺ > Ca²⁺ > Na⁺ > Li⁺, and the permeation flux reversed.

The solution diffusion model can be explained by the reason of selectivity [204,205]. The pervaporation selectivity is the product of sorption selectivity and a complex interaction of diffusion effects. Since H₂O is the penetrant with the lower molecular weight in the EtOH/H₂O mixture, it is expected that the diffusion coefficient of H₂O in the grafted membrane is somewhat higher than that for EtOH. However, high selectivity for H₂O cannot be explained by diffusion effects only, but have to be attributed to a preferential

sorption of H₂O, and an effective exclusion of EtOH from the membrane phase.

By introducing poly(*N*-isopropyl acrylamide) onto PVA membranes, significant temperature sensitivity was observed in the pervaporation processes to separate ethanol from ethanol–water mixtures [206]. The membrane showed maximum pervaporation selectivity and sorption selectivity at temperature close to the lower critical solution temperature (LCST) of pure linear poly(NIPAAm) in water/EtOH mixture. The cross-linked poly(NIPAAm) gels in water shrink abruptly as the temperature increases above 32 °C, close to the LCST of linear poly(NIPAAm) in water. This behavior results from extensive H-bonding at low temperature, which is reduced, leading to the phase separation above the critical temperature. The existence of the grafted poly(NIPAAm) changes the hydrophilic/hydrophobic balance and the polarity of the functional groups within the grafted membrane and thus alters their swelling and sorption properties.

In addition to the EtOH–water separation, there are various reports of grafted membrane to separate an organic liquid from aqueous mixtures. An acrylic acid or methylacrylic acid grafted polyvinyl alcohol membrane was prepared for CH₃OH/H₂O separation by Shantora and Huang [207]. They proposed that the separation phenomena involved H-bonding interaction. Graft co-polymers of poly(acrylic acid) onto nylon-6 are suitable for separation of AcOH–water mixture [208]. In this case, separation factors of AcOH–water up to 300 and flux rates 40–60 g/m² h were observed. The selectivity and permeation fluxes obtained for the grafted membranes were higher than those for the blended membranes [209]. Ethyl acrylate and Bu-acrylate-*g*-PE membranes showed permselectivity for chloroform, and efficiently removed chloroform from water by the pervaporation technique [210]. The Bu-acrylate grafted membrane showed higher permselectivity for trichloroethane than for chloroform. The Bu-acrylate grafted membrane exhibited higher selectivity and permeability than a cross-linked Bu-acrylate membrane [211].

Several attempts have been made to eliminate Na-alkyl benzene sulphonate (ABS) from water by reverse osmosis technique, using membranes prepared by graft co-polymerization of acrylic acid onto polypropylene in a homogeneous phase, with

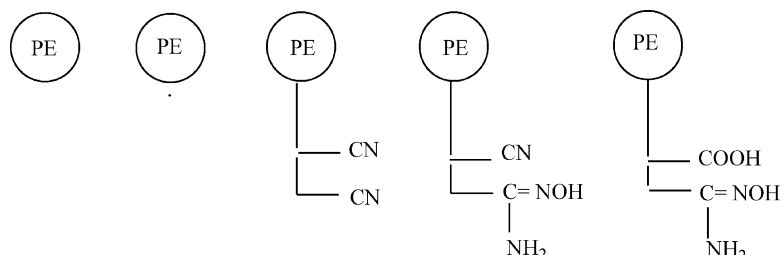
the subsequent formation of thin films on glass surfaces [212]. It has been reported that 7 l/m² h flux and 33.3% ABS rejection were obtained in a reverse osmosis operation at 50 atm. using a water conditioned 5 μm thick poly(propylene)-*g*-acrylic acid membrane. The high flux and low ABS rejection were attributed to direct permeation of water through passing channels formed by microfractures in the polypropylene matrix. They also reported the 0.5 l/m² h flux and 100% ABS rejection were obtained using a 23 μm thick-grafted membrane, brought about by water permeation through the grafted poly(acrylic acid) hydrophilic regions. The rejection was attributed to a preferential sorption and diffusion mechanism.

Yamakita and Hayakawa [213] reported that a maximum flux 5.26 l/m² h and 99.6% ABS rejection were obtained in a reverse osmosis operation at 20 atm using a nylon-*g*-poly(sodium styrene sulphonate) membrane having degree of grafting of 313.3%. The rejection of ABS was almost 100% with some non-ionic membranes, e.g. nylon-*g*-poly(vinyl pyrrolidone). Pegoraro et al. [212] assumed that the membrane behaved as a homogeneous hydrophilic polymer matrix in the latter case.

A porous, hollow-fiber polyethylene membrane containing grafted diethyl amino (DEA) groups has been reported to control water/acetone permeability [214]. The membrane was prepared by radiation induced graft polymerization of glycidyl methacrylate (GMA) on polyethylene, followed by reaction of the resulting epoxide group with an aqueous diethylamine solution (see Scheme 13).

Graft chains were formed both on the pore surface and in the amorphous domain of the porous polymer matrix, and were uniformly distributed throughout the porous membrane. The conformation of the grafted chains penetrating into the amorphous domain determines the swelling of the membrane, and stretching and shrinking of the polymer chains grafted onto the pore surface governs the permeability of water and acetone across the membrane through the pores. The density of the DEA group had a decisive effect on water/acetone permeability of the resulting DEA treated fiber.

There are many reports on the use of grafted polymeric membranes in desalination. Composite membranes comprise a porous support, a cross-linked



Scheme 14. Post-reaction of acrylonitrile grafted polyethylene membrane [225]. Reproduced from J Appl Polym Sci 1990;39:2153.

a high crystallinity of the base polymer enhanced the separation of dioxane/water azeotropic mixture. An AN/HEMA grafted PVA latex membrane composed of well-balanced hydrophilic hydrophobic components have the ability to separate phenol/water solution [221]. A polypropylene-*g*-HEMA dialysis membrane showed improved permeability towards urea and uric acid and the permeability was about 4.6–19 times larger than that obtained using a polypropylene membrane, and the urea permeation coefficient of the grafted membrane was close to that with cuprophan (regenerated cellulose, that has been strengthened by cupramonium solution treatment) [222]. Ethylene tetrafluoroethylene membrane grafted with cross-linked sulphonate styrene and cross-linked aromatic monomer is useful in acid recovery by dialysis, electro dialysis and electroelectrodialysis techniques. The grafted membranes showed excellent performance [223]. Takagami et al. [224] reported that AA/AM-*g*-nylon-6 membranes show permselective behavior towards urea and KCl, with the permselectivity increasing with the percentage of grafting. Treatments of PE-*g*-AN hollow fiber membranes [225] to create amidoxime functionality in the micropores (see Scheme 14) facilitate the diffusion of uranyl ion-species ($\text{UO}_2(\text{CO}_3)_3^{4-}$) in sea-water. A recent report [226] shows that urease immobilized on nylon membranes grafted with cyclohexyl methacrylate has potential for the removal of urea from agricultural waste water; hexamethylene diamine and glutaraldehyde were used as spacer and cross-linking agents, respectively.

4.1.2. Separation from non-aqueous systems

In membrane separation science, most of the polymer materials exhibit selectivity to water permeation, with only a few found to be selective to

the permeation of organic compounds [227]. However, the separation of binary organic mixtures, such as aromatic/non-aromatic hydrocarbon mixtures, potentially offers the largest opportunity for energy and cost savings. As a consequence, considerable efforts have been devoted to the preparation of pervaporation membranes with good performance and stability for the separation of organic–binary mixtures. Nevertheless, there are only a few reports of the use of grafted polymers for this purpose.

The separation of cyclohexane/cyclohexanone/cyclohexanol mixtures is important in connection with the production of ϵ -caprolactam in the nylon-6 industry. Cyclohexanol is prepared by the air oxidation of cyclohexane. However, since the conversion of cyclohexane reaction is only about 5–10%, the reaction mixture contains a large amount of unreacted cyclohexane, and the separation of the mixture of cyclohexanone and cyclohexanol requires a three-step distillation. In this case, the composition of each component in the feed solution is cyclohexane, 0.0216–0.9812 weight fraction, cyclohexanone or cyclohexanol 0.009–0.4892 weight fractions. The weight ratio of cyclohexanone to cyclohexanol is unity. Separation of cyclohexanol from the mixture of cyclohexane/cyclohexanone/cyclohexanol can be achieved through a nylon-6-*g*-polyoxyethylene membrane [228]. The selective separation of cyclohexanol/cyclohexanone through the membrane currently available is caused by a carrier-mediated mechanism based on an H-bonding interaction between the -OH groups of cyclohexanol and those present in the grafted chain [229]. In other words, rejection of cyclohexane from the cyclohexane/cyclohexanone/cyclohexanol mixture is achieved because of the low H-bonding ability of cyclohexane compared with that for cyclohexanol and cyclohexanone; the H-bonding

ability order is cyclohexanol > cyclohexanone > cyclohexane.

Wang et al. [230–232] prepared a poly(GMA) grafted polyethylene film, which was made homogeneous on both sides by appropriate treatment. The grafted membranes showed good performance in separating benzene/cyclohexane mixture. The membranes prepared by the homogeneous two-side treatment and under mild polymerization conditions displayed the highest performance, with a permeation flux of 0.3–0.37 kg/m² h and a separation factor of 19–22 at 60 wt% feed benzene at 70 °C. Yamguchi et al. [233–235] prepared HDPE-*g*-MA membrane by a plasma graft filling polymerization technique. In the technique, the membrane composed of two materials, the porous substrate and the filling polymer, which fills the pores of the substrate. Plasma grafting technique is employed to graft the filling polymer with the backbone polymer. The porous substrate is inert to organic liquids and the filling polymer is soluble with one component in the feed, i.e. organic liquid mixture. The filling polymer exhibits permselectivity due to the solubility difference, and the porous substrate matrix restrains the swelling of the filling polymer due to its mechanical strength. The membrane exhibits high permselectivity and flux of chloroform for the chloroform/*n*-hexane mixture. A PVC-*g*-poly(butyl methacrylate) material [236] was found to form an effective permselective membrane for the selective separation of benzene from benzene/cyclohexane mixture, as methyl acrylate has a very high affinity for benzene. The permeation rate was enhanced by the introduction of poly(butyl methacrylate) onto the PVC membrane. Polyacrylonitrile-*g*-methyl acrylate membrane prepared by heterogeneous photoinduced grafting also showed benzene permselectivity for benzene/cyclohexane mixture (50/50 v/v) during pervaporation.

4.1.3. Temperature and pH sensitive membranes

There are reports of preparation of temperature sensitive membrane by grafting *N*-isopropyl acrylamide on different polymer matrices, and pH sensitive membrane by grafting poly(acrylic acid) on a polysulfone membrane [110,237]. Poly(*N*-isopropyl acrylamide) is soluble in water, but has a LCST around 31–33 °C. As a consequence, the water filtration rate of the poly(*N*-isopropylacrylamide)

grafted PVDF membrane varies more than 10-fold between temperatures above and below the LCST, reflecting the phase change of poly(*N*-isopropyl acrylamide). The temperature sensitivity is reversible and reproducible.

Ogata et al. [238] reported that changing temperature could control the permeation rate of K/Li salts through PVA-*g*-*N*-isopropylacrylamide. The permeation rate decreased as the size of the hydrated salts increased in the order of KCl, LiCl and lithium dodecyl sulfonate (LiDS). The permeation of LiDS was considerably slower than that of other salts. The permeation of KCl and LiCl was strongly suppressed above the LCST, while the permeation of LiDS was less suppressed. The permeation rate through the well-swollen membrane below 30 °C was slower for *n*-BuOH, with its low solubility, than for *t*-BuOH, with its higher solubility, while their permeation rates were reversed above 35 °C. The permeation of the Li⁺ ion was less than that for methylene blue (MeB), with maximum permeation rates at ≈ 35 and 25 °C for Li⁺ and MeB, respectively. This implies that the depression of permeation rates of both Li⁺ and MeB at higher temperature results from the phase transition of PVA-*g*-NIPAAm membrane [239].

Polysulfone membranes grafted with poly(acrylic acid) are pH sensitive, and show different permeability of riboflavin as a function of pH [240]. The changes in the riboflavin permeation through the grafted membrane are noted particularly at pH equal to 4 and 5, due to electrostatic repulsion between the carboxylate ions. Above a pH of 4.8, the pK_a of polyacrylic acid (PAAc), the -COOH groups are dissociated into carboxylate ions and have an extended conformation because of the electrostatic repulsion forces between the chains. It results in the blocking of the pores of the polysulfone membrane, thus decrease in the permeability. At pH below 4.8, as carboxylic acid groups do not dissociate, the grafted polyacrylic acid chains will shrink and be precipitated on the surface of the polymer backbone. Thus, the pores become open and permeability sharply increases. These conformational changes are obviously due to both intra and intermolecular interaction between the grafted chains. The permeability of the modified membrane depended on the amount of grafting also, so that further grafting of PAAc on the polysulfone membrane surface does not

guarantee the retention of pH sensitivity for riboflavin permeation. An optimum grafting amount in terms of pH sensitivity was found to be $53 \mu\text{g}/\text{cm}^2$ in the grafted membrane. Such pH responsive membranes will be useful for sensing and modulating external chemical signals, and also for drug delivery applications, as they change their chain conformation according to the electrostatic interactions between charged groups.

4.1.4. Enantioselective membranes

Though their structure is similar, enantiomers (i.e. optical isomers) can differ in their permeability through membranes. Satoh et al. [241] showed that a polyacrylonitrile-*graft*-[(1 \rightarrow 6)-2,5 anhydro 3,4 dimethyl D-glucitol] membrane has enantioselective property. The permeation rate of amino acids decreased in the order phenyl glycine > phenyl alanine > tryptophane, following the molecular size of the compounds. For all the amino acids, the permeation rate of the D-isomer was greater than that of L-isomer (e.g. for phenyl glycine perchlorate, the permeation of the D-isomer is 1.17 times faster than that for the L-isomer). A microporous PP membrane with its surface modification by poly(γ -stearyl-L-glutamate) has the potentiality as chemical valves [242]. It has the amphiphilic side chains. The α -helical secondary structure of the poly(γ -stearyl-L-glutamate) is stabilized via H-bond formation, as well as hydrophobic and electrostatic interactions. The reason for the enantioselectivity for amino acids is considered to be the ordered structure [243].

4.1.5. Gas separation membranes

Although facilitated transport membranes for gas separation have attracted attention as they can have a very high selectivity compared with conventional polymeric membranes, there are few reports regarding the grafted membranes. There are two types of carrier transport membranes, one is a mobile carrier membrane (liquid membrane) where the carrier can diffuse in the membrane and the other is a fixed carrier membrane, where the carrier is immobilized into the membrane matrix and cannot move. Ion-exchange membranes have been reported and a highly swollen ion-exchange membrane prepared by grafting acrylic acid onto a microporous membrane is useful as a support for the facilitated transport of CO_2 with

ethylenediamine as the mobile carriers [244]. The membrane had a high stability as well as high selectivity for CO_2 over N_2 . The stability was attributable to both hygroscopicity of the poly(acrylic acid) gel membrane and retainment of the carrier by electrostatic forces. In the fixed carrier membrane, the permeation of the species, which can interact with the fixed carrier, is depressed compared with the mobile carrier membrane, where carriers can move freely. A PE-g-dimethyl amino ethyl methacrylate (DAMA) membrane is expected to act as a fixed carrier membrane [245]. Fixed carrier membrane are generally favorable compared with mobile carrier membrane because there is little chance of carrier effusion. In a dry membrane, the facilitated transport of CO_2 is probably based on the acid–base interaction between CO_2 and the amine moiety incorporated in the membrane. On the other hand, the CO_2 hydration reaction is thought to occur in membranes containing water. The selectivity of CO_2 over N_2 reached as high as 130 for the water containing membranes, for a CO_2 partial pressure in the feed gas of 0.047 atm. Suzuki et al. [246] reported a permselective membrane by grafting of dimethyl siloxane onto a poly(styrene-co-maleic anhydride) backbone. The gas permeation characteristics of the membrane obtained are close to the values of a pure poly(dimethyl siloxane) membrane. The permeability coefficient was of the order of magnitude of $10^{-8} \text{ cm}^3 \text{ (STP) cm/cm}^2 \text{ s cm Hg}$ for O_2 gas and gave an ideal separation factor of 2.3 for the O_2 - N_2 system.

4.1.6. Miscellaneous

Apart from the applications described above, grafting can counter the problem of membrane fouling, one of the serious limitations in membrane processes. ‘Fouling’, or adsorption of material on the membrane surface, can destroy the usefulness of the membrane. Adsorption can be avoided or minimized by the introduction of appropriate groups (hydrophilic/hydrophobic) at the surface through grafting or coating over the membrane surface. If hydrophilic groups are incorporated, they increase the wettability of membrane surface to reduce their ability to interact with species present in the solution. The advantage of grafting technique compared with coating is that graft chains are chemically bonded to the membrane matrix, which means that they will not detach from

the membrane substrate when solvent permeates through the membranes.

There are various reports in this regard. Free-radical grafting of glycine to the surface of a PVDF membrane under strongly basic conditions can render a hydrophilic surface. Similarly, grafting phosphorylcholine derivative subsequently improved the fouling resistance of PVDF and cellulose acetate [247]. Nylon tends to bind large amounts of protein, even though it is inherently wettable and hydrophilic. This fouling tendency can be reduced by radiation grafting polymers rich in hydroxyl groups (e.g. hydroxy propyl acrylate and hydroxy propyl methacrylate) [248]. Surface modification of commercial composite polyamide reverse osmosis membrane by both acrylic acid sulphoacidic monomers, as well as neutral monomers, such as polyethylene glycol methacrylate, has been used [249,250]. A commercial polyether sulfone (PES) microfiltration membrane with lower fouling properties was made by photoinduced grafting of neutral monomers (NVP and HEMA), weakly acidic monomers (AA, 2-acrylamidoglycolic acid) and two strongly acidic (sulfonic) monomers (3-sulfopropyl methacrylate (SPMA) and 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS)) and quarternary 2-dimethyl amino methyl methacrylate [251,252].

4.2. Conducting polymers

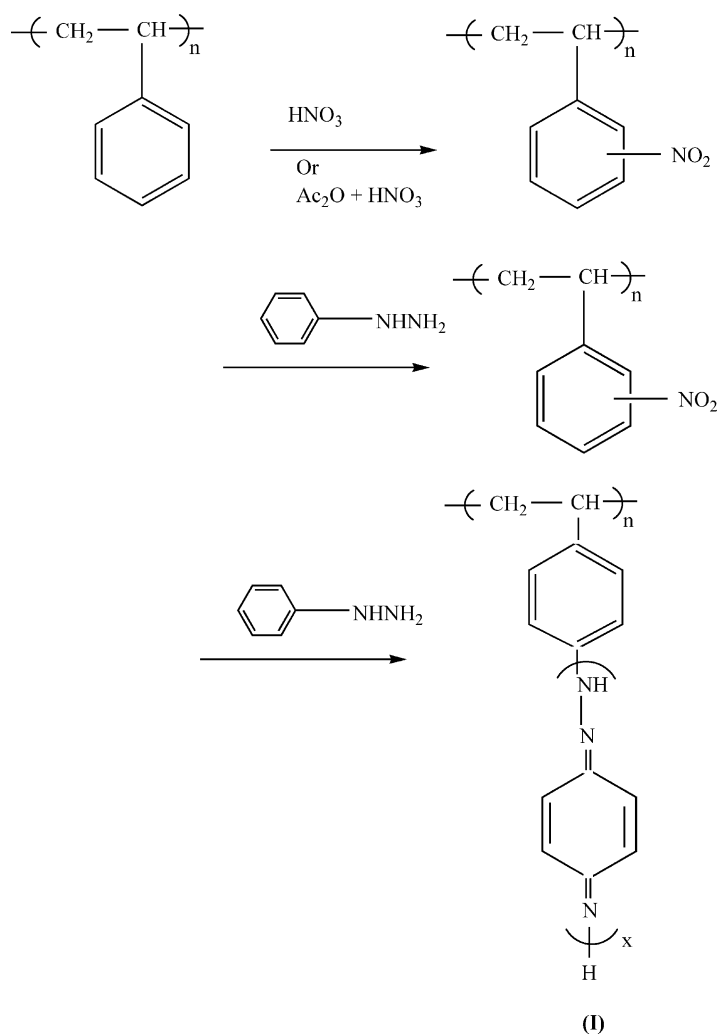
The history of the conducting polymers started in the modern age from the accidental discovery of polyacetylene by Shirakawa in 1970. Afterwards Heegar, Mac Diarmid and Shirakawa (1977) tried to explain the conductivity phenomena. They coined the term 'synthetic metals' as they are non-metallic substances with conduction properties tending toward those of metals. These materials, while being organic, have the unusual property of possessing high electrical conductivity, and can exhibit a range of properties from 'semiconducting' to 'near metallic'. In the vast insulating polymeric ocean, they present a small 'Metallic Island'. The durability, cheapness, easy processability, conductivity in semiconducting range and corrosion free properties has inspired visions to utilize them in various applications.

Conducting polymers have received attention now-a-days because of their potentiality in different fields,

such as electrochromic displays, optoelectronic devices, photovoltaic devices, modified electrodes, chemical/bio-sensors, etc. These polymeric materials can be obtained in various forms, such as powders, thin films, etc. In order to obtain a material suitable for applications in various technologies, the conducting polymer has to overcome certain limitations, such as poor mechanical properties and problems in processing, as well as instability under the relevant ambient conditions. Grafting provides a potential technique to overcome these limitations, with either or both of two objectives: to improve the processability of conducting polymers, and to obtain the particular use properties required for a target application.

Conducting polymers are often insoluble, though there are various reports of soluble variants in recent years [253]. Often, a polymer that will become conducting when doped, may be soluble in the doped state, but aggregates upon doping in solution. The exact mechanism for the aggregation is not yet clearly elucidated. Two possible causes for this aggregations are: (1) an increase in rigidity of the polymer chains on doping and (2) increased polar interactions between the polymeric chains. Conducting polymers have some similarities to conventional polymeric materials, but it is clearly the extensive main chain π -conjugation and its implicit 'stiffness' with respect to chain bending and twisting that most influences the overall physical behavior. As a direct consequence virtually all linearly unsubstituted conducting polymers are found to be intractable and infusible, presenting a significant challenge to their use.

Self-doped conducting polymers prepared by grafting techniques afford a water-soluble polypyrrole. Here, the grafting of pyrrole onto *p*-amino diphenylamine moieties of water-soluble 2-acrylamido-2-methyl-1-propane sulphonic acid-*N*-(4 aniline phenyl) methacrylate co-polymers produces the desirable property [254]. Polyaniline (PANI), was also made soluble by polymerizing aniline in an aqueous solution of poly(*p*-amino styrene) [255] to form a graft co-polymer (see Scheme 15) that is soluble in some common solvents. Apart from (I), Li et al. [256] also prepared different PANI based graft co-polymers (II) and (III), see Fig. 7. Grafting reduces the rigidity of the polymer chain, as a result solvation can occur by the solvents, imparting solubility.



Scheme 15. Reaction scheme for preparation of polyaniline based graft co-polymer [255]. Reproduced from Synth Met 1987;20:141.

Soluble, film forming chitosan-g-PANI [257] can be prepared by polymerizing aniline onto a stable aqueous solution of a soluble film-forming stable material in the presence of protonic dopants (Scheme 16).

Attempts have been made to prepare graft copolymers of MMA [258,259] and MMA-2BEMA [260] with pyrrole by grafting techniques. Graft copolymers with very low pyrrole or polypyrrole content were soluble, but they became rapidly insoluble with increasing pyrrole content, due to the presence of long pyrrole sequences. The conductivity of these composites is 10^{-2} S/cm. The reaction scheme is shown in Scheme 17.

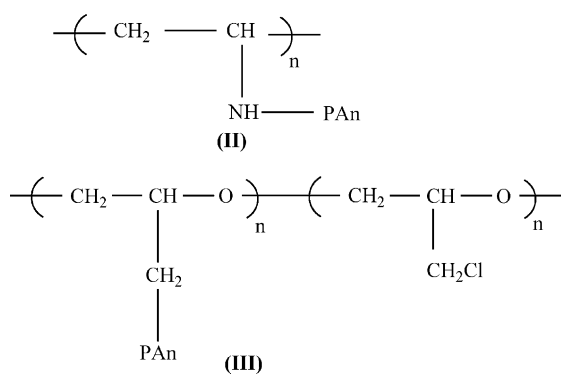
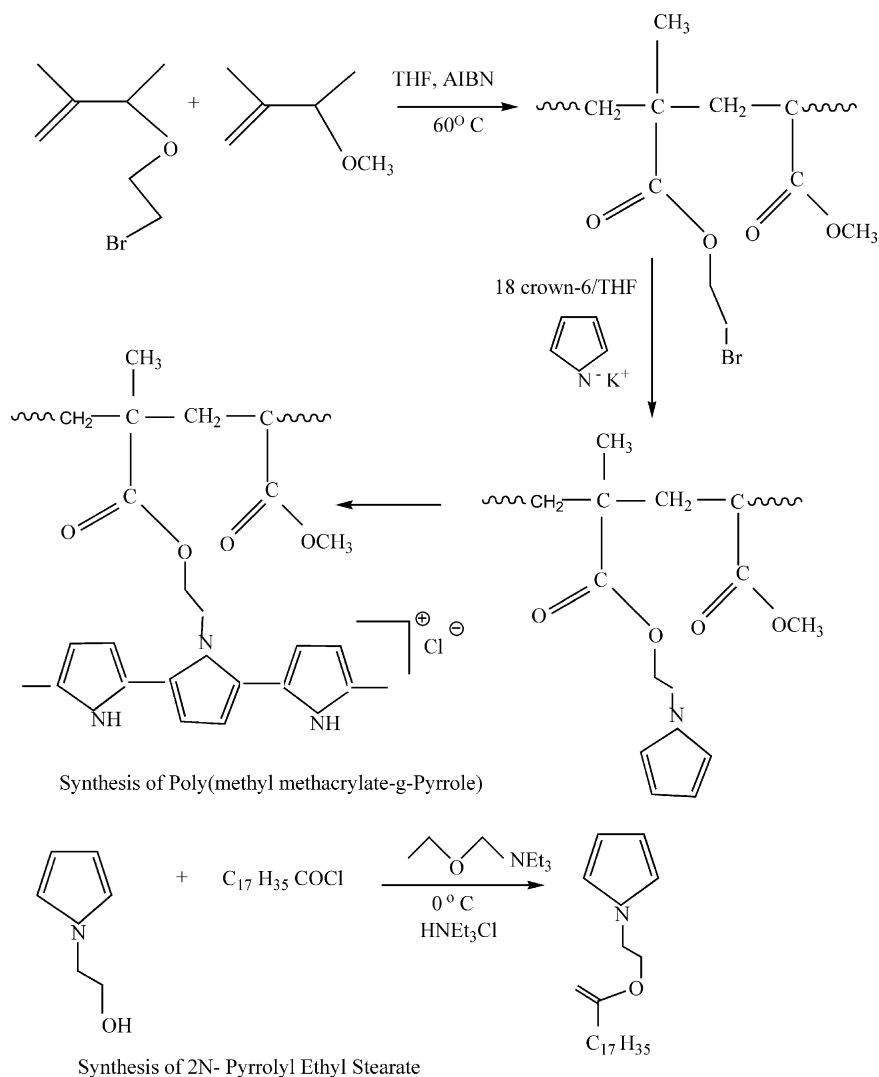


Fig. 7. Structure of aniline based graft copolymers [256]. Reproduced from Synth Met 1989;29:329.

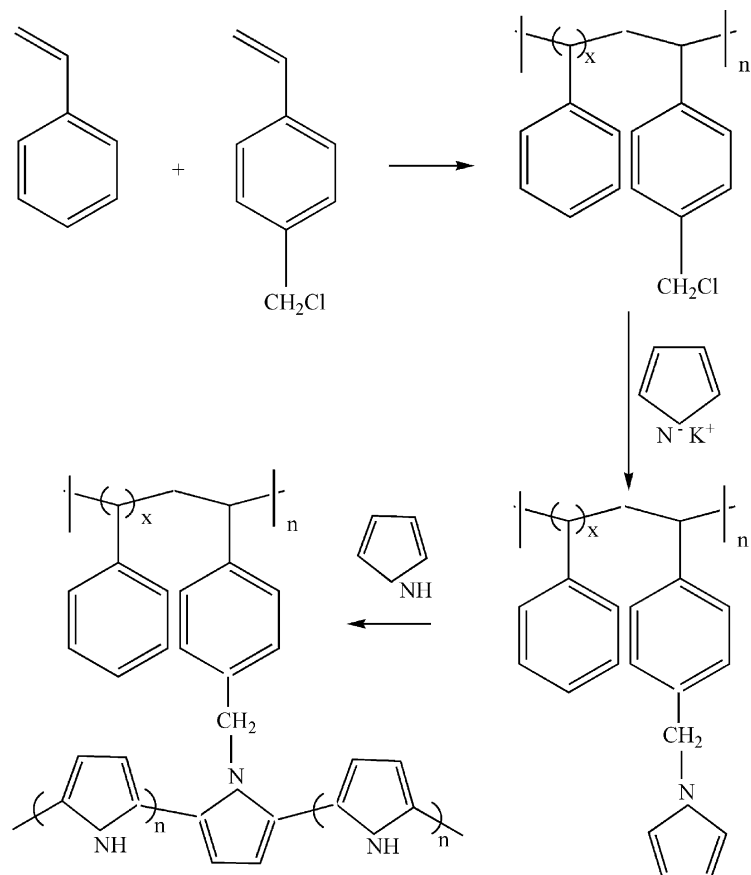


Scheme 17. Synthesis of poly(methyl methacrylate-g-pyrrole) and 2-N-pyrrolyl ethyl stearate [259]. Reproduced from Synth Met 1995;73:..261.

the nitrogen center followed by ligand coupling imparts the ion-sensitivity.

Applicability of conducting polymers in the bio-oriented field has also been reported, e.g. for PANI-(EM)-AAc and PANI-g-(PEO) [261,268,269]. Modification of the surfaces of these with bioactive molecules (i.e. molecules acting upon or influencing bodily functions) can promote biocompatibility and provide biological specificity. The PEO-grafted PANI surface decreases the amount of bovine serum albumin protein adsorption and human blood plasma platelet

adhesion on the PANI film by more than 80%. For PANI-(EM)-AAc, the functional groups of the graft provide the possibility for further functionalization of the electroactive polymer surfaces and interfaces. The coupling between the carboxyl group of the graft and the amino group of the enzyme is affected by carbodiimide. Thus, the emeraldine film with acrylic acid polymer graft was first equilibrated in a 0.05(M) phosphate buffer at pH 7.4 and 4 °C with a water-soluble carbodiimide. The activated emeraldine film was subsequently immersed in another phosphate



Scheme 18. Reaction scheme for preparation of pyrrole–styrene graft co-polymers [261]. Reproduced from Mol Cryst Liq Cryst 1985;118:137.

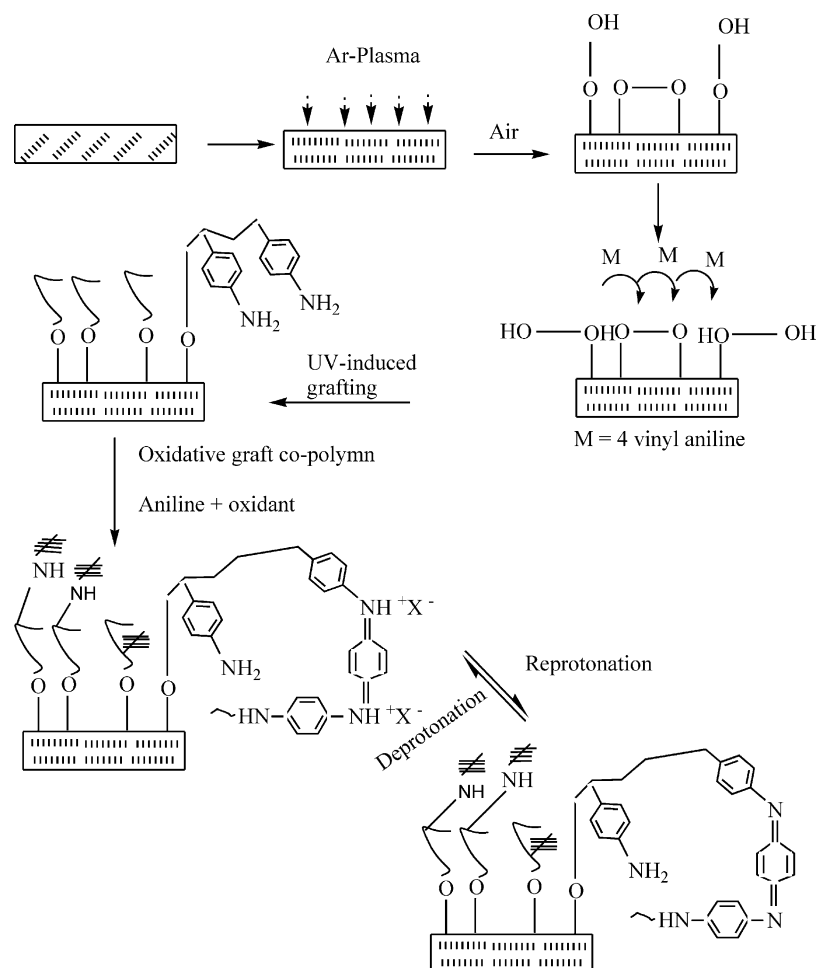
buffer solution with a dissolved enzyme, for at least 12 h at 4 °C. The resulting EM enzyme film was washed thoroughly with the phosphate buffer and showed enzyme activities toward glucose solutions of various concentration [270].

The surface modification of polymers via graft copolymerization has also been performed under relatively mild conditions for a number of polymer substrates such as polyolefins, polyesters, fluropolymers and conjugated polymers. It offers a versatile means for providing the existing polymer with new surface functionalities, without affecting the bulk properties of the substrate. In conjunction with advances in microelectronics fabrication and packaging, the surface modification of silicon wafer surface with functional monomers via UV induced graft copolymerization has been reported [271] (see Scheme 19).

5. Conclusions

The discussion above shows that through grafting one may implement a beautiful level of control of both structure and function of polymers. With this in mind, it is appropriate to consider relevant trend in polymer research.

In this review, we have sketched different mechanistic approaches for grafting by chemical methods, radiation techniques, etc. Apart from the conventional grafting process, we also focused on controlled living radical polymerization, a rapidly developing technique that provides polymers with regulated molecular weight and low polydispersities. Molecular brush or comb-like polymers can also be prepared by this technique. We have discussed different factors that can control grafting, viz. the structures of the backbone and nature of the solvent. We discussed applications of



Scheme 19. Schematic diagram illustrating the process of chemical modification of the Si(100) surface by consecutive graft co-polymerization with 4-vinyl aniline and aniline [271]. Reproduced from *React Funct Polym* 2000;46(2):145.

graft membranes in separation science and as conducting polymers. It was shown that grafted membranes have the potential to separate mixtures, viz. alcohol–water, salt–water mixtures. Fouling problems can be countered by grafting suitable monomers on the membranes. Grafting technique can be used to make the conducting polymer processable, and grafted materials based on conducting polymers have found applications as ion sensors, glucose sensors, etc.

Although grafting techniques are more than 75 years old, in spite of an enormous body of ingenious research, no large-scale commercial exploitation of the method has developed. Nevertheless, hopeful signs are beginning to appear. Fortunately, the grafting

process is now expanding rapidly through electron beam curing processes that can be achieved in a fraction of a second, and yield products in one step without further purification. Apart from the various advantages of the grafting, research takes step towards ‘bio-degradability’. It may solve some of the problems of environmental pollution caused by components that resist bio-degradation.

Acknowledgements

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