

### **1.4 Polymer surface treatment by plasma exposure**

#### **1.4.1 Surface functionalization**

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Introduction of functional groups into polymer surfaces based on the attachment of plasma species onto the surface; thus, exposure to oxygen plasma produces a broad variety of O-functional groups at polymer surfaces. The same is true if the polymer is exposed to the nitrogen plasma. Different N-containing groups were found. Exposure to the ammonia plasma did not produce the desired amino groups in significant concentration <sup>14</sup> as also found for carbon dioxide plasma and the formation of carboxyl groups <sup>15</sup>. Only the plasma exposure of polyolefins to bromine or bromoform plasma exclusively formed the desired C-Br groups in high concentration without side reactions <sup>16</sup>.

#### **1.4.2 Plasma polymerization**

Low-pressure plasma polymerization for coating and therefore for modifying polyolefin surfaces are of much significance. Two types of monomers or precursors are used in literature <sup>17</sup>, chemically easily polymerizable vinyl and acrylic monomers, such as styrene or acrylic acid and non-polymerizable precursors of any composition, which are gases or are evaporable, such as HMDSO. These monomers may be chemically hardly polymerizable monomers, such as HMDSO or allyl monomers as allyl alcohol and allylamine. By clever choice of the non-polymerizable precursors, by managing of deposition rate and plasma parameters, the film quality and therefore the surface properties can be controlled, thus the adhesion-promoting property for enhancing of both the adhesion strength of plasma polymerized layers on polymer substrates and their adhesion to coatings.

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Thus, surface functionalization, polymer etching, or plasma polymer deposition can be carried out by low pressure plasma processes. In order to characterize the modified polymer surface or the deposited layers and coatings X-ray photoelectron spectroscopy (XPS), Rutherford Backscattering (RBS), High-resolution Electron Energy Loss (HREELS), Near-Edge X-ray Absorption Fine Structure (NEXAFS) or Static Secondary Ion Mass Spectrometry (SSIMS) as well as contact angle measurements (CAM)/surface energy measurements were used <sup>18</sup>.

Polymer surface functionalization and plasma polymer deposition were used in various medical and biological applications, in microelectronics, anti-fouling, anti-corrosive, televisions, solar cells etc. Deposition of thin films includes sputter deposition <sup>19</sup>, and plasma enhanced chemical vapor deposition PECVD <sup>20</sup>.

### **1.4.3 Polymerization mechanism**

Conventional polymerization of vinyl or acrylic monomers by chain-growth polymerization <sup>21</sup> did not occur under harsh plasma conditions, at low pressure with low monomer density in the gas phase and under high energy input conditions <sup>22</sup>. The reason why is the high energy level in the plasma to sustain the steady-state of plasma and the low pressure, which causes a too seldom attachment of monomer molecules onto the active radical sites. Thus, recombination or disproportionation occur frequently and thus produce very low kinetic chain lengths and therefore low molecular weight products. Classic chain growth polymerization produces more or less linear polymers of high molecular weight and high chemical regularity. The lower the percentage of chain growth products the plasma polymer the more irregularly structured is its structure.

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The energy excess can be partially lowered by use of low wattage and use of pulsed plasmas. The very low monomer density under vacuum conditions can be minimized by use of pressure-pulsed plasmas or use of underwater plasmas<sup>23</sup>.

The dominating process in low-pressure plasma polymerization is the precursor dissociation to atoms and fragments followed by their random (poly) recombination to a chemically irregular structured crosslinked "polymer" with included monomers, oligomers, trapped C and peroxy radicals. The fragmentation of precursors is caused by inelastic collisions with electrons in the gas phase. Poly-recombination of fragments and atoms or ions occurs in both the gas phase or in the adsorption layer.

The most influential parameters for the composition of such plasma polymer layer are the power (rf power) of the plasma per amount of monomer injected into the system. The Yasuda parameter ( $W/FM$ ) describes the power density, where  $W$  is the wattage,  $F$  the flow rate, and  $M$  the molecular weight of the monomer. It was calculated that more than 1000 eV were used to transform one molecule of n-hexane to a plasma polymer<sup>24</sup>. Yasuda<sup>25-27</sup> proposed polymer forming process which can be related to the elimination of hydrogen and scission of C-C bonds forming mono-radicals  $M_i$ , and bi-radicals  $M_k$ , and thereafter, the addition of the radicals to monomer and the recombination between two radicals proceeds to make large molecules with or without radical, see Figure 1.1<sup>28</sup>.

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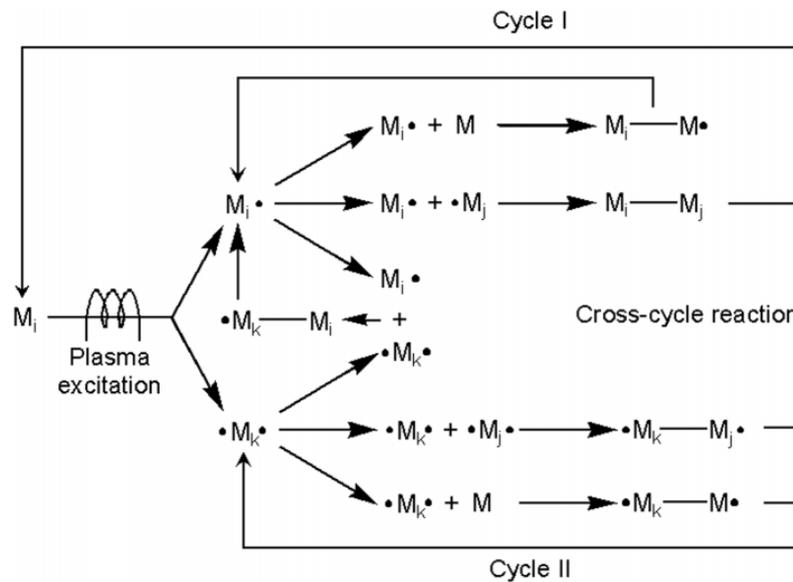


Figure 1.1 Schematic diagram of the bicyclic step-growth mechanism of plasma polymerization

Mono-radicals  $M_i \cdot$  add monomer molecules and form a new radical  $M_j - M \cdot$ . A further mono-radical  $M_i \cdot$  may recombine with  $M_j \cdot$  to build a neutral or stable molecule  $M_i - M_j$ . A bi-radical can also attack the monomer to form a new bi-radical  $\cdot M_k - M$ , or recombine with another bi-radical to form a new bi-radical  $\cdot M_k - M_j - M_k - M_j \cdot$ . This cycle I is the repeated activation of the reaction products from mono-functional activated species, cycle II describes the recombination of the mono and bi-radical to form larger radicals. However, this reaction process suggests that a more or less intact and regular linear or branched polymer is formed. Yasuda has also assumed the “Atomic Polymerization” of completely fragmented precursor molecules corresponding to the here preferred “Fragmentation-Polyrecombination Polymerization”.

Besides surface functionalization and plasma polymer coating some etching can happen simultaneously as a result of the bombardment of both the substrate and the growing coating by ions. The short wavelength plasma as radiation (vacuum ultra violet

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radiation-VUV) can modify the polymer near surface layers by  $\sigma \rightarrow \sigma^*$  processes resulting in polyene formation and crosslinking. These different processes have been described by Yasuda as competitive ablation polymerization (CAP) <sup>26,29</sup>, as seen Figure 1.2 <sup>26</sup>.

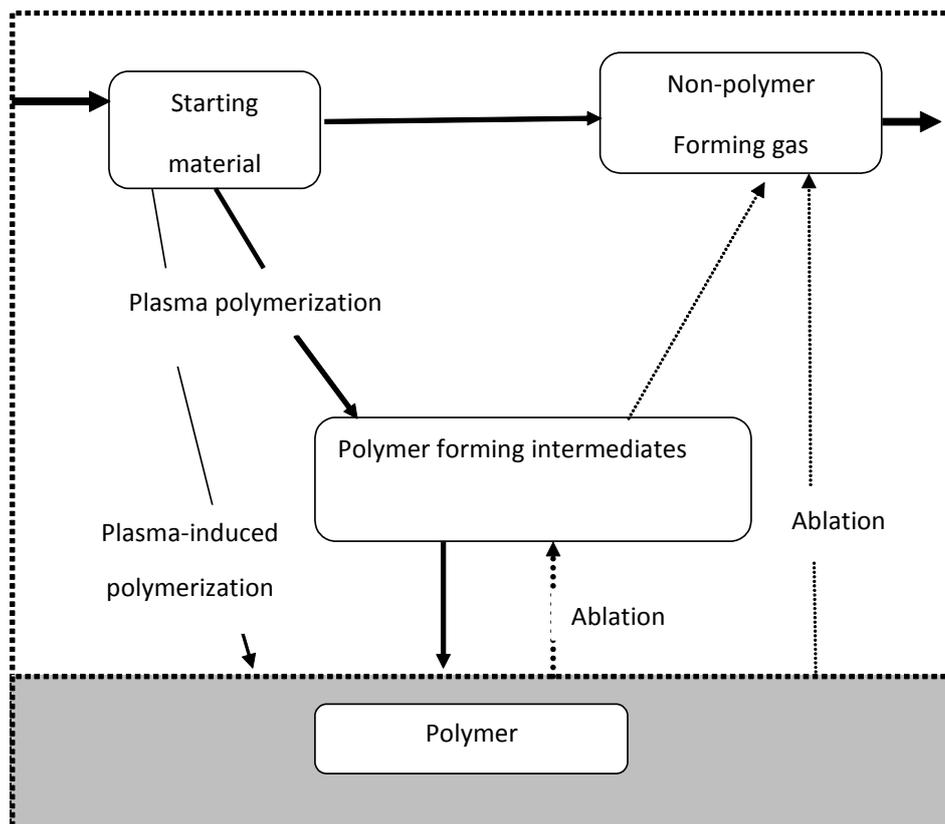


Figure 1.2 Schematic diagram of the mechanism of the plasma polymerization process

In classic polymerization monomers are linked together by chain-growth reactions without alteration of the monomer structure in the repeating units. Other variants are polyaddition as known from polyurethanes formation, ring-opening polymerization known from polyamides and caprolactame, polycondensation two monomers with release of small molecules as known from phenol-formaldehyde condensates <sup>30</sup>. Therefore, the chemical structure of the polymer is more or less fully determined by that

of the monomer. In contrast to that plasma polymerization of the same monomer forms a polymer, which has no or marginal accordance to the classic polymer and, therefore, to the monomer. This is attributed to the total monomer fragmentation, the random recombination of fragments, and the post-plasma reaction of trapped radicals in the plasma polymer layer with oxygen from air and start of auto-oxidation reactions.

### **1.4.4 Plasma polymerization of self-assembled mono-layers**

Monomolecular Langmuir-Blodgett (LB) layers offer a unique opportunity to prepare model surfaces with known thickness and molecular architecture <sup>31-35</sup>. It is a useful method to modify systematically the chemical properties of solid surfaces in order to control their functions in such processes as wetting, adhesion, and friction <sup>36</sup>. This technique is used to deposit highly oriented, ultrathin films <sup>37, 38</sup>. A well-defined monolayer is transferred onto the substrate, and highly ordered multilayers can be deposited. Self-Assembling Monolayers (SAM) were used as adhesion promoter and as corrosion-inhibiting layer <sup>39</sup>.

### **1.4.5 Plasma-induced grafting of monomers**

A method used to modify the surface chemical characteristics of natural and synthetic polymers through the activation of the polymer by exposure to the plasma, producing radical-sites, which are able to react with the introduced vinyl or acrylic monomer, thus forming regularly structured graft chains on polymer surfaces <sup>40</sup>. The second variant is plasma treatment of polymer and its exposure to air, thus transforming C-radical sites into peroxide radical sites, which can be decomposed thermally or irradiatively and then