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Modification of Polymeric Materials via Surface-Initiated Controlled/"Living" Radical Polymerization

Peng Liu *

Institute of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Lanzhou University, Gansu 730000, P. R. China; Fax number: 86-931-8912582; e@mail: pliu@lzu.edun.cn

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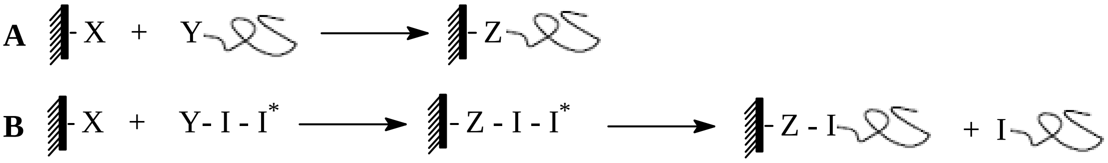
Abstract: Modification of polymeric materials has been a significant issue over last two decades in many fields of application. Among modification techniques developed to date, surface grafting has emerged as a simple, useful, and versatile approach to improve surface properties of polymers for a wide variety of applications. The synthesis of tethered block copolymer brushes via the use of controlled/"living" free radical polymerization techniques presents many significant advantages over traditional free radical polymerization techniques. This review surveys recent literature on polymer surfaces with graft chains, mainly focusing on grafting methods such as surface-initiated controlled/"living" free radical polymerization via atom transfer radical polymerization (ATRP), nitroxide-mediated radical polymerization (NMRP), reversible addition fragmentation transfer (RAFT) polymerization and iniferter techniques.

Introduction

Polymer surfaces are the phase boundaries that reside between the bulk polymer and the outer environment. The performance of polymeric materials relies largely upon the properties of the boundaries in many applications. As most polymeric materials, however, have a hydrophobic, chemically inert surface, untreated non-polar polymer surfaces often have adverse problems in adhesion, coating, painting, colouring, lamination, packaging, colloid stabilization, etc. Biomedical applications of polymeric materials have also faced many critical obstacles such as undesirable protein adsorption and cell adhesion, due to the poor biocompatibility of conventional polymer surfaces. To solve these problems, an enormous number of basic and applied researches have been devoted to the surface modifications of polymeric materials [1-3].

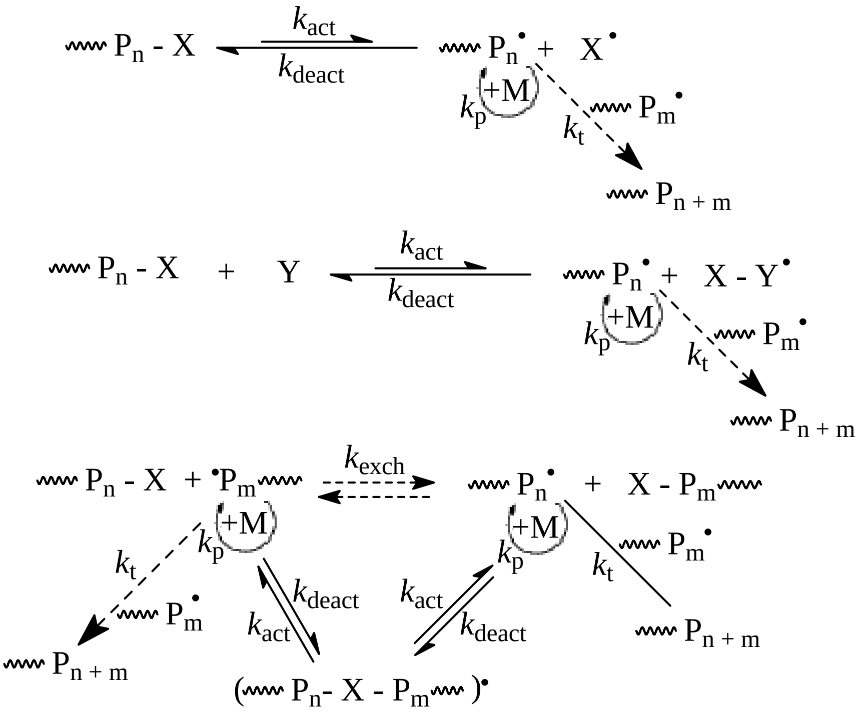
Although a variety of technologies have been proposed for improving surface characteristics, surface modification of polymers by grafting is a rather new technology. It offers versatile means for incorporating new functionalities into existing polymers. However, in spite of the potentially wide applications of such surface grafting technology, this has been applied only to a few cases in industry, probably because the basic studies required for the applications are still in their infancies. Another reason may have been that such a grafted polymer surface is relatively expensive to produce and is used mostly in aqueous environments which are rarely encountered in the conventional industrial applications of polymers. Examples of application in such aqueous environments include marine science, biotechnology, and biomedical engineering. As these fields have become active only in recent years, it is not surprising that polymer modification by surface grafting has not yet become popular in industry [4, 5].

Many different synthetic routes can be employed to introduce graft chains onto the surface of polymeric substrates depending on a system of interest. The grafting methods can be generally divided into two classifications, i.e. ‘grafting-from’ and ‘grafting-to’ processes (Scheme 1). The former utilizes active species existing on the polymer surfaces to initiate the polymerization of monomers from the surface toward the bulk phase. It is widely used for the grafting polymer chains onto various surfaces [6-11].



Scheme 1. General mechanism for “grafting to” (A) and “grafting from” (B).

To have a good control of the polymer mono-layer thickness and polymer structure, living polymerization, for example anionic [12, 13] or cationic [14] polymerizations, can be used. Among the surface-initiated grafting polymerization process, a controlled / “living” radical polymerization (CLRP) technique would be optimal, because such methods afford control over the molecular weight, molecular weight distribution, and the structure of the resulting polymer [15].



Scheme 2. Mechanism of CLRP.

Its mechanism as shown in Scheme 2, include activation and deactivation steps (with rate constants k_{act} and k_{deact}), although in reversible addition fragmentation chain transfer processes (RAFT) and degenerative transfer (DT) the scheme may be formally simplified to just the exchange process with the apparent rate constant k_{exch}. Generated free radicals propagate and terminate (with rate constants k_p and k_t), as in a conventional free-radical polymerization. Thus, although termination occurs, under appropriate conditions its contribution will be small (less than a few percent of total number of chains) and these radical polymerizations behave as nearly living or controlled systems [16].

In the recent years, the surface-initiated controlled / “living” radical polymerization (SI-CLRP) techniques are widely used for the controlled surface modification of various surfaces [17]. In this review, the focus will be on the methodology of the SI-CLRP techniques to surface modifying the polymeric materials.

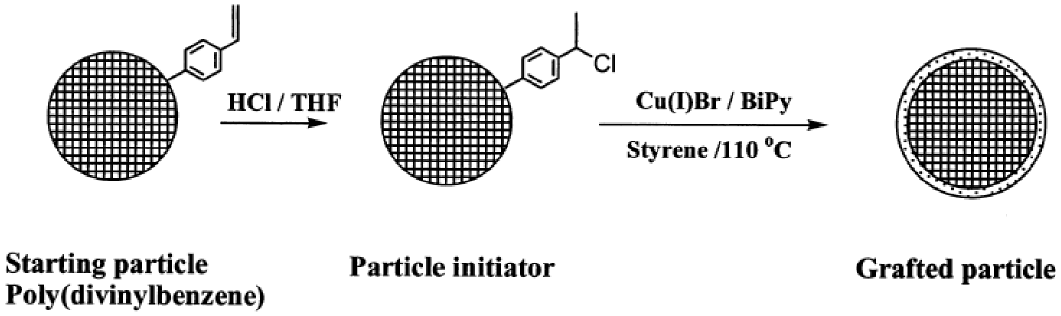
ATRP

Atom transfer radical polymerization (ATRP) is one of the most successful methods to polymerize styrenes, (meth)acrylates and a variety of other monomers in a controlled fashion, yielding polymers with molecular weights predetermined by the ratio of the concentrations of consumed monomer to introduced initiator and with low polydispersities [18]. It is widely used for the preparation of functional polymers [19], polymer brushes [20] and surface modification [21].

The use of ATRP to grow polymer brushes from initiators covalently bound to surfaces has been demonstrated and is of particular interest because control of surface properties is increasingly important in areas such as biomaterials, microelectronics and fiber composites.

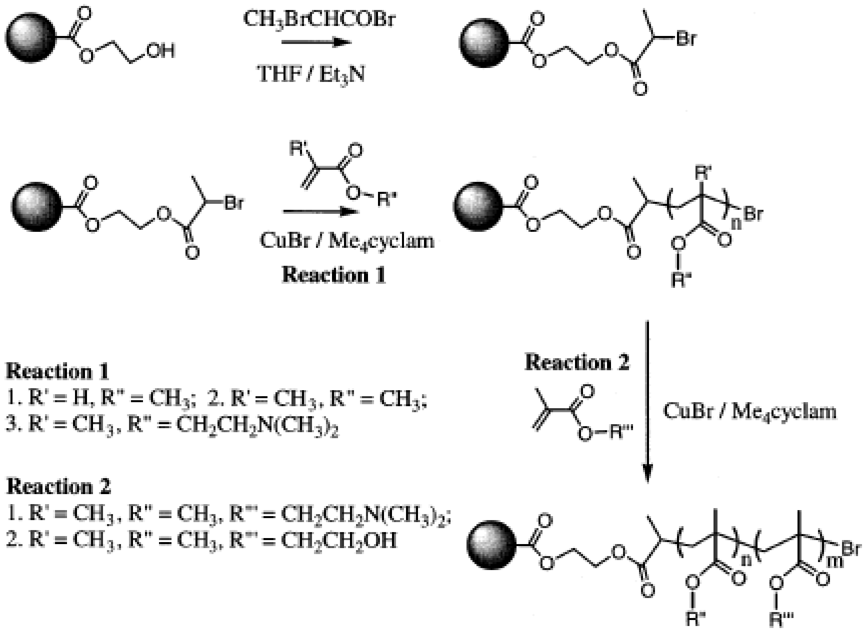
Surfaces of synthetic polymeric materials

Tirelli et al demonstrated that the waterborne surface-ATRP scheme could be conveniently used not only on latexes, but also on larger particles (and in principle on any kind of surfaces), starting from aqueous solutions and for producing multi-layered structures, also presenting chemical functionalities. A 60 lm layer of poly(HEMA) fluorescently labeled with dansyl groups was obtained via surface ATRP on an organic particle (crosslinked polystyrene-graft-PEG) [22]. They also demonstrated that the method might be adapted to create very thick structures, at least up to several tens of microns, much thicker than previously attained.



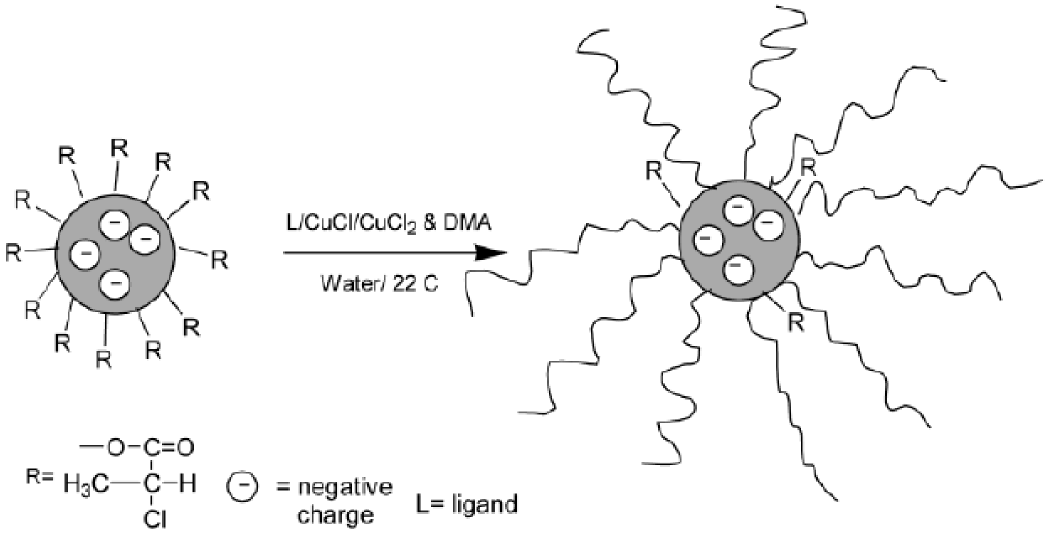
Scheme 3. ATRP from surface of particle initiators. Reprinted from ref. 23.

Grafting of polystyrene from narrow disperse polymer particles by surface-initiated atom transfer radical polymerization (SI-ATRP) was conducted by the following process (Scheme 3). Poly(DVB80) particles prepared by precipitation polymerization were used as starting particles. Their residual surface vinyl groups were hydrochlorinated to form chloroethylbenzene initiating sites for subsequent ATRP of styrene using CuBr/2bipy as catalyst system. Block copolymers of poly(styrene-*b*-4-methylstyrene) were grown from the particles [23]. The authors also reported the graft polymerization of methyl acrylate (MA), methyl methacrylate (MMA), hydroxy ethyl methacrylate (HEMA), and 2-(dimethylamino)ethyl methacrylate (DMAEMA) by ATRP from lightly cross-linked poly(DVB80-*co*-HEMA) microspheres. These poly(DVB80-*co*-HEMA) microspheres were prepared by precipitation copolymerization and subsequently modified by reaction with 2-bromopropionyl bromide to serve as ATRP macroinitiators. MMA, MA, and HEMA were then grafted from these initiator microspheres at room temperature using CuBr/Me$_4$cyclam as catalyst. Addition of a second monomer formed grafted block copolymers, indicating that a significant portion of the first grafts could be reactivated. The final particles represent novel, high-capacity polymer supports comprised of swellable core particles carrying 5.09 and 5.18 mmol/g of grafted poly(DMAEMA) and poly(MMA-*b*-DMAEMA), respectively (Scheme 4) [24].



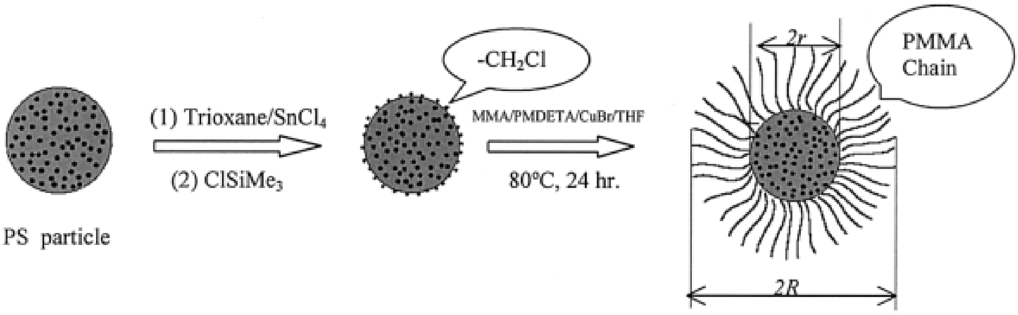
Scheme 4. Reaction of bromopropionyl bromide with precursor particles H*i* to produce initiator particles H*i*Br and the subsequent graft-polymerization and graft-block copolymerization of alky (meth)acrylates from H*i*Br. Reprinted from ref. 24.

Brooks et al described a detailed investigation of the grafting of polymers from negatively charged polystyrene latex to which a copolymer shell of styrene and ATRP initiator has been added. The negatively charged polystyrene latex was synthesized, and a copolymer shell of 2-(methyl-2'-chloropropionato)ethyl acrylate (HEA-Cl) and styrene was added, from which poly(*N*,*N*-dimethylacrylamide) (PDMA) (Scheme 5) [25, 26] and poly(*N*-isopropylacrylamide) (PNIPAM) [27] were polymerized by ATRP in aqueous suspension at room temperature. Very high grafting densities were achieved with good molecular weight control, the highest densities yet reported for high molecular weight polymer chains grown from a surface.



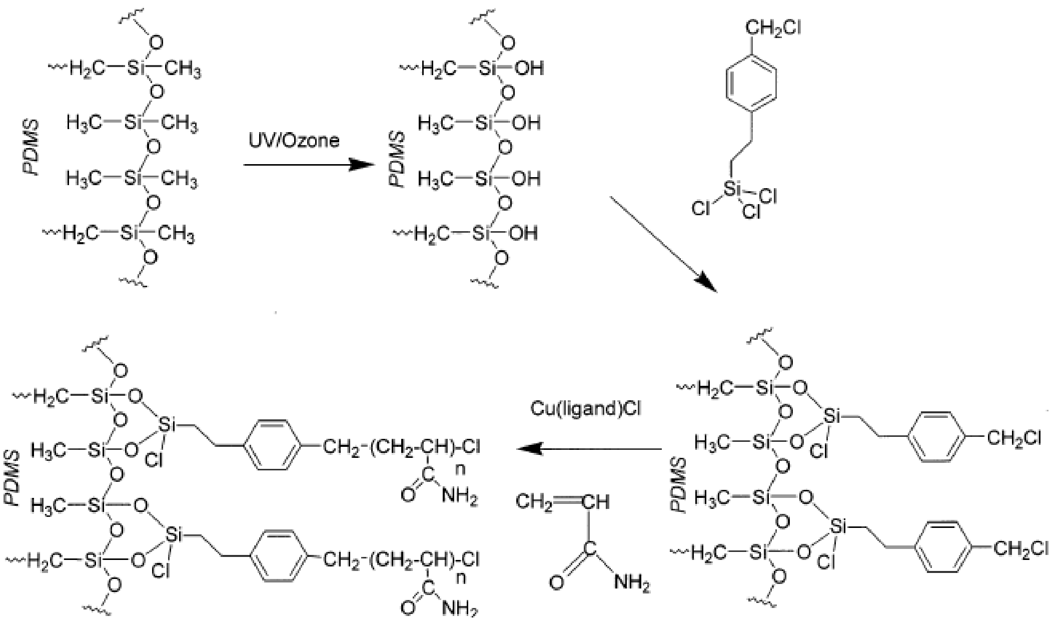
Scheme 5. Schematic representation of the surface grafting onto PS latex. Reprinted from ref. 27.

A new type of modified particle with a well-controlled modified layer, using ATRP of MMA and MA was prepared on crosslinked polystyrene (PS) seed particles. The crosslinked seed particles were first prepared using classical emulsifier-free polymerization. Second, ATRP was performed on the modified seed PS particles (Scheme 6) [28].

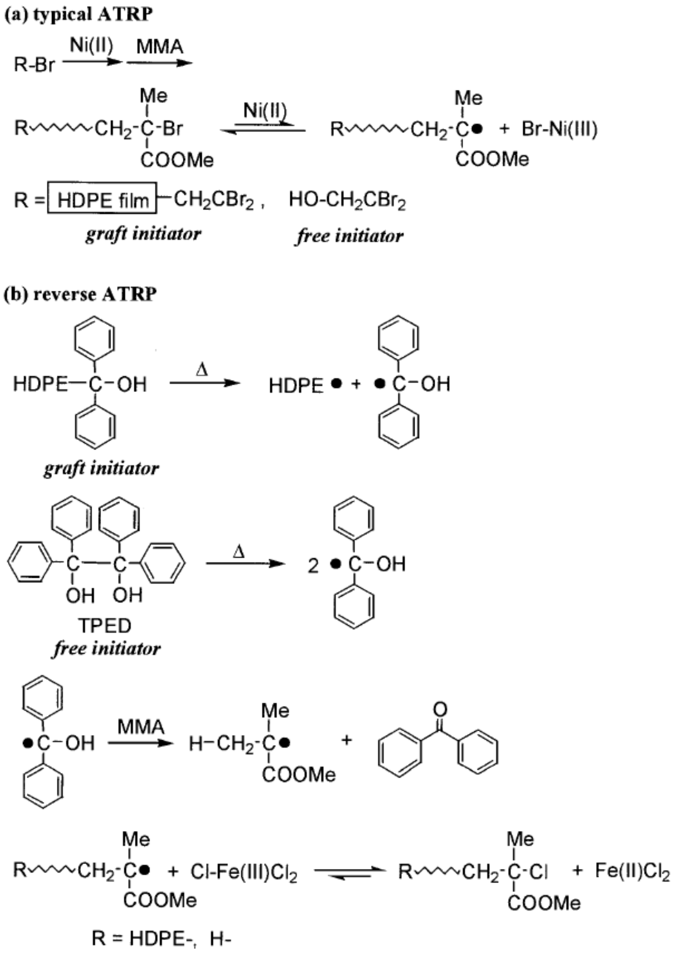


Scheme 6. Preparation of core-shell particles by ATRP. Reprinted from ref. 28.

The chemical modification of Sylgard PDMS with polyacrylamide chains achieves a hydrophilic surface that is resistant to irreversible adsorption of lysozyme. So the PDMS surface was oxidized with ozone plasma to achieve the maximum number of surface groups to silanols. The resulting silanol groups were reacted with a gaseous trichlorosilane bearing an initiator for ATRP, (1-trichlorosilyl-2-*m*-*p*-chloromethyl phenyl)ethane, and subsequent ATRP with AM was carried out in water (Scheme 7) [29]. The surface exhibited a 20-fold improvement in resisting irreversible adsorption of lysozyme, compared to bare PDMS, and a 10-fold improvement compared to bare glass. Unlike oxidized PDMS, which reverts fully to being hydrophobic after 2 days, the contact angle of the surface treated by ATRP of AM was shown to remain hydrophilic for at least 1 month.



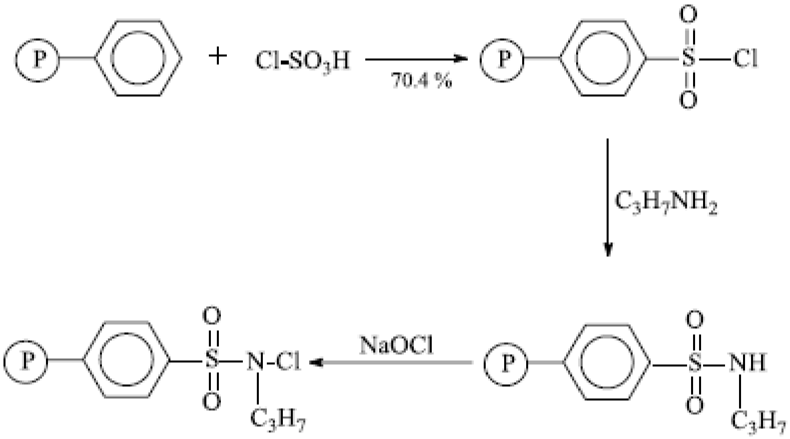
Scheme 7. The chemical modification of Sylgard PDMS with polyacrylamide chains. Reprinted from ref. 29.



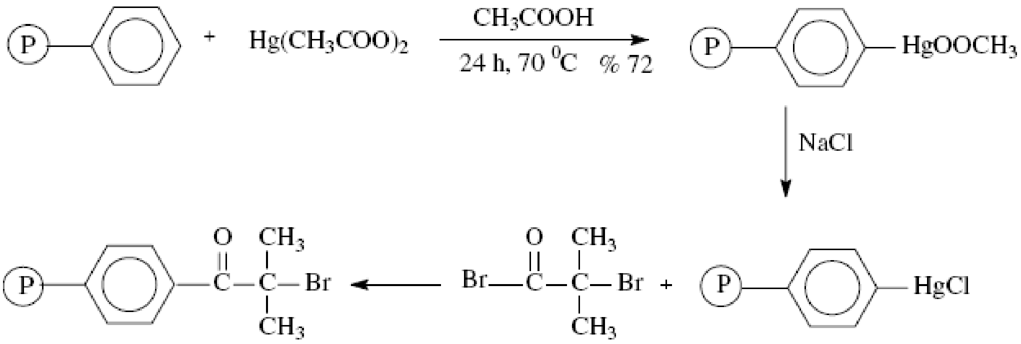
Scheme 8. Living radical graft polymerization of MMA to HDPE: (a) typical and (b) reverse ATRP with nickel and iron compounds as catalysts. Reprinted from ref. 30.

Nickel-mediated ATRP and iron-mediated reverse ATRP were applied to the living radical graft polymerization of MMA onto solid high-density polyethylene (HDPE) films modified with 2,2,2-tribromoethanol and benzophenone, respectively (Scheme 8) [30] . The graft polymerizations for both reaction systems proceeded in a controlled fashion.

Bicak et al reported the graft polymerization of AM [31], MMA and EA [32] from *N*-chlorosulfonamide groups onto crosslinked polystyrene beads using copper-mediated ATRP methodology. The beaded polymer with the graft shells were prepared in four steps, starting from styrene-divinylbenzene (10%) copolymer beads of 210-420 mm particle size; chlorosulfonation; sulfamidation with propylamine; *N*-chlorination with aqueous hypochloride; and grafting (Scheme 9). They also reported that the poly(methyl methacrylate) (PMMA) and Poly(ethyl acrylate) (PEA) have been grafted in high yields (i.e., 1000%) from 2-bromo, 2-methyl propionyl (BMP) groups on crosslinked polystyrene beads, using copper-mediated ATRP methodology (Scheme 10) [33].

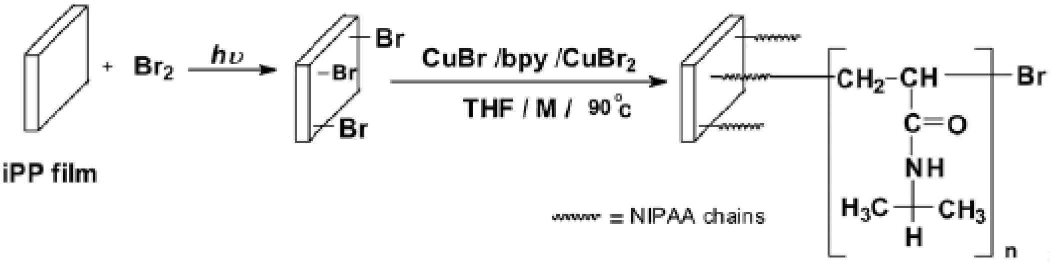


Scheme 9. Introduction of *N*-chlorosulfonamide groups onto crosslinked polystyrene beads. Reprinted from ref. 32.



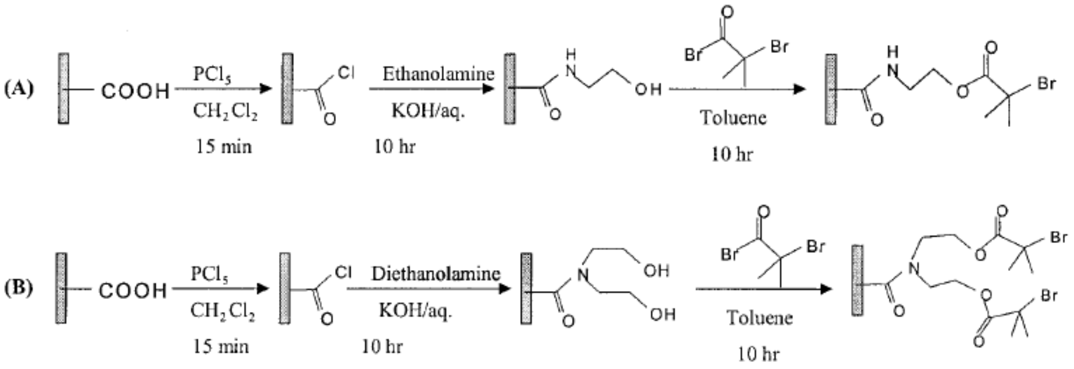
Scheme 10. Functionalization of crosslinked polystyrene beads. Reprinted from ref. 33.

SI-ATRP technique using CuBr/CuBr$_2$/bpy complex is employed to graft N-isopropyl acrylamide (NIPA) brushes onto ‘self-standing’ isotactic polypropylene (iPP) film surface via two-step mechanism involving surface bromination of iPP film by free radical gas phase photochemical reaction (which generated allyl/alkyl bromide onto the surface of the iPP films), followed by grafting (Scheme 11) [34]. The ability to control the degree of grafting of NIPA brushes reaffirms the elegance of the surface initiated ATRP technique to develop tailor-made polymer surfaces. The LCST nature of the NIPA brushes would introduce stimuli responsive character onto the surface of the iPP films used for various specialty applications, especially for biomedical purposes.



Scheme 11. ATRP of NIPA from self-standing isotactic polypropylene thin films. Reprinted from ref. 34.

Husson et al used ATRP technique to grow polyacrylamide from the surface of ethylene–acrylic acid copolymer (EAA) film. The surface functionalization constituted initiator immobilization and surface graft polymerization. For initiator immobilization, the carboxylic acid groups on EAA film were converted to acid chloride groups; further reaction with ethanolamines gave hydroxyl groups onto which 2-bromoisobutyryl bromide initiator was attached (Scheme 12) [35].



Scheme 12. Reaction procedures for preparing initiator-functionalized EAA films: (A) linear structure; (B) bifurcated structure. Reprinted from ref. 35.

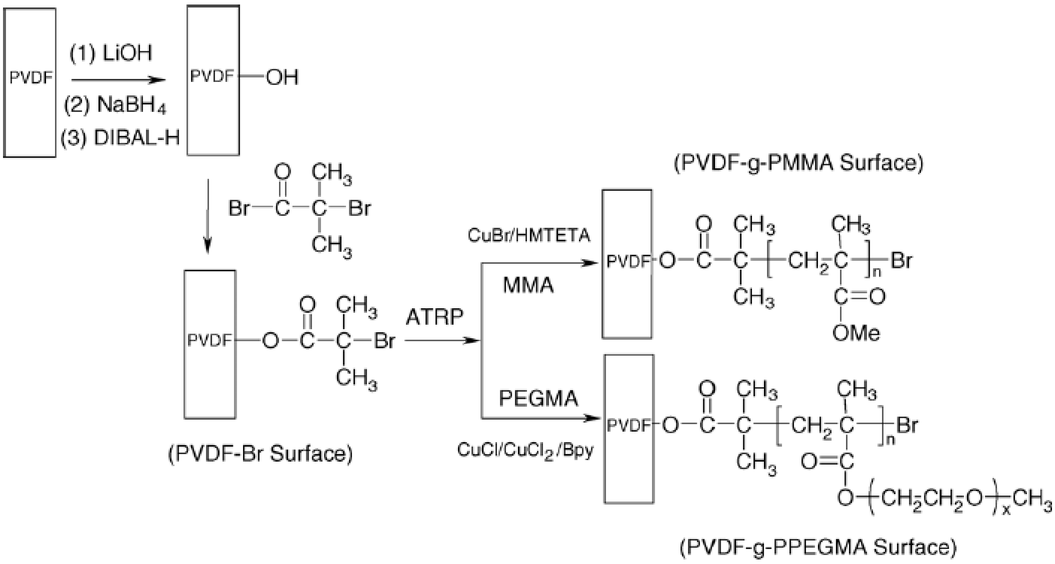
Huck et al had prepared the thermo-responsive polymer poly(N-isopropyl acrylamide) (PNIPAM) grafted polymeric surfaces of commercially important polyester films, poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN) via the ATRP technique. These plastic films were modified prior to polymerization by plasma oxidation, exposing surface hydroxyl groups, in order to immobilise patterned self assembled monolayers (SAMs) of trichlorosilane initiator, through the soft lithographic method of microcontact printing (lCP). Subsequently, polymerizations were initiated from the surface, under aqueous conditions, to create patterned brushes of the thermo-responsive polymer PNIPAM [36].

Kang et al had prepared polymer microspheres with permanent antibacterial surface via SI-ATRP technique. Cross-linked poly(4-vinylbenzyl chloride) (PVBC) microspheres were first synthesized by suspension copolymerization of 4-vinylbenzyl chloride (VBC) in the presence of a cross-linking agent, ethylene glycol dimethacrylate (EGDMA). Subsequent modification of the microsphere surfaces via SI-ATRP of 2-(dimethylamino)-ethyl methacrylate (DMAEMA), using the VBC units of PVBC on the microsphere surface as the macroinitiators, gave rise to well-defined (nearly monodisperse) and covalently tethered poly-[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) brushes. Quaternization of the tertiary amine groups of the PDMAEMA brushes with alkyl bromides (1-bromododecane or 1-bromohexane) gave rise to a high concentration of quaternary ammonium salt (QAS) on the microsphere surfaces [37]. The PVBC latex particles were used as templates and modified with silyl groups via SI-ATRP of 3-(trimethoxysilyl)propyl methacrylate. The silyl groups were then converted into a silica shell, via a reaction with tetraethoxysilane in ethanolic ammonia. Hollow silica nanospheres were finally generated by the thermal decomposition of the PVBC template cores [38].

They also prepared the surface-active microporous membranes from the poly(vinylidene fluoride)-graft-poly(2-(2- bromoisobutyryloxy)ethyl acrylate) copolymer (PVDF-g- PBIEA) by phase inversion in water. The PBIEA side chains could function as initiators for the ATRP of 2-(N,N-dimethylamino)-ethyl methacrylate on the membrane surfaces to give rise to the PVDF-g-PBIEA-ar-PDMAEMA membranes. N-alkylation with hexyl bromide and nitromethane gave rise to the quaternized PVDF-g-PBIEA-ar-QPDMAEMA membranes with polycation chains chemically tethered on the membrane surface, including the pore surfaces [39]. The bactericidal effect of the functionalized microspheres on *Escherichia coli* and *Staphylococcus aureus* was demonstrated. The permanence of the bactericidal activity was also demonstrated through the repeated applications of the surface-modified polymeric materials without any significant loss of their surface activity or functionality.

A new methodology was developed to convert commercially available, microporous membranes into ion-exchange membranes using primary anchoring polymer (mono)layers and graft polymerization from the surfaces of the membranes. ATRP was used to modify the membranes with pyridinium exchange groups. Polymerization time was used as the independent variable to manipulate the amount of grafted poly(2-vinylpyridine) on the membrane surface [40]. Chen et al reported the direct preparation of grafting polymer brushes from commercial poly(vinylidene fluoride) (PVDF) films with SI-ATRP technique. The direct initiation of the secondary fluorinated site of PVDF facilitated grafting of the hydrophilic monomers from the PVDF surface. Homopolymer brushes of 2-(N,N-dimethylamino)ethyl methacrylate (DMAEMA) and poly(ethylene glycol) monomethacrylate (PEGMA) were prepared by ATRP from the PVDF surface. Protein adsorption experiments revealed a substantial antifouling property of PPEGMA-grafted PVDF films and PDMAEMA-grafted PVDF films in comparison with the pristine PVDF surface [41].

Surface modifications of the PVDF film with well-defined polymer brushes from a combination of surface hydroxylation and SI-ATRP were also reported. Surface hydroxylation is first generated on the PVDF surface by chemical treatment. The wet chemical treatment is applicable for modification of the larger bulky materials whereas the other traditional treatments are unsuitable. Immobilization of initiators is carried out by esterification of surface-tethered hydroxyl group and 2-bromoisobutyryl bromide. The tethered 2-bromoisobutyrate is used as the surface immobilized initiator for ATRP. Homopolymer brushes of MMA and poly(ethylene glycol) monomethacrylate (PEGMA) are prepared by ATRP on the bromoester functionalized PVDF surface. Diblock copolymer brushes were prepared by using the homopolymer brushes as the macroinitiators for the ATRP of the second monomer (Scheme 13) [42].



Scheme 13. The processes of hydroxylation of PVDF surface, formation of the 2-bromoisobutyrate-functionalized PVDF surface, and surface graft polymerization via ATRP from the bromoester-functionalized PVDF surface. Reprinted from ref. 42.

Poly(hydroxy ethyl methacrylate) (PHEA) had been grafted from the surfaces of crosslinked poly(vinyl chloride) (PVC) beads with their surface labile chlorines as initiation sites, using copper-mediated SI-ATRP methodology [43]. The ester groups of the poly(hydroxy ethyl methacrylate)-grafted crosslinked poly(vinyl chloride) beads (PHEA-PVC) were then hydrolyzed to yield carboxyl groups. Then the bare PVC beads, PHEA-PVC beads, and the hydrolyzed product, poly(acrylic acid)-grafted crosslinked poly(vinyl chloride) beads (PAA-PVC), were used for the extraction of heavy metal ions such as Cu(II), Hg(II), Zn(II), and Cd(II) in weak acidic aqueous solution. Polyacrylamide was also grafted from the PVC thin films via the SI-ATRP technique for the selective adsorption of Hg(II) ion [44].

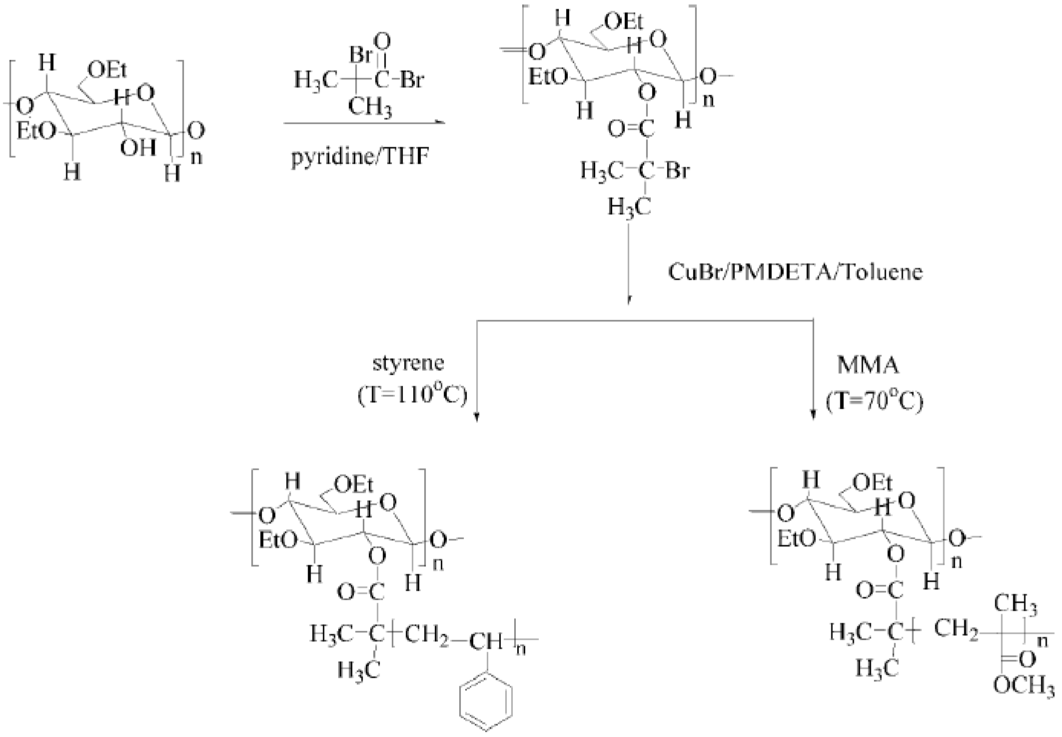
The undoped PANI powders had been modified by first bromoacetylating of the surface amine groups of the undoped PANI with bromoacetylbromide and then the bromoacetyl modified PANI (BrA-PANI) was used for the SI-ATRP of MMA to obtain the core-shell PMMA- PANI with PMMA brushes on the surfaces [45]. The surface-initiated ATRP technique had also been used for the modification of poly(ether imide) membranes after the chloromethylation of the phenyl groups in the main chain [46].

Surfaces of natural polymeric materials

Surface modification of various solid polysaccharide substrates was conducted by grafting MA and styrene via atom transfer radical polymerization (ATRP) to produce well-defined polymer grafts. The hydroxyl groups on the surfaces of the substrates were reacted with 2-bromoisobutyryl bromide followed by graft copolymerization under ATRP conditions. The studied substrates were filter paper, microcrystalline cellulose, Lyocell fibers, dialysis tubing, and chitosan films [47].

Cellulose fibers, in the form of a conventional filter paper, have been modified by reacting the hydroxyl groups on the fiber surface with active groups, followed by grafting using ATRP conditions. Styrene (S), MMA, methacrylamide (MAm) and acrylomorpholine (AcM) were grafted onto powder cellulose by ATRP. Cellulose chloroacetate (Cell-ClAc), as a macro-initiator, was first prepared by the reaction of chloroacetyl chloride with primary alcoholic OH groups on powder cellulose [48]. Cellulose fibers had been grafted with block-copolymer of MA and 2-hydroxyethyl methacrylate (HEMA) after reacting the hydroxyl groups on the fiber surface with 2-bromoisobutyryl bromide [49]. And it was also modified with bromoacetyl bromide for the SI-ATRP of MMA [50].

Densely grafting copolymers of ethyl cellulose with PS and PMMA were synthesized through ATRP. First, the residual hydroxyl groups on the ethyl cellulose reacted with 2-bromoisobutyrylbromide to yield 2-bromoisobutyryloxy groups, known to be an efficient initiator for ATRP. Subsequently, the functional ethyl cellulose was used as a macroinitiator in the ATRP of methyl methacrylate and styrene in toluene in conjunction with CuBr/N,N,N',N'',N''-pentamethyldiethylenetriamine as a catalyst system (Scheme 14) [51, 52].

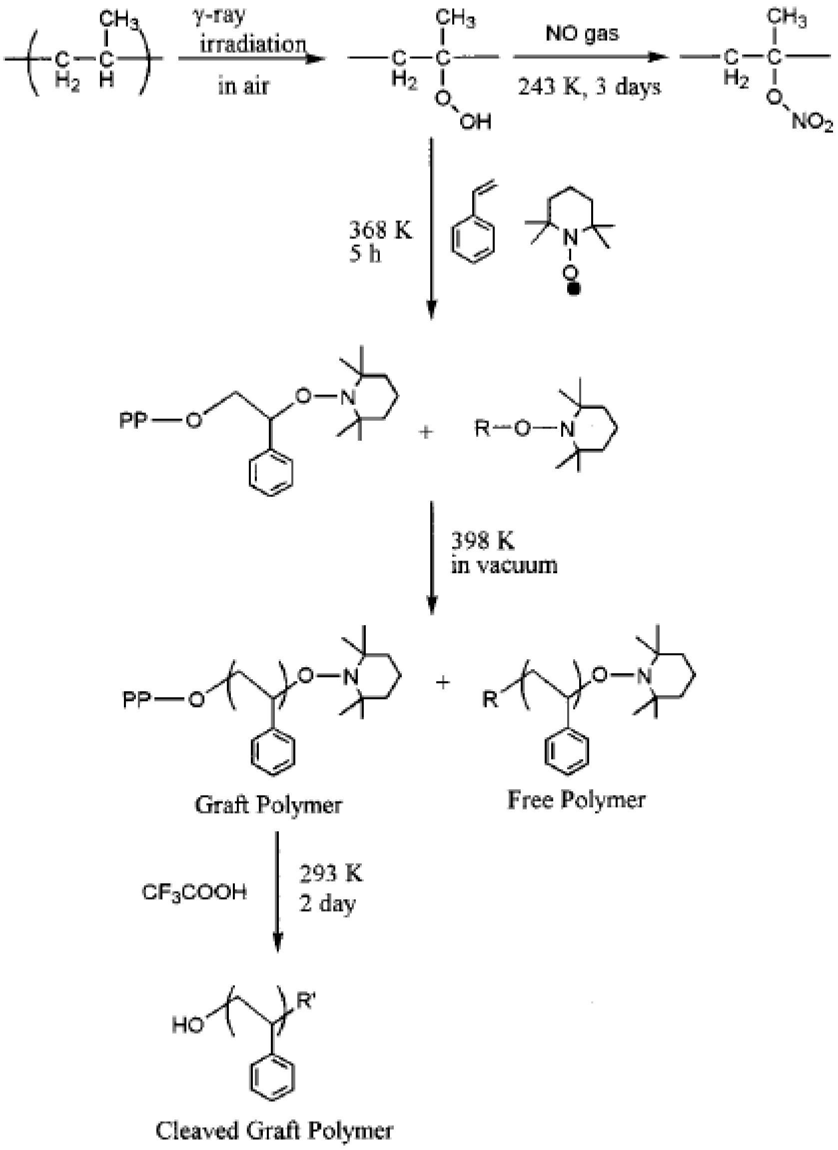


Scheme 14. Synthesis of the EC graft copolymer. Reprinted from ref. 51.

The covalently bonding polystyrene to jute (*Corchorus capsularis*) [53], poly(n-butyl acrylate) to starch granules [54], polyacrylamide [55] and polystyrene [56] to chitosan beads or particles were also reported via the SI-ATRP technique after the conversion of the surface hydroxyl or amino groups into initiating groups.

NMRP

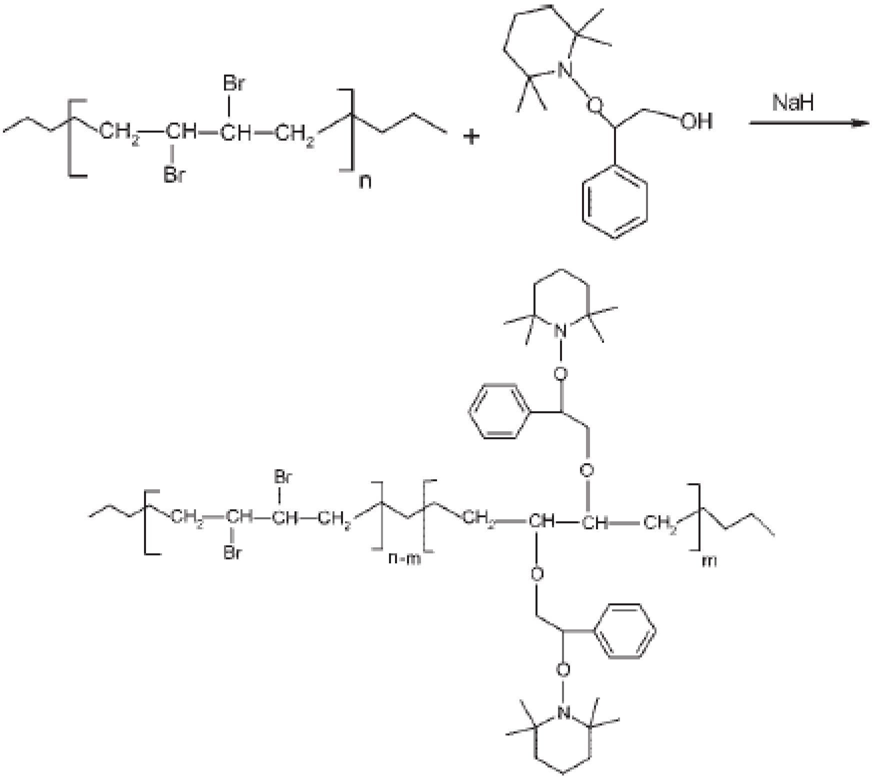
In 1993, Georges et al. reported the pseudoliving free radical polymerization in the synthesis of polystyrene by nitroxide-mediated radical polymerization [57]. Then, a number of homopolymers, block copolymers, star-shaped polymers, and random copolymers with low polydispersities were prepared by the nitroxide-mediated radical polymerization (NMRP) or stable free radical polymerization (SFRP) technique [58-63]. Hybrid silica particles comprised of an inorganic core and an organic polymer shell which can be synthesized by surface-initiated nitroxide-mediated polymerization (SI-NMP) in the presence of a grafted alkoxyamine as initiator [64].



Scheme 15. Graft polymerization of styrene to PP. The most likely end structures of R are groups generated through Diels-Alder reaction of ST and hydroxyl group generated by decomposition of the PP-peroxide. Reprinted from ref. 67.

Frechet et al reported the first use of a “living” radical polymerization for the preparation of macroporous polymers by the direct copolymerization of monovinyl and divinyl monomers in the presence of a porogenic solvent. The porous polymer monoliths have been prepared by polymerization of styrene and divinylbenzene in the presence of porogenic solvents initiated by 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane. They found that the combination of slower kinetics and elevated reaction temperatures characteristic of the TEMPO-mediated polymerization employed enables the preparation of materials with completely different porosity profiles. The porous properties of the monolithic materials were easily controlled in a broad range by adjusting the composition of the porogenic solvents in the polymerization mixture. The capped radicals located at the surface of the pores of the monolith were used for subsequent grafting of functionalized linear chains from monomers such as tert-butyl methacrylate, chloromethylstyrene, or vinylpyridine and thus potentially impart additional unique properties to these monolithic flow-through supports. The extent of grafting within the pores could be controlled by adjusting the reaction time or diluting the monomer with an inert solvent [65, 66].

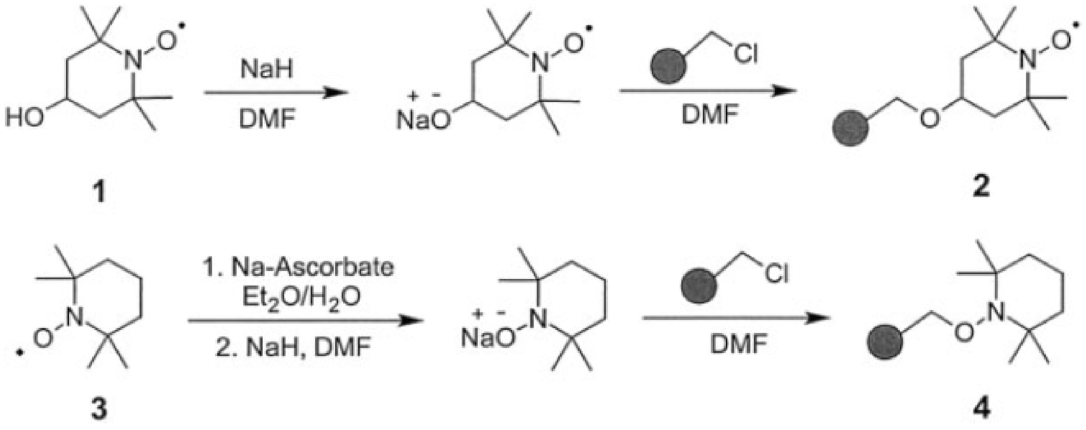
A stable free radical (2,2,6,6-tertamethylpiperidinyl-1-oxy, TEMPO) polymerization technique was applied to a graft polymerization of styrene to polypropylene (PP) (Scheme 15) [67] and polyethylene (PE) [68]. PP and PE peroxides, produced by γ-irradiation (7.2, 12, and 35 kGy) in air, were used as macromolecular initiators for grafting. Then the surface-initiated “living” radical graft polymerization of styrene or controlled random graft copolymerization of styrene and n-butyl methacrylate were successfully conducted with TEMPO [69, 70].



Scheme 16. Preparation of macroinitiator SBR-TEMPO. Reprinted from ref. 71.

A new TEMPO substitute, 1-benzoyl-2-phenyl-2-(2’,2’,6’,6’-tetramethyl-piperidinyl-10-oxy)ethane (BZ-TEMPO), was synthesized and hydrolyzed to the corresponding 1-hydroxyl derivative. This functional nitroxyl compound was coupled with brominated styrene-butadiene rubber (SBR-Br). The resulting macroinitiator (SBR-TEMPO) for “living” free radical polymerization was then heated in the presence of styrene for the formation of the controlled graft copolymer. Thus the well-defined graft copolymers with styrene-butadiene rubber (SBR) backbones and polystyrene branches were synthesized by living free radical polymerization (LFRP) techniques (Scheme 16) [71].

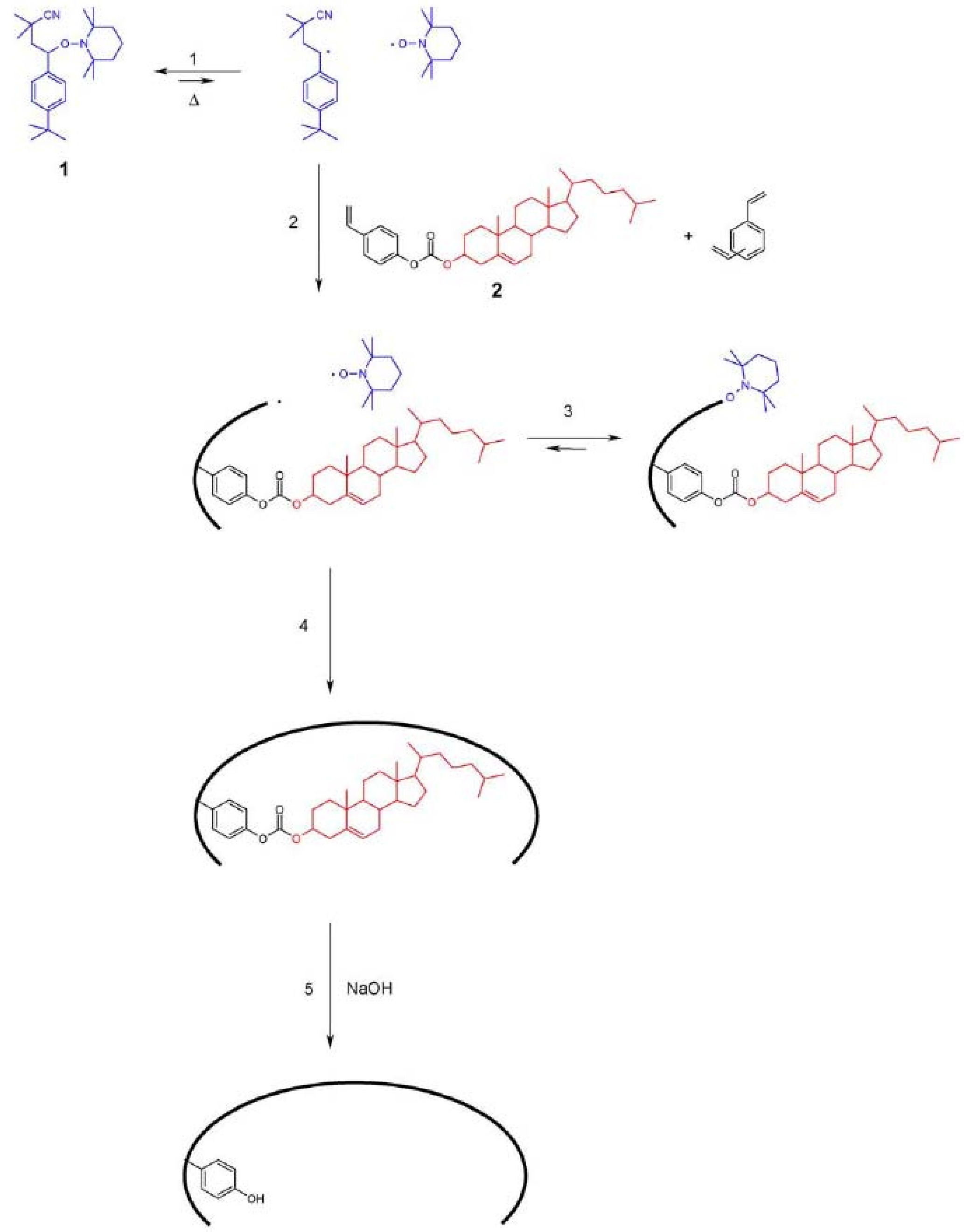
Merrifield resin is converted to a solid-supported free radical initiator by reacting with the TEMPO-Na. Heating TEMPO-methyl resin with a variety of functionalized styrene and acrylate monomers gives larger resin beads via living free radical polymerization as a solvent-free suspension polymerization [72]. It is particularly well suited for preparation of resin beads from monomers which contain electrophilic groups that would be destroyed upon suspension polymerization in water. With judicious choice of co-monomers and polymerization strategy, the solvent affinity, loading capacity, and distance of functionality from the cross-linked core may be controlled giving beads with properties that are tailored to specific uses as synthesis supports and scavenging resins. PS, poly(acetoxystyrene), and poly[styrene- b-(methyl methacrylate-co-styrene)], poly(acetoxystyrene-b-styrene), and poly-(styrene-co-2-hydroxyethyl methacrylate) copolymers were also successfully grafted onto 2,2,6,6-tetramethyl-1-piperidinyloxy nitroxide bound Merrifield resins (Scheme 17) via NMP [73].



Scheme 17. Preparation of 2,2,6,6-tetramethyl-1-piperidinyloxy nitroxide bound Merrifield resins. Reprinted from ref. 73.

The NMP technique is very useful for the preparation of molecularly imprinted polymers (MIPs). NMP can also simplify surface modification for MIPs to bring about better compatibility with different solvent systems. Furthermore, NMP has the potential to be used in both covalent and non-covalent imprinting systems. Ye’s group utilized the nitroxide-mediated living radical polymerization technique to prepare molecularly imprinted polymers for the first time (Scheme 18) [74]. The imprinted hydrolyzed polymer prepared by NMP also displayed an imprinting effect that was clearly superior to that obtained using traditional radical polymerization, particularly for the high affinity sites that were easily characterized by radio ligand binding analysis.

Polystyrene grafted crosslinked poly (methyl methacrylate) microspheres [75] and poly(ethyl methacrylate) grafted crosslinked polystyrene microspheres [76] were reported via an in-situ polymerization of the monomers on the crosslinked microspheres initiating with benzoyl peroxide (BPO) in the presence of 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO ·). MMA was also in-situ grafted onto the surface of PS film initiated with UV light with wave length of 253-254 nm to generate a polymer brush in the presence of TEMPO [77].



Scheme 18. Preparation of cholesterol-imprinted polymer using nitroxide-mediated polymerization. The transient free radicals generated from **1** (Step 1) initiate chain polymerization of **2** and DVB (Step 2). The majority of the growing chain radicals are stabilized by their reversible association with TEMPO (Step 3), so that permanent chain termination is avoided. This living polymerization finally leads to the formation of imprinted sites in the cross-linked polymer network (Step 4), which after hydrolysis (Step 5) afford specific cholesterol binding cavities. Reprinted from ref. 74.

RAFT

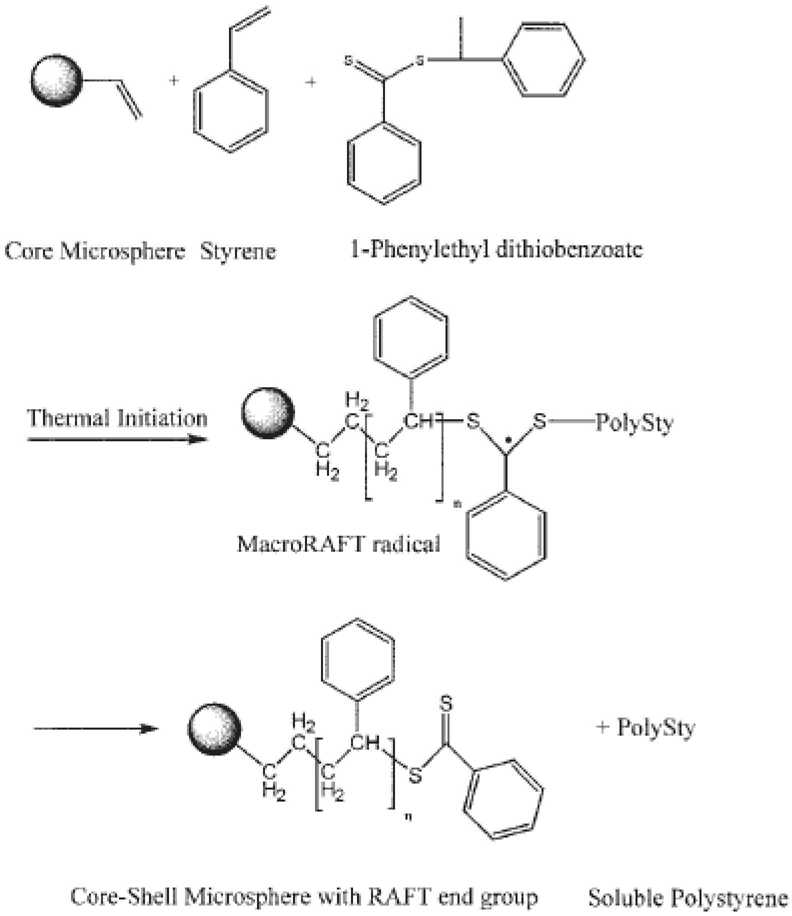
The reversible-addition-fragmentation-chaintransfer (RAFT) polymerizations is a versatile technique for the preparation of living polymers with both low polydispersity and functionalizable end groups [78]. In recent years, syntheses of polymers with complex molecular architectures via the RAFT process have been reported. The RAFT method utilizes thiocarbonylthio compounds to mediate the polymerization via a reversible chain-transfer process. RAFT polymerizations can be initiated by thermal initiators or by UV-, electron beam- or gamma-irradiation. Modified polymeric surfaces play an important role in combinational chemistry and biotechnology. It is therefore a matter of priority to develop methods for controlled surface grafting in order to further improve the performance of polymeric surfaces and to facilitate novel applications. The RAFT methodology is particularly attractive for the controlled modification of surfaces, because it allows for the formation of a uniform polymeric layer or shell with various functionalities in a one-pot process. The grafted polymeric chains often cannot be readily cleaved off the surface. Therefore, some characterization techniques (such as molecular weight analysis) prove too difficult to employ.

Grafting onto polymeric surface is accompanied by the formation of polymer in the solution surrounding the polymeric surface. The formation of this free polymer is also governed by the RAFT process and analysis of the free polymer can therefore provide information about the grafted polymer [79].

Narrowly distributed linear poly (N-isopropylacrylamide) (PNIPAM) chains can be effectively grafted on spherical PNIPAM/HEA copolymer microgels via free-radical reversible-addition-fragmentation-chaintransfer (RAFT) polymerization, resulting in a novel core-shell nanostructure. The results showed that such a structure had two different kinds of temperature-induced transitions in terms of the thickness of the grafted PNIPAM layer. In the low temperature range 25-32 °C, the layer thickness decreased, which was attributed to the coil-to-globule transition of linear grafted PNIPAM chains. While, in the high temperature 32-35°C the layer thickness increases linearly with the grafting density due to the repulsion among the grafted chains on the surface, which was related to the globule-to-brush transition of the collapsed PNIPAM chains on the PNIPAM/HEA microgel [80].

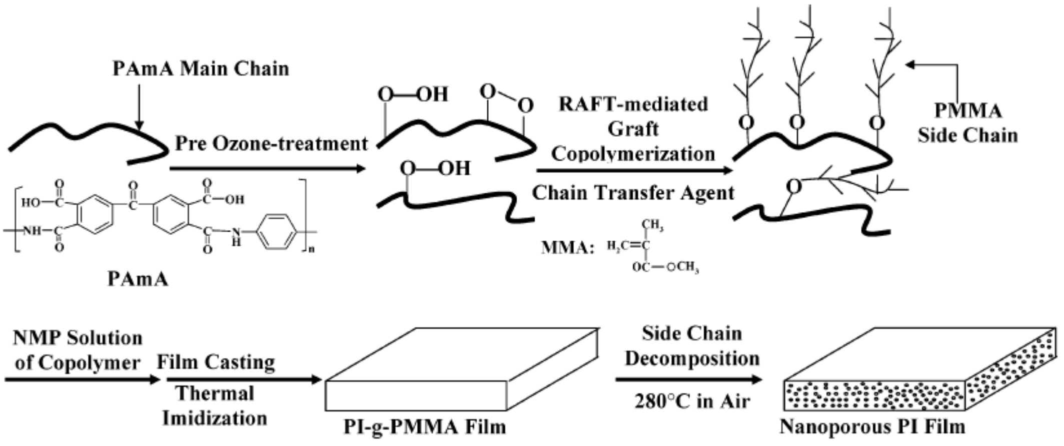
The γ-initiated reversible addition–fragmentation chain-transfer (RAFT)-agent-mediated free-radical graft polymerization of styrene onto a polypropylene solid phase has been performed with cumyl phenyldithioacetate (CPDA) [81]. The RAFT graft polymerization is compared with the conventional free-radical graft polymerization of styrene onto polypropylene. Both processes show two distinct regimes of grafting: (1) the grafting layer regime, in which the surface is not yet totally covered with polymer chains, and (2) a regime in which a second polymer layer is formed. The grafting ratio of the RAFT-agent-mediated process is controlled via the initial CPDA concentration. The molecular weight of the polystyrene from the solution (PS free) shows a linear behavior with conversion and has a low polydispersity index. Furthermore, the loading of the grafted solid phase shows a linear relationship with the molecular weight of PS free for both regimes. Regime 2 has a higher loading capacity per molecular weight than regime. The γ-initiated RAFT-mediated free-radical graft polymerization of styrene and m-isopropenyl-a,a'-dimethylbenzyl isocyanate (TMI) from a PP solid phase was performed with CPDA as the chain-transfer agent [82].

Barner et al also used the RAFT agent1-phenylethyl dithiobenzoate (PEDB). PEDB is a well-known RAFT agent, frequently used in polymerizations of styrene. They also synthesized core poly(DVB) microspheres that contain RAFT end groups instead of residual vinyl bonds via the precipitation polymerization technique in the presence of a RAFT agent (PEDB). The RAFT agent mediated the growth of oligomers until they aggregated and subsequently precipitated to form microspheres containing RAFT end groups on the surface and within the particle (Scheme 19) [83].



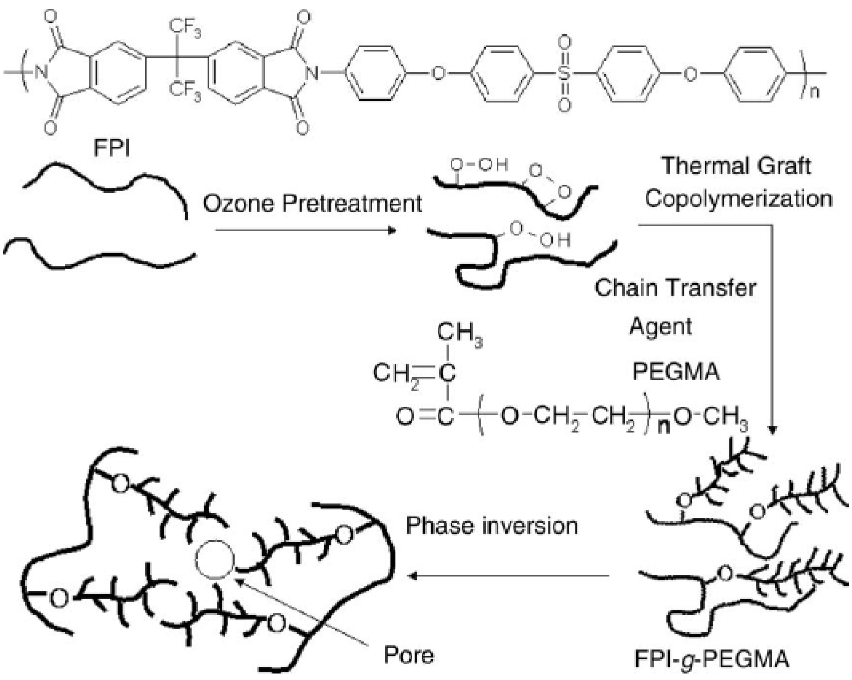
Scheme 19. Schematic for the graft reversible addition fragmentation chain transfer (RAFT) polymerization of styrene from core microspheres. Reprinted from ref. 83.

Kang et al reported the synthesis of poly (vinylidene fluoride) (PVDF) with grafted living poly (acrylic acid) (PAAc) side chains. The PVDF-g-PAAc copolymers are prepared from the RAFT-mediated graft copolymerization of AAc with the ozone-pretreated PVDF, using 1-phenylethyl dithiobenzoate as the chain transfer agent (CTA). The copolymer can be readily cast into pH-sensitive microfiltration (MF) membranes with enriched living PAAc graft chains on the surface (including the pore surfaces) by phase inversion in an aqueous medium. The MF membranes with surface-tethered PAAc macro-CTAs, or the living membrane surfaces, were further functionalized via surface-initiated block copolymerization with NIPAAM to obtain the PVDF-g-PAAc-b-PNIPAAM MF membranes. The membrane exhibited both pH- and temperature-dependent permeability to aqueous media [84].



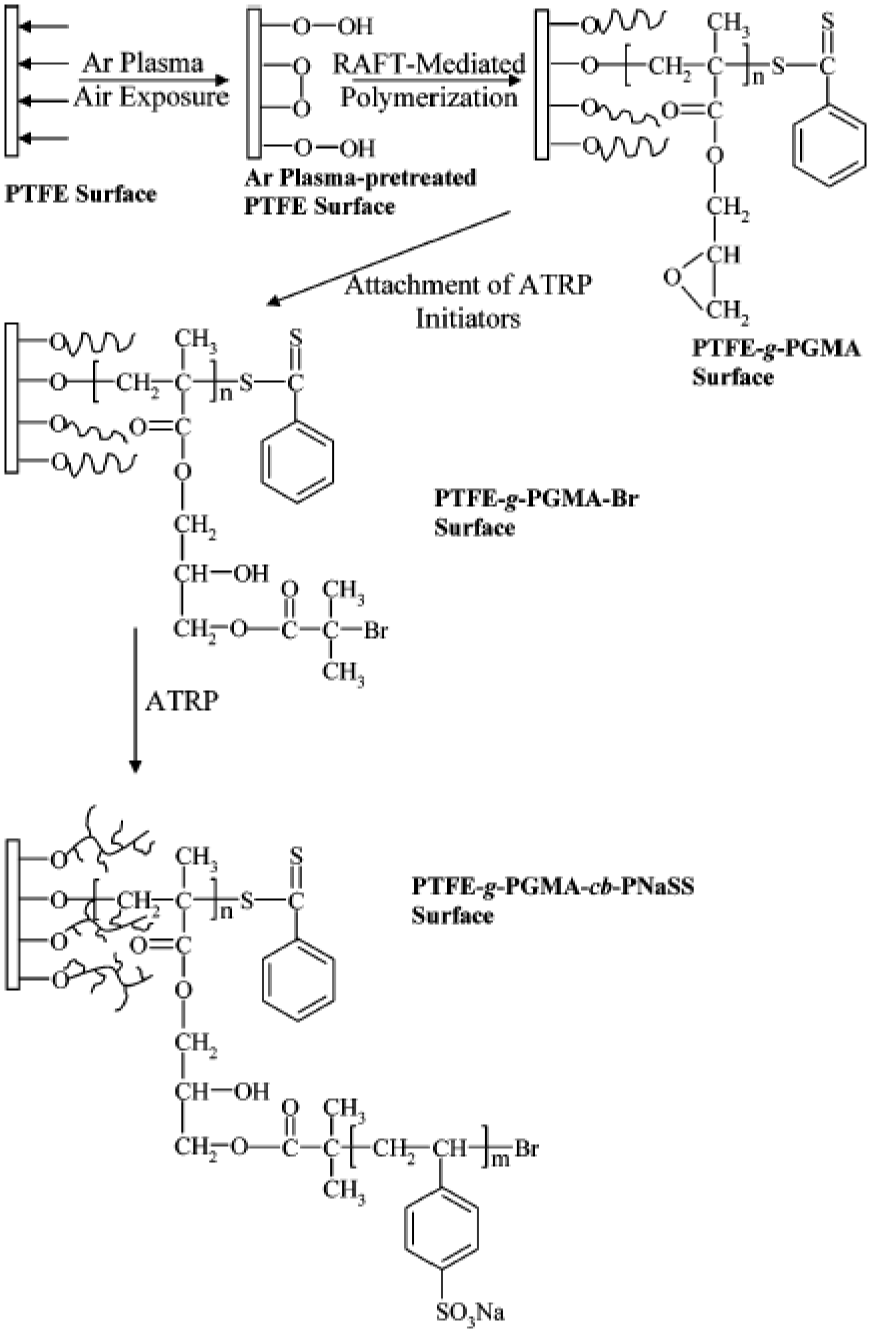
Scheme 20. Schematic illustration of the processes of thermally induced graft copolymerization of MMA with the ozone-preactivated PAmA backbones in the RAFT-mediated process and the preparation of a nanoporous PI film. Reprinted from ref. 85.

The nanoporous low dielectric constant (low-κ) polyimide (PI) films with narrow pore size distribution were prepared from the RAFT-mediated copolymers of poly [N,N'-(1,4-phenylene)-3,3',4,4'-benzophenonetetracarboxylic amic acid] (PAmA) with grafted PMMA side chains (PAmA-g-PMMA copolymers) (Scheme 20). Nanoporous PI films, with the PI backbones intact, were obtained after thermal imidization of the PAmA backbones in an inert atmosphere, followed by thermal decomposition of the labile MMA polymer side chains in air [85].



Scheme 21. Schematic illustration of PEGMA graft polymerization with the ozone-pretreated FPI backbone under the RAFT-mediated process and the preparation of the FPI-*g*-PEGMA MF membrane by phase inversion. Reprinted from ref. 86.

Poly(ethylene glycol) methyl ether methacrylate (PEGMA) was grafted from fluorinated polyimide (FPI) by the RAFT-mediated process (Scheme 21). The peroxides generated by the ozone treatment on FPI facilitated the thermally-initiated graft copolymerization from FPI backbone. The "living" character of the graft chain growing was ascertained in the subsequent chain extension of PEGMA. Microfiltration (MF) membranes were fabricated from the FPI-*g*-PEGMA comb copolymers by phase inversion in aqueous media [86].



Scheme 22. Schematic diagram illustrating the processes of Ar plasma pretreatment of the PTFE surface, surface-initiated RAFT polymerization of GMA, attachment of the ATRP initiators to the PGMA brushes, and preparation of the comb copolymer brushes on the PTFE surface. Reprinted from ref. 87.

Surface modification of poly (tetrafluoroethylene) (PTFE) films by well-defined comb copolymer brushes were carried out by the two-step process combination of RAFT and ATRP techniques. Peroxide initiators were generated directly on the PTFE film surface via radio frequency Ar plasma pretreatment, followed by air exposure. Poly(glycidyl methacrylate) (PGMA) brushes were first prepared by surface-initiated RAFT polymerization from the peroxide initiators on the PTFE surface in the presence of a chain transfer agent. Kinetics study revealed a linear increase in the graft concentration of PGMA with the reaction time, indicating that the chain growth from the surface was consistent with a “controlled” or “living” process. R-Bromoester moieties were attached to the grafted PGMA by reaction of the epoxide groups with 2-bromo-2-methylpropionic acid. The comb copolymer brushes were subsequently prepared via surface-initiated ATRP of two hydrophilic vinyl monomers, including poly(ethylene glycol) methyl ether methacrylate and sodium salt of 4-styrenesulfonic acid (Scheme 22) [87].

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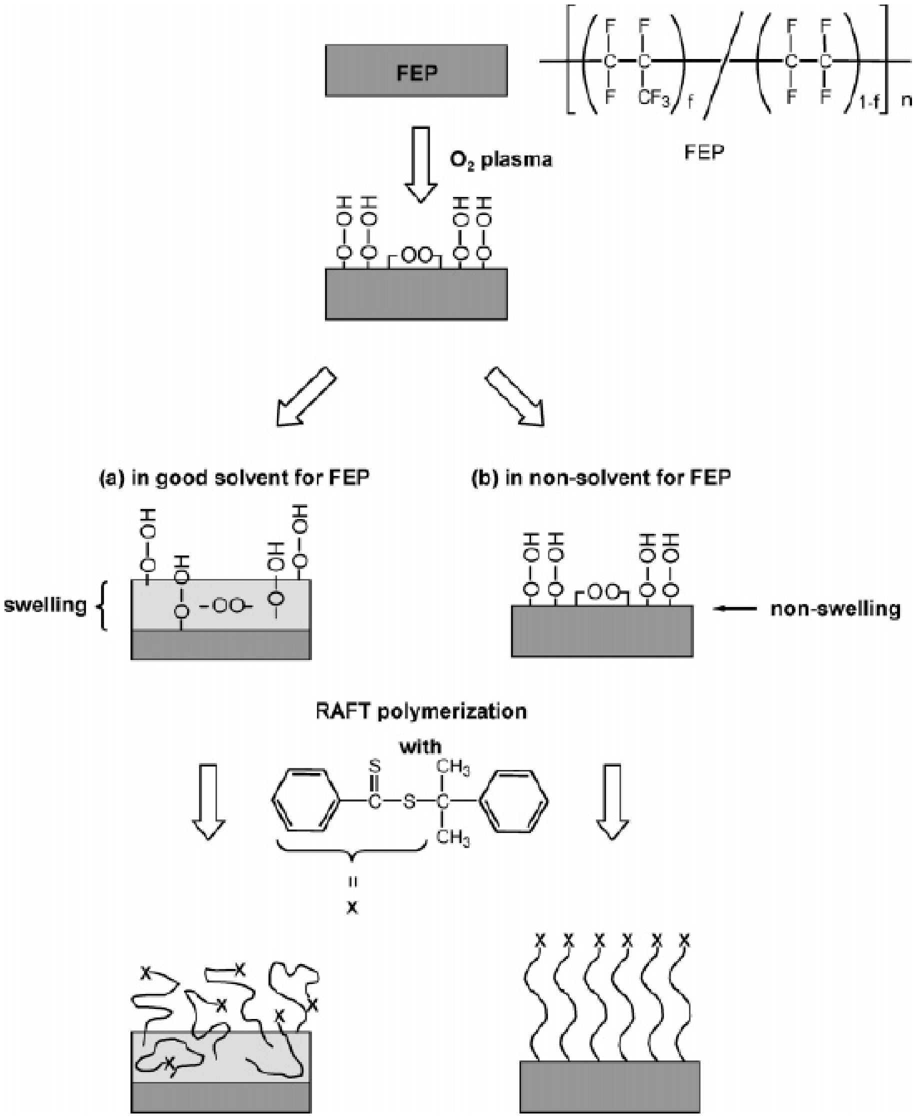
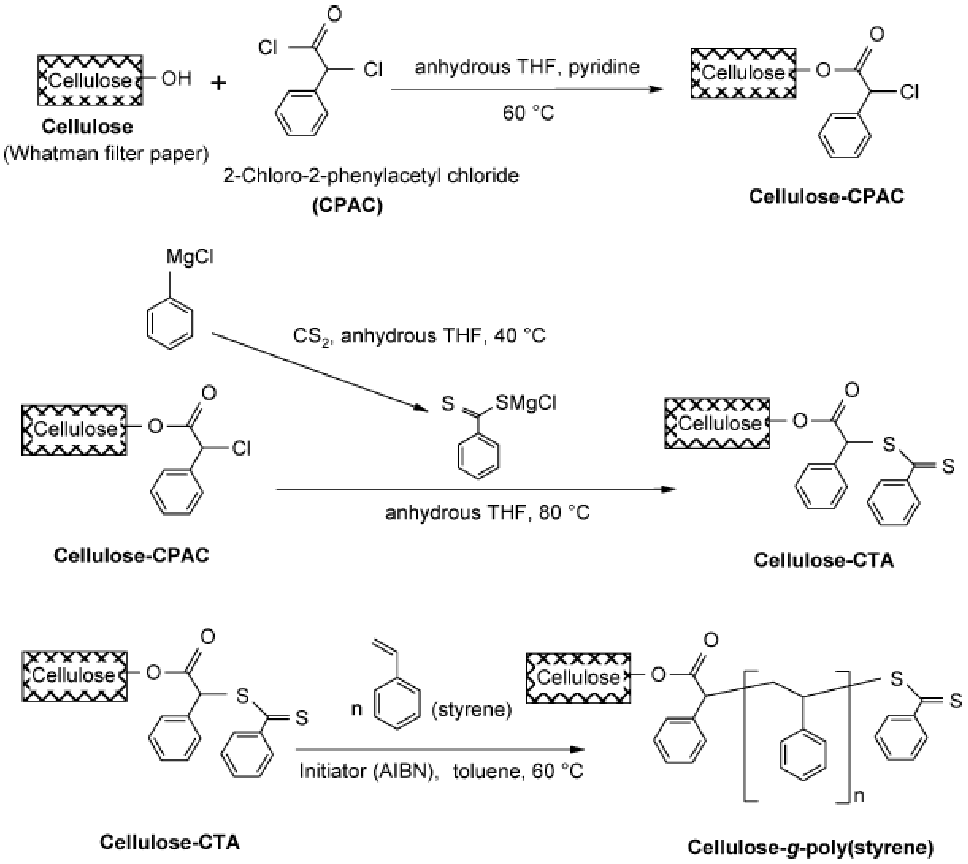


Scheme 23. Schematic illustration of the graft polymerization on the FEP film in (a) good and (b) non-solvents for FEP. Reprinted from ref. 89.

Betz et al reported the post-radiation-induced-graft polymerization on solid substrate using RAFT mechanism for the first time. Radiation-induced graft polymerization onto polymers is a potentially interesting technique to create easily new materials from highly resistant polymers, e.g. surface graft polymerization of acrylic acid (AA) onto PVDF improves its surface properties without losing its excellent mechanical properties. The graft polymerization of AA onto electron-beam irradiated a-PVDF was performed using trithiocarbonic acid bis(1-phenylethyl) ester as a RAFT agent to control the radical polymerization [88]. Hydrolysis of PAA chains was also studied in order to remove the trithiocarbonate functionality from the grafted polymer. A mild chemical condition was achieved in order to have thiol groups that were detected onto the modified PVDF by specific enzymatic reaction

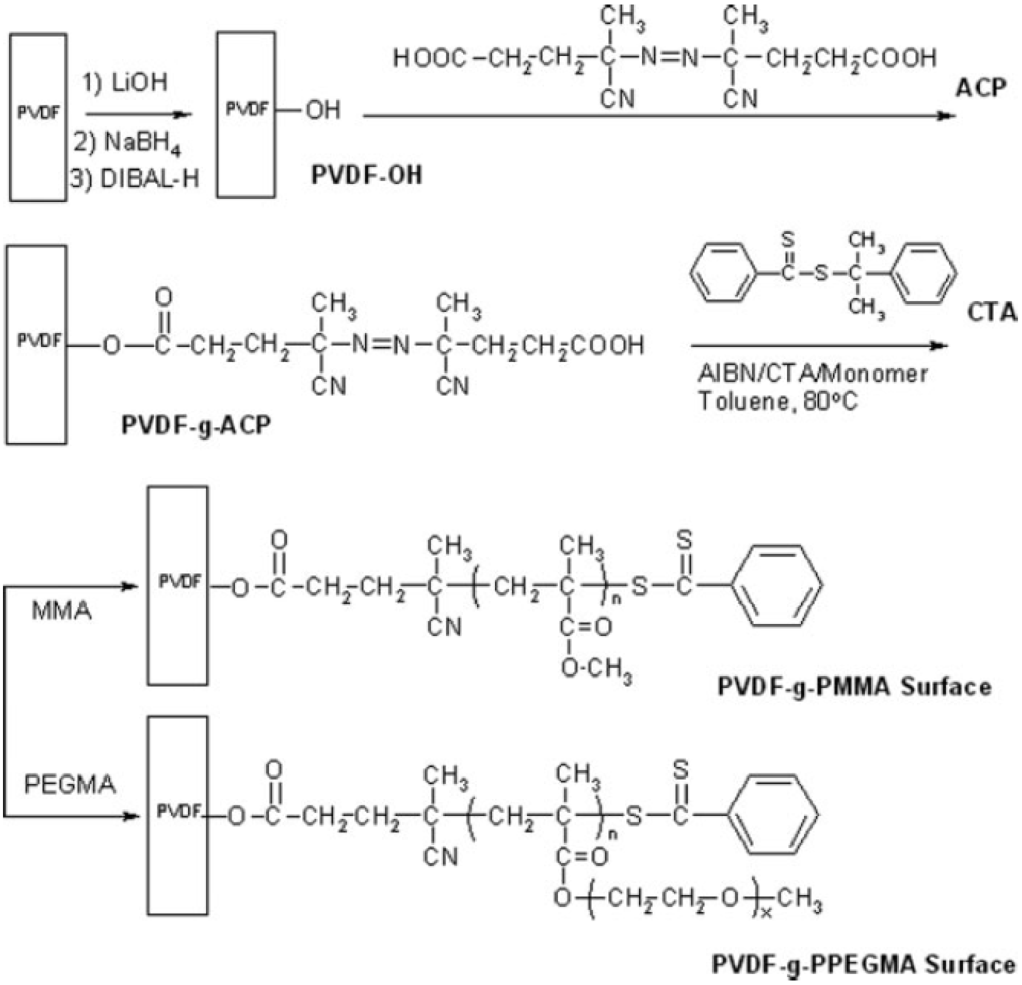
Fukuda et al reported the well-defined, high-density poly (2-hydroxyethyl methacrylate) (PHEMA) brush fabricated on the surface of a poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) film by surface-initiated living radical polymerization (SI-LRP). First, a sufficient amount of peroxides as initiating moieties were successfully introduced on the film surface without causing etching by the O_2-plasma treatment. Subsequently, the polymerization mediated by RAFT was carried out at a mild temperature in a nonsolvent for FEP to minimize the swelling of the FEP film surface and avoid the growth of chains from deep inside of the film (Scheme 23) [89].



Scheme 24. Synthesis of cellulose chain transfer agent for RAFT polymerization and their use to mediate styrene polymerization. Reprinted from ref. 90.

A hydrophobic cellulose surface was prepared by grafting poly(styrene) onto a cellulose substrate (Whatman No. 1 filter paper) via the RAFT polymerization method with a view to use the hydrophobic cellulose fibers in composites. The cellulose-based RAFT agent were prepared by the conversion of the hydroxyl groups of the cellulose fiber into thiocarbonyl-thio chain transfer agent, and were further used to mediate the RAFT polymerization of styrene (Scheme 24) [90, 91].

Graft polymerized brushes of PMMA and PPEGMA from PVDF surfaces were also conducted by the surface-initiated RAFT. PVDF surfaces were exposed to aqueous LiOH, followed by successive reductions with NaBH4 and DIBAL-H to obtain hydroxyl functionality. Azo-functionalities, as surface initiators for grafting, were immobilized on the PVDF surfaces by esterification of 4,40-azobis(4-cyanopentanoic acid) and the surface hydroxyl groups. Kinetics studies revealed a linear increase in the graft concentration of PMMA and PPEGMA with the reaction time, indicating that the chain growth from the surface was consistent with a ‘‘controlled’’ or ‘‘living’’ process. The living chain ends were used as the macroinitiator for the synthesis of diblock copolymer brushes (Scheme 25) [92].



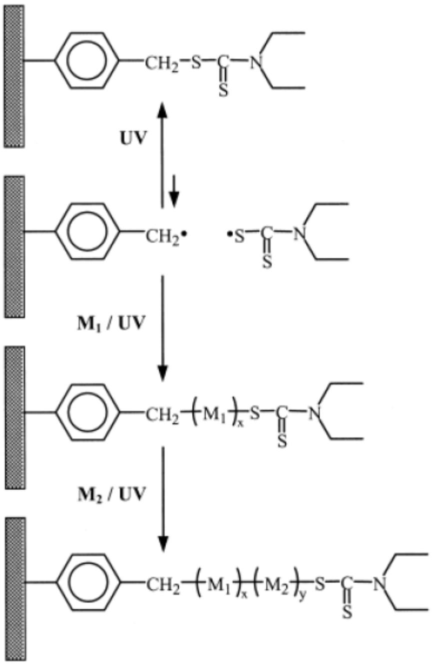
Scheme 25. Schematic diagram illustrating the formation of hydroxyl functionalities from PVDF surface, formation of the azo-functionalized PVDF surface, and surface graft polymerization via RAFT from the azo-functionalized PVDF surface. Reprinted from ref. 92.

Fu et al prepared surface molecularly imprinted polymers (SMIP) via the RAFT polymerization on the chloromethyl polystyrene resin (CPR) in the presence of the template D-phenylalanine [93].

Iniferter

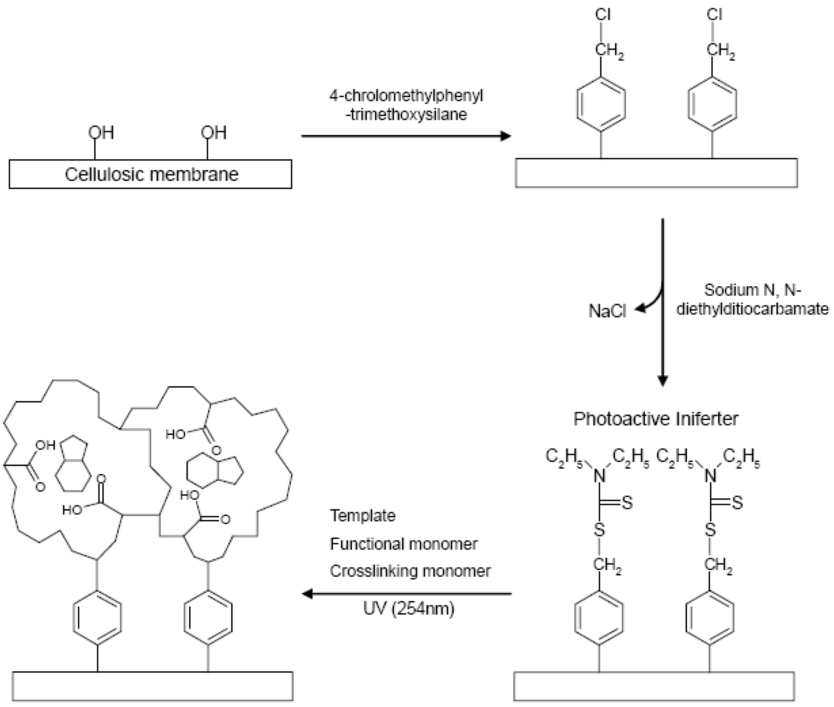
Living radical polymerization is also induced by “iniferter” (initiator-transfer agent-terminator). Iniferters are initiators that induce radical polymerization that proceeds via initiation, propagation, primary radical termination, and transfer to initiator. Because bimolecular termination and other transfer reactions are negligible, these polymerizations are performed by the insertion of the monomer molecules into the iniferter bond, leading to polymers with two iniferter fragments at the chain ends. The use of well-designed iniferters would give polymers or oligomers bearing controlled end groups [94] or block and graft copolymers [95, 96]. If the end groups of the polymers obtained by a suitable iniferter serve further as a polymeric iniferter, these polymerizations proceed by a living radical polymerization mechanism in a homogeneous system. In these cases, the iniferters (C-S bond) are considered a dormant species of the initiating and propagating radicals.

Living radical polymerization induced by iniferter is a desirable method for the surface modification of polymers for a number of reasons. First, photochemically produced triplet states of carbonyl compounds facilitate hydrogen abstraction, so graft polymerization is initiated without prior modification of a surface with conventional or living radical initiators. Second, a high concentration of active species is produced locally at the interface between the substrate polymer and the monomer solution. Third, the procedure is relatively simple, energy-efficient, and cost-effective. Fourth, UV-induced polymerization is well suited for integration with other technologies, such as microcontact printing and photolithography, to produce desired surface chemistry changes in well-defined two-dimensional regions on a surface [97-100].



Scheme 26. Mechanism of the photopolymerization by diethyldithiocarbamate chemistry. Reprinted from ref. 103.

The segmented polyurethane (SPUs) surfaces were photografted with PEGMA or N, N-dimethylacryl amide (DMAAm) via a surface photograft polymerization method based on the photochemistry of the dithiocarbamate group that functions as an iniferter [101]. The phenyl groups in the SPUs were chloromethylated with chloromethyl methyl ether and then the dithiocarbamate groups were introduced by the reaction of the chloromethylated SPUs with sodium N, N-diethyldithiocarbamate trihydrate. The platelet adhesion of the products were investigated and it was found that the poly(DMAAm)-grafted SPU surface reduced platelet adhesion and the poly(PEGMA)-grafted SPU surface showed little platelet adhesion or activation (note that the round spots scattered all over the surface were not adhered platelets).

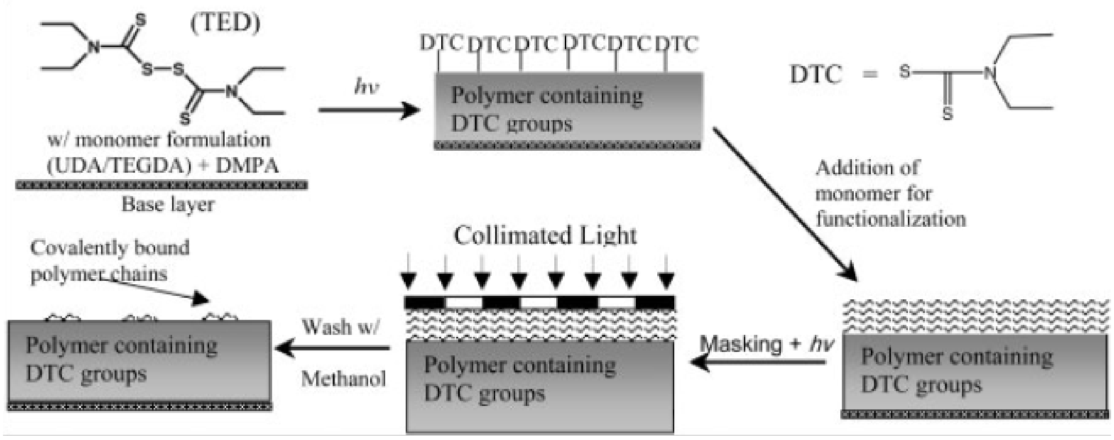


Scheme 27. MIP-grafting onto a cellulosic membrane by living radical copolymerization. Reprinted from ref. 105.

The “living” radical polymerization with an iniferter was used to create micropatterned biomedical surfaces. Novel, photosensitive biomedical polymers were created by the incorporation of dithiocarbamate groups from iniferters. A second monomer layer was then irradiated onto the photosensitive polymer substrate created with the iniferter to form a copolymer. Patterns were created on the films by application of modified microfabrication-based photolithographic techniques. The technique was used to create patterns with depths from 5 to 80 mm. In addition, various polymers were incorporated, including polyethylene glycol methacrylates, styrene, and methacrylic acid, to synthesize regions with different physico-chemical properties. Applications include novel surfaces for biosensors and biomaterials for the selective adhesion of cells and proteins [102].

Bowman et al had developed a novel, photopatternable grafting technology from polymer substrate [103, 104]. The diethyldithiocarbamate-containing polymer substrate was prepared by copolymerization of a mixture of methacrylic monomers with a methacrylic diethyldithiocarbamate molecule, (methacryloyl ethylenedioxy carbonyl) benzyl N,N-diethyldithiocarbamate (HEMA-E-In), which serves as a photoiniferter that is chemically anchored on the surface and throughout the substrate. Then surface-initiated photopolymerization of the poly (ethylene glycol) methyl ether methacrylate (m-PEGMA) was conducted from the surface of the polymer substrate (Scheme 26). Elevating the concentration of the monomer iniferter increases the rate of graft polymerization, and differences in water contact angles reveal surface bound functionality.

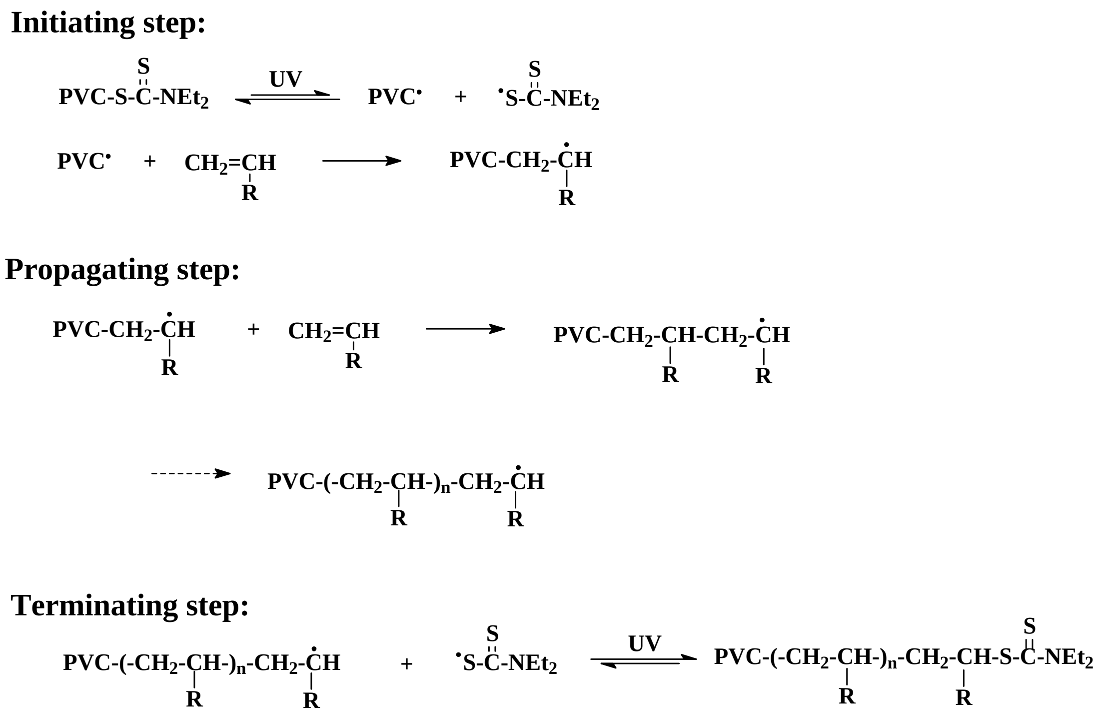
Yoshimi et al applied living polymerization for the grafting of the molecularly imprinted polymers (MIPs) using photoactive iniferter immobilized on the cellulose membrane with the benzyl N,N-diethylditiocarbamate group (Scheme 27). In a model system described here MIP was successfully grafted to dialysis membrane surface and used for studying gate effect. It was shown that the grafting degree, diffusive permeability and selectivity of Theo-MIP vary upon the time of UV irradiation [105].



Scheme 28. Controlled/living radical photopolymerization grafting chemistry with the DTC surface functionality. Reprinted from ref. 106.

The dithiocarbamate functionalities were introduced onto polymer surfaces using tetraethylthiuram disulfide (Scheme 28). It enables integration of LRP based grafting for the development of an integrated, covalent surface-modification method for microfluidic device construction. The unique photolithographic method enables construction of devices that are not substrate-limited [106]. It offers a way of surface-modifying substrates for applications varying from directed fluid flow to surface-assisted cell patterning.

Poly(n-butyl acrylate) grafted cross-linked poly(vinyl chloride) beads (PBA-PVC) [107] and polyacrylamide grafted cross-linked poly(vinyl chloride) beads (PAM-PVC) [108] were successfully prepared by the surface-initiated controlled/”living” radical polymerization (SI-CLRP) methodology from the cross-linked poly(vinyl chloride) beads with surface modification with diethyldithiocarbamyl groups under UV irradiation (Scheme 29). The macro-iniferter, diethyldithiocarbamyl cross-linked poly(vinyl chloride) beads (DEDTC-PVC) were prepared by the reaction of the surface C-Cl groups with sodium N,N-diethyl dithiocarbamate. The PBA-PVC showed higher adsorption capacities for organic solvents such as acetone, ethanol, toluene, and chloroform. And the PAM-PVC was found to be a selective adsorbent for Hg(II) ion.



Scheme 29. The mechanism of surface-initiated photopolymerization (R: COOBu or $CONH_2$).

Conclusions

The use of controlled/”living” free radical polymerization techniques to modify the surfaces of various polymeric materials offers many advantages on molecular weight, molecular weight distribution, and the structure of the resulting polymers over traditional radical polymerization techniques. It is expected that the methods might play an important role in the surface functionalization and designing of polymeric materials for advanced applications. And the introduction of initiating groups onto the surfaces for the controlled/”living” free radical polymerization and the characterization techniques for the modified surfaces will be further developed in the future years. The review has been summarized in Table 1.

Tab. 1. A summary.

Substrate	Method	Polymer grafted	Reference
crosslinked polystyrene-graft-PEG	ATRP	PHEMA	22
Poly(DVB80)	ATRP	poly(styrene-*b*-4-methylstyrene)	23
poly(DVB80-*co*-HEMA)	ATRP	PMA, PMMA, PHEMA, PDMAEMA) and poly(MMA-*b*-DMAEMA)	24
negatively charged PS	ATRP	PDMA	25, 26
negatively charged PS	ATRP	PNIPAM	27
PS	ATRP	PMA, PMMA	28
Sylgard PDMS	ATRP	PAAm	29
HDPE	ATRP	PMMA	30
Crosslinked PS	ATRP	PAAm	31

Crosslinked PS	ATRP	PMMA, PEA	32, 33
iPP	ATRP	PNIPA	34
EAA	ATRP	PAAm	35
PET, PEN	ATRP	PNIPAM	36
Cross-linked PVBC	ATRP	PDMAEMA	37
Cross-linked PVBC	ATRP	Poly(3-(trimethoxysilyl)propyl methacrylate)	38
PVDF-g- PBIEA	ATRP	PDMAEMA	39
PVDF	ATRP	PVP	40
PVDF	ATRP	PPEGMA, PDMAEMA	41
PVDF	ATRP	PMMA, PEGMA	42
Crosslinked PVC	ATRP	PHEA	43
PVC	ATRP	PAAm	44
PANI	ATRP	PMMA	45
poly(ether imide)	ATRP	PMMA	46
filter paper, microcrystalline cellulose, Lyocell fibers, dialysis tubing, and chitosan films	ATRP	PMA, PS	47
Cellulose	ATRP	PS, PMMA, PMAAm, PAcM	48
Cellulose	ATRP	P(MA-*b*-HEMA)	49
Cellulose	ATRP	PMMA	50
Ethyl cellulose	ATRP	PMMA, PS	51, 52
jute	ATRP	PS	53
starch	ATRP	PBA	54
chitosan	ATRP	PAAM	55
chitosan	ATRP	PS	56
porous polymer monoliths	NMRP	P(*t*-BMA), PCMS, PVP	65, 66
PP	NMRP	PS	67
PE	NMRP	PS	68
PP	NMRP	Copolymer of styrene and n-butyl methacrylate	69
PE	NMRP	Copolymer of styrene and n-butyl methacrylate	70
SBR	NMRP	PS	71
Merrifield resin	NMRP	PS	72
Merrifield resin	NMRP	PS, poly(acetoxystyrene), and poly[styrene- b-(methyl methacrylate-co-styrene)], poly(acetoxystyrene-b-styrene), and poly-(styrene-co-2-hydroxyethyl methacrylate) copolymers	73
PDVB	NMRP	Poly(4-tert-butylstyrene)	74
Crosslinked PMMA	NMRP	PS	75
Crosslinked PS	NMRP	PMMA	76, 77
spherical	RAFT	PNIPAM	80

PNIPAM/HEA copolymer			
PP	RAFT	PS	81, 82
PDVB	RAFT	PS	83
PVDF	RAFT	PAAc-b-PNIPAAM	84
PI	RAFT	PAmA-g-PMMA copolymers	85
FPI	RAFT	PEGMA	86
PTFE	RAFT	PGMA	87
PVDF	RAFT	PAA	88
FEP	RAFT	PHEMA	89
cellulose	RAFT	PS	90, 91
PVDF	RAFT	PMMA, PPEGMA	92
CPR	RAFT	PMAA	93
SPU	Iniferter	PEGMA, PDMAAm	101
PS	Iniferter	PEGMA-co-PEGDMA	102
PEGDMA	Iniferter	PEGMA-co-PMAA	102
copolymerization of a mixture of methacrylic monomers	Iniferter	Poly(m-PEGMA)	103, 104
cellulose	Iniferter	copolymer of MAA and EGDMA	105
DTC-incorporated UDA/TEGDA	Iniferter	Polymer of fluorescently labeled PEG acrylate	106
cross-linked PVC	Iniferter	PBA	107
cross-linked PVC	Iniferter	PAAm	108

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