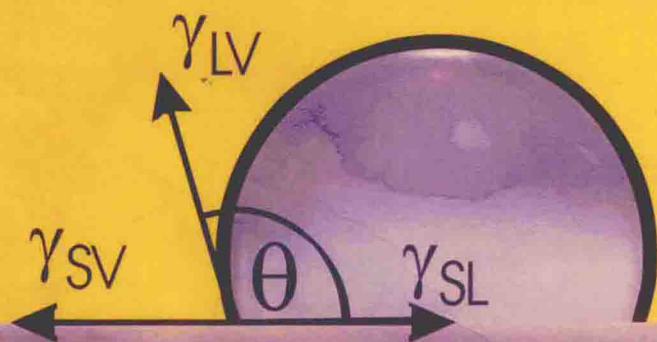


Polymer Assisted Surface Modification by Photons



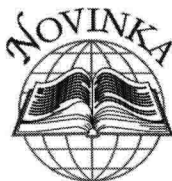
Daniel Eduardo Weibel

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POLYMER ASSISTED SURFACE MODIFICATION BY PHOTONS

DANIEL EDUARDO WEIBEL



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PREFACE

Polymers have been applied successfully in many different fields such as membrane and thin-film technologies, biomaterials and biocompatibility, sensors, adhesion, protective coatings, microelectronic devices, composites, etc. Success or failure in a particular application depends many times on special surface properties of the material with regard to chemical composition, hydrophilicity, roughness, crystallinity, conductivity, lubricity, and cross-linking. Polymers very often do not possess the surface properties needed for these applications. However, surface modification techniques, which can transform these inexpensive materials into highly valuable finished products, have become an important part of the plastics and many other industries. In recent years, many advances have been made in developing surface treatments to alter the chemical and physical properties of polymer surfaces without affecting their excellent bulk properties. In particular, the past two decades have seen the rapid development of new strategies for the design of polymer functional surfaces. As one of the main techniques developed to achieve efficient surface modification of polymeric materials, electromagnetic radiation-induced surface modification has been widely applied as simple, useful and versatile approach to improve the surface properties of polymers. This book surveys the recent advances in electromagnetic radiation-induced surface modification of polymers, predominantly focusing on the research work carried out in the last decade and covering the modification and functionalization of polymer surfaces using: (1) Ultraviolet (UV); (2) Vacuum-UV (VUV); (3) Laser and (4) Synchrotron radiation sources. Each radiation source combined with traditional or new experimental approaches has the ability to tailor specific applications.

The academic interest in this area is driven by two reasons: the first one is the advance in the understanding and manipulation of nano and microstructures designs at surfaces together with the chemistry involved at the molecular level. The second is associated with the unique potential associated in use light to transform and pattern surfaces. The extensive base of knowledge of photochemistry accumulated in the last half century, in particular the advances in surface photochemistry, offers exciting potential for modification of surfaces with control of both the density and nature of surface chemical groups. Electromagnetic radiation permits a high selective control of the changes produced at the surfaces due to quantum allow transition rules. Simultaneously the use of ultrafast laser sources, where ablation takes place because of non-resonant process by multi-phonon absorption, can be used even in materials normally transparent to the laser wavelength. Additionally, electromagnetic radiation treatments offer solutions in terms of industrial applications, which need for materials to compete in the increasing low-cost consumer market. The materials for these applications should be cheap, easy to make, and, last but not least, be environment-friendly, combustible, or better yet biodegradable or photodegradable. These characteristics, which can not usually be obtained by traditional wet and dry surface modification techniques of polymer surfaces, offer great potential for expansion of modification methods based in electromagnetic radiation.

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Chapter 1

INTRODUCTION

The field of polymer photochemistry is recognized as an active and very important area in applied photochemistry, with rapidly extending applications in industrial development. Light source-driven technologies such as UV-hardening, photolithography, photopolymerization, photohardening and photochemical grafting became very common as surface modifications techniques. In particular, photopolymerization and photocuring science and technologies are being developed toward designing novel and specific initiators and materials for special applications. Photocrosslinking of polymers is also very attractive in terms of enhancing the physical and mechanical properties of conducting materials.

Optical properties of polymers remain an active area of strong development, with a continued growth in photochromic and liquid crystalline materials. New polymer-based composite materials containing nanoparticles is a rapid growing field[1], particularly in relation to fast optical switches, magneto-optics data storage, interferometers, nonlinear optical properties, etc. Photoactive polymer films by immobilization of photoactive complexes in polymer matrices enable the study of the electro- and photochemistry of species in non-diffusive conditions. Research in polymer based solid state electrochemoluminescent[2] and dye based solar cell systems[3] have shown the widespread applications of those approaches in recent years. Those and other examples[4] demonstrate that processes, such as, electrochemoluminescence seen in solution can be achieved also in immobilized systems.

Surfaces that can respond to a specific external stimulus in a specific manner, the so called smart surfaces[5], are of increasing interest in areas as diverse as organic electronics, cell culture, microfluids and coatings. The

combination of those smart surfaces with the flexibility provided through molecular synthesis, supramolecular chemistry, and surface science, open a series of exciting opportunities for the development of new materials and devices. Photoswitchable molecules immobilized in polymers are a recent attempt for the generation of photoswitchable polymers. For example, a photo/electrochromic dithienylcyclopentene can be immobilized on a surface as a thin film (<10 nm) through the electropolymerization of a methoxystyryl unit attached to the photoactive unit[6]. The limited conductivity of the polymer backbone limits the oxidative electropolymerization of the methoxystyryl unit. The polymer film is formed consistently as a thin film and can be switched both optically and electrochemically between the open and closed state of the photochromic dithienylethene moiety, although problems with oxidation and extended UV irradiation leads to rapid destruction of the photochromic functional unit.

Photodegradable polymer is receiving increasing attention in the last decade, due there are compelling economic and social reasons for using degradable plastics in certain applications and, therefore, considerable research is now devoted to devising new polymers with improved performance. The ideal photodegradable polymer would be such material that should end up as litter rather quickly after light activation. Basically, there are two methods to obtain polymers photochemically degradable[7,8]. One method is to introduce chemically a chromophore into the polymer chains. Indeed, the most commercially successful chromophore is the carbonyl group[7,8]. Ultraviolet radiation absorption leads to typical photoreactions of the carbonyl chromophore, *i.e.*, the well known Norrish type I and II processes or by an atom abstraction process[9], all of which produce the degradation of the polymer material. The second general method for making polymer materials photochemically degradable is to mix a radical initiator into the polymer[10,11]. Although direct irradiation of polymers might be the simplest method, in some cases, the use of photosensitive structures has some advantages. The photosensitization method should be preferred when there is a need of controlling the photodegradation, as well as when the irradiation is performed at wavelengths that are not absorbed by the polymer. The excitation of the sensitizers may result in the production of free radicals that can initiate polymer degradation processes. In general, these radicals abstract hydrogen atoms from the macromolecule forming polymeric alkyl radicals that react with oxygen, initiating an oxidative chain reaction. Both the carbonyl-containing and the radical initiator require ultraviolet light for degradation. Recently, some research groups tried to synthesize visible light photo-

degradable polymers based in a new class of polymers that contain metal-metal bonded organometallic dimmers interspersed along the polymer backbone[12]. These polymers are photodegradable because the metal-metal bonds can be cleaved with visible light and the resulting metal radicals captured with oxygen or other traps.

In the polymer photochemical processes described above, the surface of the solid material is a very important property in successful applications and among all parts of a material, the outmost surface of the solid will probably interact physical and chemically with its environment in the largest extend. The microstructure and chemical functional groups present at the surfaces are usually different from those in the bulk. To achieve materials with desired surface properties for specific applications, the surface of solids are modified by a wide range of surface treatment techniques. Surface modification has many advantages, such as, no need to redesign the bulk material to achieve a target surface performance, improvement of the surface properties without affecting its bulk properties and in many cases reduction in cost, since all chemistry is confined to the surface. In recent years, many advances have been made in developing surface modification techniques for polymers to tailor specific applications which change their original chemical and physical surface properties and keep their bulk properties intact. The more common surface modification techniques now a day available are treatments by plasma, corona, photons, electron beams, ion beams, X-rays, γ -rays, chemical grafting and combinations of different methods, including modern hybrid techniques. By using those treatment technologies different polymer surfaces can be modified to achieve the following objectives:

1. Increase hydrophilicity.
2. Increase hydrophobicity.
3. Introduce special functional groups at the surface.
4. Modify surface free energy.
5. Improve chemical inertness.
6. Introduce surface cross-linking.
7. Modify surface morphology increasing or decreasing roughness.
8. Remove weak boundary layers or contaminants.
9. Increase separation efficiency in membranes.
10. Increase surface electrical conductivity.
11. Avoid or decrease corrosion rate.
12. Decrease friction.

Surface functionalization of polymeric materials by using polychromatic or monochromatic electromagnetic radiation is a relatively new research field, in particular when monochromatic radiation is used as a tool to introduce new surface functionalities. UV-light treatment of polymer surfaces provides similar effects with other techniques, such as plasma treatment modifying their hydrophilicity, chemical properties on surfaces, and so on. The use of UV-light for surface treatment is a classical application of this methodology for surface modification. However, there are significant differences, advantages and disadvantages of UV-treatments compared with plasma modification techniques. Plasma treatments are generally limited to surfaces, but photochemical reactions can be surface-limited or can take place deep inside the bulk depending on the UV absorption coefficient at the specific UV-wavelength. Plasma can treat wide surface areas, while UV-treatment can process wide areas as well as very small spots. Another difference is the power-intensity control. Controlling plasma intensity is generally limited although with some methods like a magnetic field confinement it can be enhanced locally. In UV-photo treatment, one can use continuous wave (CW) UV-lamps with a moderate light intensity to very high power output of a pulsed laser. In general, UV processes do not require costly equipment and offer the advantage of patterned surface modification by use of lithographic techniques. In the last decade, new applications of UV surface functionalization have been published combining reactive gas or vapors atmospheres with simultaneous UV irradiation of the polymer[13-18].

The developments of excimer lasers and vacuum-ultraviolet (VUV) sources based on dielectric barrier discharges, DBDs, is inciting increasing interest as means to oxidize polymer surfaces. Although low-pressure radiofrequency (r.f.) plasmas were used to study VUV since the early 1970s[19], the field of materials processing with VUV radiation has only recently received much attention[20-27]. Organic materials with multiple bonds or with atoms which have non-bonding electron pairs such as oxygen or nitrogen absorb light with a wavelength shorter than 200 nm very strongly[28]. This property limits the penetration depth of the photons and 90% of the radiation is absorbed within a surface layer between 50 and 100 nm. The penetration depth contrast with UV light, where, depending on the intensity of the source, the wavelength or the polymer structure, the radiation is absorbed nonuniformly within microns (1-6 μm). Principal advantages of VUV excimer radiation sources are high monochromatic radiant exitances, simplicity of construction, large emission area with high energy photons, low cost, and availability of different wavelengths. Excimer VUV lamps are very promising

for surface modification for large area industrial applications. Excimer radiation sources may be preferred to laser and plasma techniques for the treatment of large surface areas as well as for the simplicity of the irradiation equipment used, taking into account that plasma systems require most often vacuum lines and controlled gas mixtures.

The understanding of the interaction of a laser radiation with a material has contributed to the increase application of lasers to surface modification, machining, laser ablation deposition, and chemical analysis. The availability of eximer laser sources in the VUV spectral region has increased the number of publications in polymer surface modification using lasers as excitation sources. In particular, laser technology has found interesting applications in the fabrication of polymer based sensor arrays by applying conventional patterning steps on appropriate photosensitive materials[29]. Further polymer engineering should maximize the number of areas with different sensing properties on the same substrate producing a novel class of polymer sensor arrays with enhanced detection efficiency of liquid/gas analytes[30]. The photo induced changes in the VUV in one hand modulate the physical/chemical functionality of the polymeric surfaces such as hydrophilicity, wettability, or biocompatibility and on the other hand, lead to surface modification with nanoresolution. The high value of the absorption coefficient and the high molecular photo-dissociation probability allow atomic resolution depth control. In addition, modification of chemical composition and roughness of the irradiated part of the organic films is achieved, enhancing thus the surface-probe binding strength and the detection sensitivity in a predetermined way.

Within the wide range of photochemical sources used to modify polymer surface properties, synchrotron radiation (SR) is the less explored way of treatment. A synchrotron yields a continuous spectrum of radiation extending from the far IR to the hard X-ray regime. Third and projected fourth SR sources have much more intense photon flux than can be obtained by most conventional sources. UV and X-ray monochromators provide an adjustable spectral resolution for all photoemission experiments. Further advantages of SR are its 100% polarization in the plane of the ring, its high degree of collimation, its high stability and well-defined time structure for time-resolved measurements. In spite, the unique properties of this source a few studies have been carried out to modify the surface properties of polymeric materials[31-36]. Surface modification by SR exposure in the soft X-ray region under gas atmosphere is effective in controlling surface properties; however, it has not been extensively reported because of its experimental difficulties originating

from the lack of a suitable window material in this energy region and the use of ultra high vacuum conditions. Probably, new kind of studies will start to appear in the future using SR radiation to modify selectively polymer surfaces due to the increasing importance of this radiation to characterize, modify and synthesized new materials.

This book is intended to review the status of worldwide research in surface modification of polymeric materials using mainly electromagnetic radiation as excitation source and covering from the UV up to soft X-ray region. Second section reviews various techniques to perform surface modifications of polymeric materials and typical experimental techniques used to characterize the changes produced at the treated surfaces are presented in Section 3. Thereafter the electromagnetic radiation treatment of polymer surfaces are discussed depending on the source used, UV, VUV, laser and SR, in sections 4, 5, 6 and 7 respectively. Finally, a few conclusions and outlooks in surface modification by electromagnetic radiation are summarized in section 8.

TECHNIQUES IN SURFACE MODIFICATION

2.1. WET CHEMICAL

In wet chemical surface modification, a material is treated with liquid reagents to generate reactive functional groups on the surface. This classical approach to surface modification does not require specialized equipment and thus can be conducted in most laboratories. It is also more capable of penetrating porous three-dimensional substrates than plasma and other energy source surface modification techniques[37], and allows for in situ surface functionalization of microfluidic devices. For example, cyanuric chloride was used as a coupling molecule between hydroxyl groups on the surface of an epoxy resin and polyamines[38]. In this way two polyamine, diethylenetriamine and branched polyethylenimine, were successfully coupled to the surface via chemical modification. Recently, an interesting application of TiO_2 self cleaning coatings on polycarbonate (PC) substrates was reported[39]. TiO_2 coatings on plastics may find widespread application in auto and construction industries if the coating produces a polymeric material with new differentiated photocatalytic and mechanical properties. A chemical surface treatment method was used to create hydrophilic groups on the PC surface. Then TiO_2 was deposited based on wet coating using an anatase sol of TiO_2 nanoparticles of 30 nm size. PC with a self cleaning TiO_2 layer exhibited better hardness and scratch resistance, as well as good photocatalytic and mechanical properties.

Chromic acid and potassium permanganate in sulfuric acid have been used to introduce reactive oxygen-containing moieties to poly(ethylene) (PE) and poly(propylene) (PP)[40, 41]. PP, like PE and other polyolefins, has become an increasingly important material. The ability to tailor the bulk properties of

polyolefins through catalyst design makes these already important polymers derived from relatively inexpensive feedstocks even more important. However, these polyolefins are generally hydrophobic materials and in many practical instances, improved adhesion, wettability, printability, or biocompatibility is desired. As a result, there is continuing and widespread interest in new chemistry capable of modifying these polymer surfaces. For example, PP was initially oxidized by etching to produce a modified surface[41]. Then, a series of repetitive grafting experiments using a diamine derivative of poly(*tert*-butyl acrylate) were used to produce surfaces containing significant amounts of poly(acrylic acid) obtaining water contact angles of approximately 20-30°. On the other hand, treatment of the modified PP surfaces by chemical etching with alkali produced a more hydrophilic carboxylate surface. Treatment of these surfaces first with ethyl chloroformate followed by pentadecylfluorooctylamine produced a hydrophobic fluorinated surface. Modifying a pristine polyolefin surface allows for further processing of the polymer increasing the application range and impact of the material in the market.

Fluorinated polymers, like poly(tetrafluoroethylene) (PTFE) has widely used in several fields of industry because of its excellent properties, such as thermal and chemical stability, low surface energy and high resistivity. PTFE membranes are frequently used for filtration, as gas permeable membranes in gas electrodes and diffusion cells and can be used in the construction of biosensors based on an oxygen sensor or an ammonia gas electrode. Membranes and powders prepared from PTFE were investigated for their potential use as multifunctional supports for proteins, enzymes and sugars[42]. PTFE surfaces have been modified by refluxing for 8 h with elementary sodium in toluene to generate double bonds. In a next step, samples were oxidized at 120 °C in a 1:1 mixture of trifluoroacetic acid and hydrogen peroxide (38%) which improved membrane wetting and allowed immobilization of the enzyme *alliinase*.

Unfortunately, these wet chemical methods are non-specific, introducing a range of oxygen-containing functional groups. Chain surface orientation, as in PMMA ester modification, for example, adds additional complexity in the treatment processes and the degree of surface functionalization may therefore not be repeatable between polymers of different molecular weight, crystallinity, or tacticity. These wet chemical methods also generate hazardous chemical waste and can lead to irregular surface etching[43]. Many of these techniques also require extended treatment in concentrated corrosive solutions.

For these reasons, while useful in the laboratory environment, these wet chemical processes may not be suitable for larger scale, industrial applications.

2.2. PLASMA

Broadly, a plasma can be defined as a gas containing neutral and charged species, including electrons, positive and negative ions, radicals, atoms and molecules in ground and excited states and electromagnetic radiation (mainly UV and VUV). In a plasma, the average electron temperature ranges between 1 and 10 eV, the electron density varies from 10^9 to 10^{12} cm⁻³, and the degree of ionization can be between 10^{-6} and 0.3[44]. There are a wide range of scientific published reviews[44-47] and books (see the review of Denes, et al.[45] and references therein) concerning plasma treatment of polymers and only a brief account will be given in this section.

Plasma treatments in its different forms have moved from the academy to become important industrial processes for modifying the surface properties of polymers. The main advantages of plasma modification techniques can be summarized in the following:

1. Bulk properties of the polymer remain intact after treatment because the surface modification can be confined to the surface layer, typically less than ~ 100 nm.
2. Choosing the gas in the plasma, it is possible to graft particular chemical functionalities at the polymer surface.
3. Common problems encountered in wet chemical techniques (section 2.1) such as residual solvent on the surface and swelling of the substrate can be avoided with the use of a gas plasma.
4. Excited species in gas plasma can modify the surfaces of all polymers, regardless of their structures and chemical reactivity, and this modification is fairly uniform over the treated surface.

The disadvantages of the plasma processes are as follows:

1. A vacuum system is required in traditional plasma treatments increasing the operation cost.
2. Optimal parameters developed for one system usually cannot be adopted for another system. Because the plasma process is extremely complex; it is necessary a very good control of the plasma

parameters such as Radio Frequency (r.f.), power level, gas flow rate, gas composition, gas pressure, sample temperature, and reactor geometry. In consequence, it is difficult to achieve a good understanding of the mechanisms involved between the plasma species and the surface.

3. It is difficult to control the concentration of a particular functionality formed on a polymer surface.
4. Usually, polymers substrates modified by plasma have to be further processed after treatment, between hours and up to a few days, because polymers recover pristine properties, commonly in a short period of time.

Plasma occurs naturally on the sun and other stars[45] and it is also artificially produced in fluorescent lights, plasma displays and flat panel TV. The generation and sustenance of a plasma requires an energy source to produce ionization of the gas species. The use of direct current (DC) in a plasma requires that electricity has to be conducted through the electrodes, where in one of them, the sample is set for treatment. Frequently, polymer films are insulators which it would charge up the electrode and terminate the discharge. To solve the problem an AC power source is used because positive charges accumulated during one half-cycle can be neutralized by electron bombardment during the next cycle. To provide a continuous discharge a frequency of 50-100 kHz is sufficient to obtain many of the qualitative features observed in a DC glow discharge. A r.f. plasma can be initiated and sustained by external electrodes outside the reactor vessel or the coil wound around the reactor vessel. A typical plasma system is constituted by a vacuum pumping system, a reactor vessel, a matching network, a power source and a gas handling or flow control system. A schematic diagram of a typical r.f.-plasma reactor including the generated species in a plasma is shown in Figure 1.

In general, the interaction of the reactive species generated in a gas plasma can react with polymer surface according the following processes[44]:

1. Surface reactions: Reactive plasma gas-phase species can react directly with the polymer surface. Alternatively, surface species can produce new functional groups after exposition to oxygen or other gases. In addition, those reactive species can give place to crosslinking reactions at the surface. Examples of these reactions include plasma treatment by argon, ammonia, carbon monoxide,

carbon dioxide, fluorine, hydrogen, nitrogen, nitrogen dioxide, oxygen, and water.

2. Plasma polymerization: A thin film on the surface of a polymer is formed via polymerization of an organic monomer such as CH_4 , C_2H_6 , C_2F_4 , C_3F_6 , acrylic acid, etc. in a plasma. These complex processes involve reactions between species in the gas phase, reactions between surface species and reactions between gas-phase species and surface species.
3. Etching and surface cleaning: Undesirable materials at the polymer surface or atmospheric contaminants are removed from a surface by chemical reactions and physical etching at the surface to form volatile products. Organic contaminants presented at the surface are usually removed by oxygen-containing plasmas. Etching differs from cleaning only in the amounts of materials that are removed from the surface.

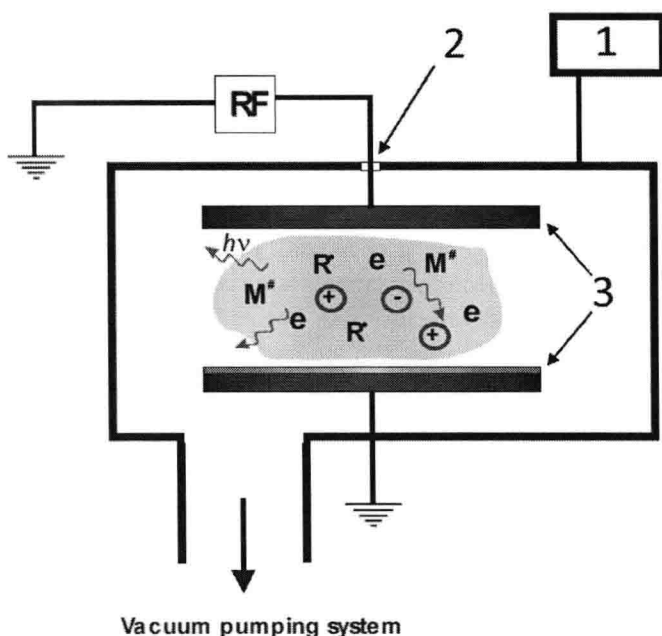


Figure 1. Schematic diagram of a parallel plate cold-plasma reactor representing the plasma-generated species. 1: gas supply and flow control; 2: electric insulator; 3: electrodes; RF: r. f. generator; R^* : radical species; $M^\#$: metastable excited species; $h\nu$: UV and VUV emitted radiation.