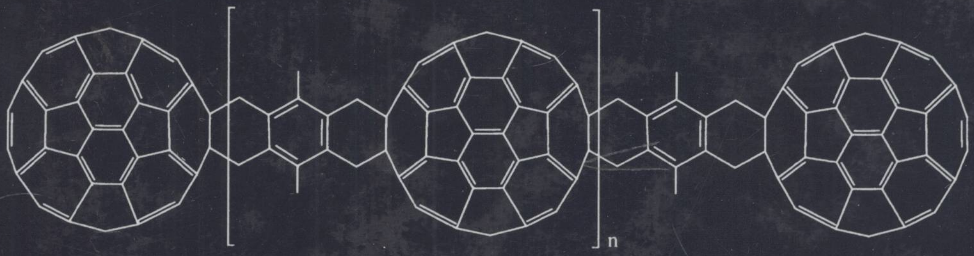
Advanced Functional Molecules and Polymers

Volume 2

Processing and Spectroscopy

Edited by
Hari Singh Nalwa



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Advanced Functional Molecules and Polymers

To my most honorable Gurus
Professor Satya Vir Arya
and
Professor Padma Vasudevan

Preface

Organic polymers are the most fascinating materials in the modern industrial era and have emerged as one of the most valued classes of materials in our everyday life. Organic polymers offer widespread applications in many fields of science ranging from solid state technology to biomedical engineering. The applications of polymeric products cover almost every area of consumer products such as telecommunications, the internet, optical fibers, light-emitting devices, displays, aircraft, audio-video systems, television sets, computers, insulators, electronic devices, contact lenses, kitchenware, home appliances, fabrics, sportswear, toys, building materials, automobiles, adhesives, paints, fillers, plastic wall and floor coverings, furniture, pipes, technical instruments, etc. Almost every corporation and institute in the entire world is involved in polymeric materials one way or the other because of their increasing demands. The superiority of polymeric materials is due to the aspects of their tremendous versatility and astonishing degree of tailoring to bring them closer to the novel applications. From a technological point of view, organic polymers offer enormous advantages over traditional materials such as metals, ceramics, glasses, wood, leather, etc. Polymeric materials are light weight, flexible and tough materials, they can be processed in the form of ultrathin films, fibers and even as liquid cystals, they offer low-cost mass production, they manifest good durability and environmental stability, and some are biocompatible.

The polymeric materials discussed in this book are key elements of continued scientific and technological advances in the 21st century and belong to one of the most diverse research fields. The four volume set of *Advanced Functional Molecules and Polymers* consolidates the current knowledge of science and technology of polymers and other low molecular weight organic materials into a single reference source including their synthesis, processing, theory, spectroscopy, and structure–property relationship to device applications. This book aims to bring together all aspects of functional molecular and polymeric materials currently studied in academic and industrial research by covering every single aspect of their science and engineering. The book draws on two decades of pioneering research on functional materials and their technology for the first time, while emphasizing the multidisciplinary nature. This book has 34 chapters presented in four volumes, written by 74 authors coming from 18 countries. The cutting edge state-of-the-art review chapters contain the most up-to-date research in the field of functional polymeric materials.

Volume 1 focuses on different topics related to synthetic aspects that include oligomers and polymeric fullerene derivatives; functional polymers; block and graft copolymers; metal-containing macromolecules; highly crosslinked polymers based on mesogenic monomers; synthesis of block copolymers with combination of different polymerization routes; syntheses and structures of thermotropic liquid crystalline polymers; structure–property relationships in polyurethane ionomers; and novel photoreactions of azadienes and related compounds.

Volume 2 is focused on processing and spectroscopy of polymeric materials covering various spectroscopic techniques. The topics in this volume include surface modification of polymers *via* molecular design; nanostructured polymers *via* microemulsion polymerization; polymer-stabilized metal nanoparticles; monolayers and membranes formed from polymers with surface active head groups; stereochemical and compositional assignments of polymers by NMR spectroscopy; infrared spectroelectrochemistry on conducting polymers and fullerenes; spectroelectrochemistry of intrinsically conducting polymers and fullerenes; structural studies of polymer systems using small angle neutron scattering; and methyl-group; dynamics in glassy polymers by neutron scattering.

Volume 3 focuses on electronic and photonic properties of defined chain length oligomers and polymers. The topics include thin film photoconductors; synthesis and properties of electrically conducting polymers such as polythiophenes, polypyrroles, polyacetylenes, polyanilines, poly(*p*-phenylenes) and rigid-rod polymers; electronically conducting ion-exchange polymers; photoinduced non-centrosymmetry in azo-polymers using dual-frequency interferences; second-order nonlinear optical molecules and polymers; poly(*p*-phenylene vinylene) derivatives as photonic materials; and fluorescence probes used in characterization of materials.

Volume 4 focuses on various physical properties and applications of polymeric materials. The topics include photodegradation and stabilization of polymers; properties of immobilized proteins; conduction of heat in polymers, polymer composite propellants; polyimides; ion beam processing and modification of polymers; polymeric membranes for reverse osmosis, ultrafiltration, microfiltration, gas separation, pervaporation and reactor applications; tribology of engineering polymers; use of functional polymers for metal ion complexation and separation; polymer-supported reagents; and the use of polyacetals in biomedical applications.

This book summarizes the current status of the field, covering important scientific and technological developments made over past decades with contributions from internationally recognized experts from all over the world. Fully cross-referenced, the book has clear, precise and wide appeal as an essential reference source long overdue for the scientific community involved in polymer science and engineering. With more than 8,000 bibliographic citations and nearly 1,500 illustrations, tables, chemical structures and equations, this book is an invaluable reference source for graduate and advanced level undergraduate students and scientists working in chemistry; polymer chemistry; polymer engineering; solid-state physics; materials science; electrical, optical and chemical engineering.

I greatly appreciate the tremendous efforts and cooperation of all the contributing authors who devoted their valuable time in preparing state-of-the-art chapters for this book. I would like to thank Professor Seizo Miyata of the Tokyo University of Agriculture and Technology (Japan), and many colleagues at the Hitachi Research Laboratory, Hitachi Ltd., Japan for their kind support during my stay in Japan. I would like to give my special thanks to my friends Krishi Pal Raghuvsnshi, Rakesh Misra, Jagmer Singh, Ranvir Singh Chaudhary, Ashish Kumar and other colleagues who supported my efforts in the compilation of this book. I have great appreciation for my wife Dr Beena Singh Nalwa for her continuous cooperation and patience in enduring this work at home during weekends and late nights, the moral support of my parents Kadam Singh and Sukh Devi and the love of my children, Surya, Ravina and Eric in this exciting enterprise.

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Biographical Note

Dr Hari Singh Nalwa is the Director at the Stanford Scientific Corporation in Los Angeles, USA. He was previously the Head of Department and R&D Manager at the Ciba Specialty Chemicals Corporation in Los Angeles (1999–2000) and a staff scientist at the Hitachi Research Laboratory, Hitachi Ltd., Japan (1990–1999). He has authored over 150 scientific articles in journals and books. He also has 18 patents either issued or applied for on electronic and photonic materials and their based devices. He has published eleven books including this 4 volume set: *Ferroelectric Polymers* (Marcel Dekker, 1995), *Nonlinear Optics of Organic Molecules and Polymers* (CRC Press, 1997), *Organic Electroluminescent Materials and Devices* (Gordon and Breach Science Publishers, 1997), *Handbook of Organic Conductive Molecules and Polymers*, Volumes 1–4 (John Wiley & Sons, 1997), *Low and High Dielectric Constant Materials* Volumes 1–2 (Academic Press, 1999), *Handbook of Nanostructured Materials and Nanotechnology*, Volumes 1–5 (Academic Press, 1999), *Advanced Functional Molecules and Polymers*, Volumes 1–4 (Gordon and Breach Science Publishers, 2001), *Handbook of Advanced Electronic and Photonic Materials and Devices*, Volumes 1–10 (Academic Press, 2001), *Photodetectors and Fiber Optics* (Academic Press, 2001), *Silicon-Based Materials and Devices* (Academic Press, 2001), *Supramolecular Photo-sensitive and Electro-active Materials* (Academic Press, 2001), *Handbook of Surfaces and Interfaces of Materials*, Volumes 1–5 (Academic Press, 2001) and *Handbook of Thin Film Materials*, Volumes 1–5 (Academic Press, 2001). The *Handbook of Nanostructured Materials and Nanotechnology* received the 1999 'Award of Excellence' in Engineering Handbooks from the Association of American Publishers.

Dr Nalwa is the founder and Editor-in-Chief of the *Journal of Nanoscience and Nanotechnology* (from 2001). He was the founder and Editor-in-Chief of the *Journal of Porphyrins and Phthalocyanines* published by John Wiley & Sons (1997–2000) and serves on the editorial boards of the *Journal of Macromolecular Science-Physics* (from 1994), *Applied Organometallic Chemistry* (1993–1999), the *International Journal of Photoenergy* (from 1998) and *Photonics Science News* (from 1995). He also serves as a referee for many international journals, that include the *Journal of the American Chemical Society*, the *Journal of Physical Chemistry*, *Applied Physics Letters*, the *Journal of Applied Physics*, *Chemistry of Materials*, the *Journal of Materials Science*, *Coordination Chemistry Reviews*, *Applied Organometallic Chemistry*, the *Journal of Macromolecular Science-Physics*, *Applied Physics*, *Materials Research Bulletin* and *Optical Communications*.

Dr Nalwa is a member of the American Chemical Society (ACS), American Physical Society (APS), Materials Research Society (MRS), Electrochemical Society (ECS) and the American Association for the Advancement of Science (AAAS). He has been awarded a number of prestigious fellowships that include a National Merit Scholarship, Indian Space Research Organization (ISRO) Fellowship, Council of Scientific and Industrial Research (CSIR) Senior fellowship, NEC fellowship and a Japanese Government Science & Technology Agency (STA) fellowship. He was also an Honorary Visiting Professor at the Indian Institute of Technology in New Delhi. Dr Nalwa has been cited in the Who's Who in Science and Engineering, Who's Who in America, Who's Who in the World and the Dictionary of International Biography.

Dr Nalwa received a B.Sc. degree in biosciences from Meerut University in 1974, a M.Sc. degree in organic chemistry from the University of Roorkee in 1977, and a Ph.D. degree in polymer science from the Indian Institute of Technology in New Delhi in 1983. He was a guest scientist at the Hahn-Meitner Institute in Berlin, Germany (1983), research associate at the University of Southern California in Los Angeles (1984–1987) and the State University of New York at Buffalo (1987–1988). In 1988, he moved to the Tokyo University of Agriculture and Technology, Japan as a lecturer (1988–90) where he was teaching and conducting research on electronic and photonic materials. His research activities include studies of ferroelectric polymers, nonlinear optical materials for integrated optics, low and high dielectric constant materials for microelectronics packaging, electrically ducting polymers, electroluminescent materials, nanocrystalline and nanostructured materials, photocuring polymers, polymer electrets, organic semiconductors, Langmuir-Blodgett films, high temperature-resistant polymer composites, water-soluble polymers, rapid modeling and stereolithography.

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Contents

Surface Modification of Polymers *via* Molecular Design

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Contents

1 Introduction

Objects made from polymeric materials are incredibly useful. In most of the engineering application, a polymer is selected because of its favorable bulk properties, such as mechanical strength, electrical and dielectric properties, thermal stability and processability. Many applications require that a polymeric material be attached to or in contact with another material or with a specific environment. In this regard, special surface properties with respect to chemical composition, hydrophilicity, hydrophobicity, roughness, biocompatibility, crystallinity, conductivity, lubrication, adhesion, crosslinking density etc. are required. Often, however, the selected

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polymer has surface and interfacial characteristics which are less than optimum for interacting with other materials or with the environment. Certain applications require low-energy surfaces which are chemically inert. Other applications require good adhesion and strong interactions between the polymer and other substrates.

The problem can usually be overcome to a large extent through controlled modification and functionalization of polymer surfaces and interfaces without altering the bulk physicochemical properties. The polymer literature is extremely rich in methods and strategies directed towards the modification of polymer surfaces for specific applications and services [1–9]. Common surface modification techniques applicable to polymers include treatments by flame, corona discharge, plasma, photons, electron beams, (x-rays, γ-rays), wet chemical oxidation, chemical functionalization, grafting and graft copolymerization. Controlled chemical and physical modification of polymer surfaces has been made possible by recent advances in two areas. First, there has been a steady increase in the availability of surface analytical techniques and instruments [10–12]. Secondly, the expanded surface analytical capability has resulted in a steady growth in fundamental understanding of relations between surface microstructure and various aspects of surface performance. This fundamental understanding, in turn, has substantially increased our ability to redesign and re-engineer the molecules at the polymer surfaces for specific applications, and to develop related technologies for surface molecular engineering [5]. More recently, Hoffman has summarized the surface modification technologies involving physical, chemical, mechanical and biological methods [13].

Although a variety of techniques have been proposed and employed for improving the surface characteristics of polymers, surface modification by grafting and graft copolymerization are used to a much lesser extent, for example, than gas plasma treatments [8]. Nevertheless, the technique offers an unequaled versatility and specificity for incorporating new molecular functionalities into the existing polymer in a well-controlled manner. In fact surface modification by grafting and graft copolymerization offers a simple and unique method for redesigning and re-engineering the surface molecules of all polymers, including the most inert fluoropolymers [14]. With continuous improvement in and simplification of the technique, as well as the availability of reliable methods for characterizing the chemical composition and microstructure of the modified surface, the process should become increasingly popular and attractive to the various industries. In fact, batch and continuous processes for surface modification of polymers *via* grafting and graft copolymerization have been designed [15–17]. Figure 1 illustrates a continuous surface photografting process for fibers.

2 Surface Molecular Design by Grafting and Graft Copolymerization

Molecular design or re-design of polymer surfaces can be achieved *via* two convenient approaches: grafting by coupling reactions and surface graft copolymerization. Grafting by coupling reactions refers to the direct attachment of previously synthesized polymer chains to the substrate surface, whereas graft copolymerization is the synthesis of polymer chains from monomer molecules by initiating chain growth from the active centers on the substrate surface. Both processes result in covalently tethered polymer chains on the substrate surface.

2.1 Grafting by Coupling Reactions

Most of the earlier studies on the surface modification by direct attachment of polymer chains have involved adsorptive attachment rather than covalent attachment or have involved inorganic surfaces rather than organic polymer surface [18–25]. Ikada and Uyama [5] have reviewed the various techniques and analytical methods associated with the chemical modification of polymer surfaces by grafting. The mechanism of surface grafting involves chemical coupling of the reactive groups

Table 1 Properties of polymer surface and related technologies for achieving such properties.

Property	*Related technology*	*Surface nature and related characteristics*
Adhesion	Polar groups anchoring	Hydrophilicity, surface free energy
Wettability	Acidic, alkaline treatment	Hydrophilicity, antifogging, adhesion, electroconductivity
Printability	Corona treatment	Hydrophilicity, adhesion
Antistaticity	Metal-coweaving, surfactant mixing	Electroconductivity
Antifogging	Hydrophilic-polymer coating, heating, extremely low surface energy	Hydrophilicity, hydrophobicity
Antifouling	Hydrophilic-polymer coating, micro-vibration, printing with organic tin compounds, extremely low surface energy	Hydrophilicity, hydrophobicity, mechanicaln removal
Biocompatibility	Enzyme mixing, protein immobilization, surface grafting	Hydrophilicity, hydrophobicity, bioinertness, antithrombogenicity
Lubricity	Hydrophilic or hydrophobic lubricious coating	Hydrophilicity, hydrophobicity

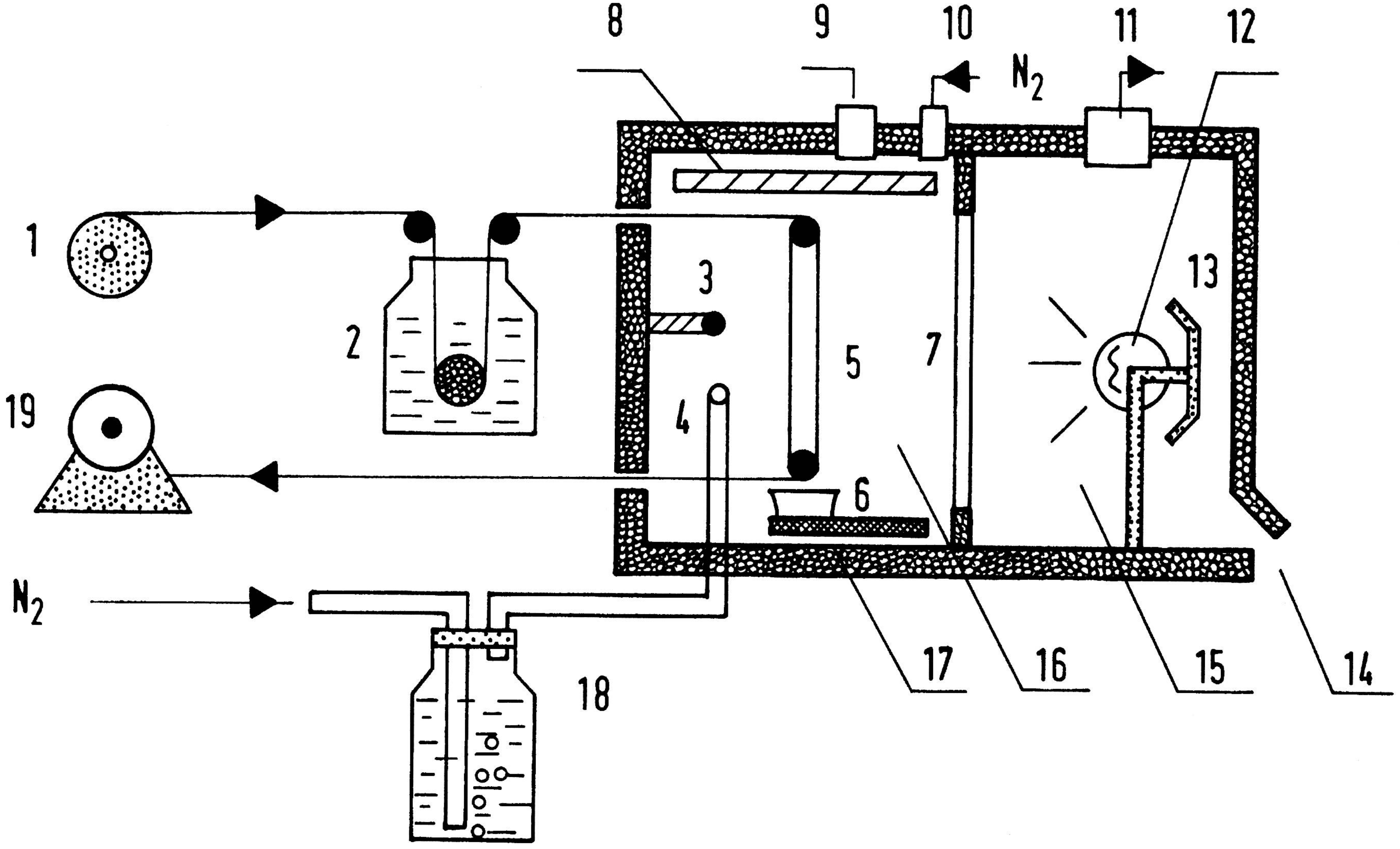

Figure 1 Surface photografting device. 1. fiber feed roll; 2. presoaking solution; 3. thermocouple (screened form UV lamp); 4. vapor inlet of monomer and initiator solution; 5. running rolls; 6. container of solid monomer; 7. quartz window; 8. cooling water pipe; 9. exhaust outlet; 10. nitrogen inlet; 11. air outlet (ventilation); 12. UV lamp; 13. parabolic reflector (of aluminium); 14. air inlet; 15. lamp box (water cooled); 16. reaction chamber; 17. electric heater; 18. monomer and initiator bubble solution; 19. pulling-off roll with driving motor. (Reproduced from reference 15 with permission of John Wiley & Sons, Inc.)

present on both the substrate and the chain to be grafted. For example, the poly(ethylene oxide) chains were grafted onto the silica surface by direct esterification of the silanol groups with the hydroxyl end groups of the polymer at 230 °C under a nitrogen atmosphere according to [24]:

$$\mathrm{SiOH + ROH \rightarrow SiOR + H_2O}$$

Kishida *et al.* [25] had directly immobilized poly (ethylene glycol) (PEG) chains onto a cellulose surface through esterification reactions. The terminal hydroxyl group of the PEG molecule was first derivatized to carboxylic acid using succinic anhydride. The modified PEG molecules were then chemically immobilized on the hydroxyl goup of the cellulose surface *via* a carbodiimide intermediate in a non-aqueous medium. Kramer [26], on the other hand, had proposed kinetic expressions for the grafting of a pure end-functional polymer melt to a reactive interface by assuming that the free energy of reaction was very large and negative.

A number of other studies also involved the grafting of PEG chains. Han *et al.* [27] and Park *et al.* [28] reported the grafting of PEG and heparin onto the surface of polyurethane (PU) and polyurethaneureas by the use of diisocyanate coupling agents or by isocyanate end-capped PEG prepolymer. A decrease platelet adhesion to the modified surface was observed. Bergstrom *et al.* [29], on the other hand, grafted PEG on the surface of polystyrene (PS) labware for the purpose of reducing the non-specific adsorption of protein. Grafting was accomplished *via* a multi-step process which involved prior amination of the PS surface and conversion of some of the PEG hydroxyl groups to epoxide groups, followed by chemical reaction between the epoxide groups and the amine groups to covalently attach the PEG chains. In yet another study, PEG chains were grafted onto the poly(ether urethane) film in a two-step process [30]. In the first step, the film surface was treated with hexamethylene diisocyanate in toluene and in the presence of triethylamine as a catalyst. In the subsequent step, the PEG chains were allowed to react in toluene with the surface bound isocyanate groups.

Dextran has also been grafted onto the surface of ethylene-vinyl alcohol copolymer through the coupling reaction with or without the primary amine groups [31]. The coupling reaction took place *via* a urethane linkage when unmodified dextran was used, and *via* urea linkage when the dextran contained amino groups. Tezuka *et al.* [32], on the other hand, immobilized block copolymers onto poly(vinyl alcohol) (PVA) and PU surfaces. The polystyrene-poly(dimethyl siloxane) (PS-PDMS) block copolymers containing vinyl silane or diol at the end of the chain (the 'macromers') were synthesized by living polymerization of styrene and dimethylsiloxane. The 'macromers' were then allowed to react chemically with the PVA and PU surfaces. In another study, Han *et al.* [33] prepared poly(ethylene oxide) (PEO)-grafted PU beads. The PU beads were first treated with hexamethylene diisocyanate in toluene and in the presence of stannous octate. They were subsequently grafted with PEO in benzene in the presence of the same catalyst.

Surface modification of chemically-inert substrates *via* grafting has also been widely reported. The poly(tetrafluoroethylene) (PTFE) film has been modified through bonding of polymeric silicic acid [34]. The porous PTFE film was first exposed to a silicon tetrahalide atmosphere to allow the low molecular weight species from the gaseous phase to penetrate the film. The absorbed silicon tetrahalide was subsequently hydrolyzed to silicic acid in water. On the other hand, polyethylene (PE) films functionalized with diphenylmethyl groups have been deprotonated to form a nucleophilic lithiated surface. The so-modified surface has, in turn, been used for the covalent binding of C_{60} to PE film surface [35]. Finally, a carboxyl-terminated PS has been converted to a triethoxy silane end-capped polymer, which can be surface grafted onto a cleaned silicon wafer [36]. The surface grafting is made possible by the fact that a triethoxy silane group can bond strongly to the silanol group of the silicon oxide surface.

2.2 Surface Graft Copolymerization

Surface molecular design *via* graft copolymerization is a simpler and more versatile technique than that of the coupling reactions, and has been explored much more extensively. Unlike the surface coupling reaction, which requires the presence of reactive groups on both the substrate and the polymer chain to be grafted, graft copolymerization of monomers normally requires only the generation of active species at the substrate surface to initiate polymerization. Surface graft copolymerization is based most commonly on the free radical reaction of vinyl or acrylic monomers, although cationic and anionic polymerization mechanisms can also be used. For graft copolymerization *via* the free radical mechanism, either free radicals or peroxides have to be generated in the surface region of the substrate to initiate chain growth. Surface graft copolymerization proceeds *via* the diffusion of the vinyl or acrylic monomers, present either in vapor or in solution, to the substrate surface and react with the active centers there. Since an active center is regenerated after each monomer addition, the reaction continues and the chains propagate from the substrate surface. In addition to chain growth from the surface, ungrafted homopolymer chains are also produced and can become adsorbed on the substrate. They must be removed by vigorous extraction.

The active species can be generated on the substrate surface in several ways. The two most widely practiced initiation mechanisms are: (i) the introduction of a polymerization photoinitiator or thermoinitiator in the reaction mixture, and (ii) the direct generation of active species on the substrates surface prior to the graft coplymerization process.

2.2.1 Initiation by Polymerization Initiators

For the first initiation mechanism, the initiator decomposes to form free radicals. The radicals in contact with the substrate surface will create unpaired electrons by abstraction of hydrogen from the polymer chains at the surface. The process is depicted in Figure 2(a), using benzophenone (PB) as the photoinitiator [17]. Upon UV irradiation in the absence of oxygen, BP is excited first to the singlet excited state ($^1BP^*$), which rapidly reverts to the triplet excited state ($^3BP^*$) by intersystem crossing. The BP molecule in the triplet state abstracts hydrogen from the polymer surface (P-H) by inelastic collision to produce a polymer radical (P•) and a ketyl radical (BH•). The C-H bond dissociation energies for various compounds are summarized in Table 2 [17]. The ketyl radicals are rather unreactive. They are inactivated or terminated by dimerization or by combination with other radicals. The polymer radical, on the other hand, can react with a monomer (M) to produce a covalently tethered surface macroradical which can initiate graft polymerization. The inelastic collisions of the triplet excited state with the monomers at the surface of the substrate are relatively more efficeint than its elastic collisions with the solvent and monomer molecules in solution, resulting in a high grafting efficiency [17]. Nevertheless, the grafted polymer layers are very thin, usually less than 10 nm. Even for substrates with very large area per weight ratio, the amount of grafting cannot be determined gravimetrically with accuracy [37]. Absolute amounts of grafted polymers, for example, have been analyzed by acid-base microtitration of polypropylene (PP) yarn grafted with acrylic acid (AAc) polymer. The thickness of the graft layer was calculated to be not more than 7.6 nm.

Table 2 C—H bond dissociation energy of various compounds.

Compound	*Abstracted H*	*C—H bond energy* (kcal/mol)
$CH_2{=}CH\text{-}CH_2\text{-}H$	Allylic	88
$(CH_3)_3C\text{-}H$	Tertiary	91
$(CH_3)_2CH\text{-}H$	Secondary	95
$CH_3\text{-}CH_2\text{-}H$	Primary	98
$H_2C{=}CH\text{-}H$	Ethylenic	104

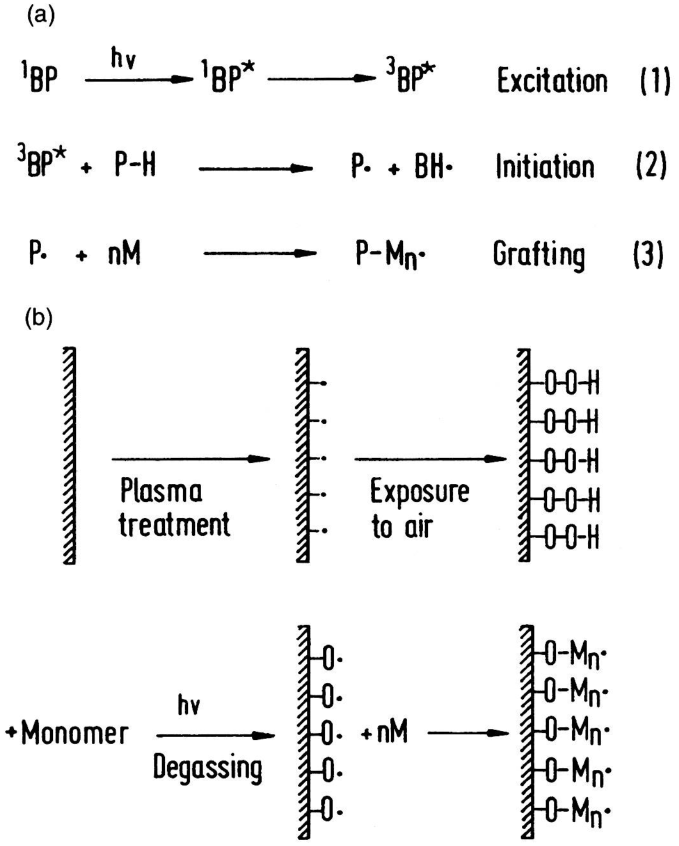

Figure 2 Schematic illustration of surface graft copolymerization (a) in the presence of a photo-initiator, benzophenone, and (b) in the presence of plasma activation of the substrate surface.

2.2.2 Initiation by Surface Pre-activation

The peroxide and hydroxyl peroxide species required for the initiation of surface graft copolymerization can also be generated on the substrate surface by gas plasma treatment [38], high voltage corona discharge [39], ozone [40], or UV exposure [41]. Alternatively, the unpaired electrons can also be generated on the polymer surface by bombarding it with high energy radiation, such as γ-rays [42], and electron and ion beams [43]. In any case, the surface treatment must not result in the over-oxidation of substrates surface and must leave the bulk unperturbed. The mechanism for the initiation of graft copolymerization from a substrate surface pretreated with plasma is illustrated schematically in Figure 2 (b). When a polymer surface treated with argon, hydrogen or oxygen gas plasma is exposed to air, peroxides and hydroxyl peroxide species are introduced on the surface. If the pretreated surface is exposed to UV irradiation or to the elevated temperature in the presence of a thoroughly degassed monomer or monomer solution, the decomposition of the surface peroxide species readily results in the initiation of surface graft copolymerization.

Strobel *et al.* [44] have compared the five gas-phase surface oxidation processes, viz., corona discharge, flame treatment, ozone exposure, remote air plasma treatment, and a combined UV/ozone treatment of polypropylene (PP) and poly(ethylene terephthalate)

(PET) films. The results indicate that the polymer surfaces are readily oxidized by the flame, corona discharge, and remote plasma treatments within a short period of time. Among the five techniques, flame treatment appears to give the shallowest oxidation depth. In the generation of surface oxidized species for the initiation of graft copolymerization, not all the methods are applicable to a specific polymer substrate. For instance, florinated polymers, such as PTFE films, are not susceptible to significant oxidation by ozone and corona discharge. The active species for surface graft copolymerization are effectively produced only by glow discharge treatemnt. On the other hand, fluorinated polymers are more suscceptible to chain scission than PE and PET when exposed to vacuum ultraviolet radiation [45]. The concentrations of peroxides introduced onto the poly(methyl methacrylate) (PMMA) substrate by the different activation methods, such as ozone exposure, UV irradiation, corona discharge and glow discharge, and their effect on the graft yield of the acrylamide (AAm) polymer have been investigated [46]. The most suitable surface activation method for the graft copolymerization of AAm onto PMMA substrate was concluded to be the UV irradiation.

3 Graft-Modified Polymer Surfaces

In this section, the graft-modified surfaces of a number of commonly encountered families of polymers are reviewed. For each family, the initiation methods used to achieve the graft copolymerized surfaces are further distinguished.

3.1 Polyolefins and Acrylate Polymers

Both the high-density polyethylene (HDPE) and low-density polyethylene (LDPE) films are by far the most widely used substrates for surface graft copolymerization. A pH sensitive LDPE surface has been prepared by immobilization of the AAc polymer [47]. In this case, the substrate surface was first functionalized with phenylpyrenyl methyl group, followed by graft polymerization of *t*-butyl acrylate monomer, and subsequently hydrolysed to form the AAc polymer. Pyrene groups were found to localize near the interfacial region, and the average degree of polymerization (DP) of acrylate polymer was estimated to be 20 to 30. An oxidative method by chromic acid had also been reported [48]. The esterified LDPE surface was then irradiated by UV to introduce the radicals for graft copolymerization of acrylonitrile. The surfaces of polypropylene (PP), PS, and polyacrylonitrile have also been oxidized by immersion in aqueous solution of oxidizing agents, such as potassium peroxy disulfate, under a nitrogen atmosphere at high temperature [49]. Graft copolymerization of water-soluble monomers, such as AAm, methacrylic acid, and 3-aminopropyl methacrylate has been performed in aqueous solution in the presence of 2×10^3 M ceric ammonium nitrate solution at 50 °C.

A number of studies involved the use of thermal or photoinitiators for surface graft copolymerization. In fact, the earliest work on surface modification in the 1950's involved photografting on substrates pre-coated with benzophenone [50]. The technique was also extended to the UV-induced vapor-phase graft copolymerization of functional monomers on photo-sensitized polyolefin films. The photoinitiators used included benzophenone, anthraquinone and benzoyl peroxide. Ogiwara *et al.* [51] later reported on the photo-induced graft copolymerization of AAc and methacrylic acid (MAA) on benzophenone-coated LDPE film in aqueous medium. However, it was not easy to graft copolymerize other hydrophilic monomers, such as AAm, to a high extent on these initiator-coated surfaces and a two-step initiator coating process was required for the photo-induced graft copolymerization [52]. A number of subsequent studies were also devoted to the surface modification of LDPE, PP and PS by photo-induced graft copolymerization with AAc and AAm in the presence of a photoinitiator, either in liquid or in vapor phase [16, 53–56]. In the case of vapor phase reactions, grafting was affected by the combination of the solvent/carrier used and the type of polymer substrate. The UV-photo-initiated process was also extended to the vapor phase graft copolymerization of glycidyl acrylate (GA) and glycidyl methacrylate (GMA) on PE, PP and PS [57, 58]. Other monomers which are susceptible to photoinitiated graft copolymerization with PE and PP include 4-vinyl pyridine [59] and HEMA [60]. More recently, radical living graft copolymerization on PE films with AAc and MAA in the presence of a photoinitiator, such as benzophenone, xanthone and 9-fluorenone, had been reported [61]. Finally, a scale-up process for the continuous photoinduced graft copolymerization of AAm and AAc on HDPE films had also been developed [62, 63].

The earlier work on the physical pretreatment of HDPE powders involved the exposure to a high γ-frequency discharge from a Tesla coil prior to the graft copolymerization of acrylonitrile [64, 65]. The ionization radiation-induced graft copolymerization can be carried out by three methods: (1) simultaneous irradiation and graft copolymerization through free radicals formed in situ, (2) graft copolymerization through peroxide groups introduced by pre-irradiation, and (3) graft copolymerization initiated by trapped radicals from pre-irradiation [42]. The pioneering work on the surface modification of PE films and silicone rubber substrates involved surface graft copolymerization with the hydrophilic 2-hydroxyethylmethacrylate (HEMA) and AAm using a simultaneous surface activation and graft copolymerization technique from irradiation by a ^{60}Co source [66]. The modified substrate surface was carefully characterized