Polymer Surface Modification and Micropatterning for Biomedical Applications

Hui Sun, Yingkai Xu, Guozhi Xu

Chemical Industry Press

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· Beijing ·

精确控制细胞行为是细胞和组织工程学研究的最终目标，材料表面形貌特别是微/纳米图案化形貌对细胞行为产生重要影响。本书基于著者近年来在高分子生物材料领域的科研成果撰写而成，系统地介绍了温和的无溶剂气相光接枝用于高分子材料的新方法和该法与微流体孔道技术相结合提出的掩模光接枝的高分子表面微/纳米图案化新技术，适合化学、化工、材料、生物工程等领域科研工作者阅读使用。

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Preface

Nowadays, polymers have been increasingly used as cell-culture substrates. Studies show that both polymer surface chemistry and surface topography play important roles in cell-surface interactions. Polymer surface modification and patterning have enabled the fabrication of model surface for cell-surface interaction studies.

In this book, we describe surface modification of polymers via solvent-free vapour-phase photografting and electron-beam induced grafting polymerization as well as hydrolysis approaches. Grafted molecules of interests are acrylamide, maleic anhydride and acrylic acid. Polymer substrates chosen are both conventional and biodegradable, such as poly(ethylene terephthalate), poly(methyl methacrylate) and polycaprolactone. A variety of surface functionalities including XPS probe molecules are incorporated into modified polymer surfaces. Cell-recognizing RGD peptides were immobilized onto polymer surface for cell-surface interaction studies. Contact angle measurements, X-ray photo-

electron spectroscopy, ultraviolet-vis spectroscopy are employed to precisely characterize surface properties.

We also describe masked vapour phase photografting as a novel approach to micropatterning polymer surfaces. The development of this method is based on the combination of vapour phase photografting and microfluidic channel technique. It provides a new means of modifying and patterning polymer surface at the same time.

I am indebted to many persons who have in one way or another helped make this book possible. I would like to thank my co-authors Dr. Yingkai Xu and Prof. Guozhi Xu for their time spent. I am particularly grateful to Beijing Technology and Business University for financial support. I would like to express my gratefulness to prof. Zhonglong Wei and colleages for their encouragement.

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Photografting of Acrylamide onto Poly (ethylene terephthalate)

1.1 Summary

Poly (ethylene terephthalate) (PET) films were photografted under reduced pressure in a solvent free vapour of acrylamide and benzophenone without pre-treatment of PET by impregnation or sorption of reactants. Characterization of grafted samples by ESCA and contact angles showed that the grafting increased with grafting time and temperature. The amide groups obtained by the acrylamide grafting were converted into amine groups by the Hofmann rearrangement to be used in coupling reactions. These were confirmed with an acid chloride compound containing fluorine as label for ESCA. Surface grafting of polymeric substrates in the vapour phase induced by plasma or high energy and UV irradiation is reviewed.

The surface modification of PET for biomedical applications is of major interest since this polymer is a structural component in artificial vascular grafts and heart valves.

In this investigation we have studied the photo-

grafting of PET in a solvent free vapour phase of AAm and BPO at reduced pressure. The resulting acrylamide grafted surfaces were converted to contain amino groups by the Hofmann reaction for additional modification by coupling reactions with model compounds suitable for ESCA evaluation of the coupling efficiency.

1.2 Introduction

The chemical or physical functionalization of polymeric surfaces with amino, carboxylic or other reactive groups is a primary step for attaching additional reagents to the surface directly or via spacer molecules. For these secondary steps a range of high yield coupling reactions are available based on well established organic chemical reactions[1~5]. Common applications are attachment of enzymes and antibodies in bioassays[6], heparin in non-thrombogenic devices[7] and cell binding peptides in cell and tissue engineering[8,9].

Although the initial functionalization often uses adsorption methods covalent linking of the chemical groups to the substrate is desirable to increase environ-

mental stability. This regards pH, ionic strength, temperature and solvents in the subsequent coupling and purification steps as well as in the final applications.

In the selection of methods for the covalent binding of chemical groups to a solid polymeric substrate also the substrate material as such has to be concerned. This is not only with regard to its response to a certain graft initiating reaction and inertness towards processing conditions. Also in the chemical modification of a surface provided with submicro- or nanodimensional patterns such topographies should remain after the grafting operation. For these reasons we started to search for a mild but yet efficient surface grafting process with the ambition to confine the grafting to a thin surface layer.

The advantages of supplying the monomer in a vapour phase in comparison to liquid phase have long been recognized comprising more efficient use of monomer, less homopolymerization and easy separation of the grafted substrate.

Plasma techniques operate in a heterogeneous phase system where a solid substrate is reacted with a

vapour phase plasma at low pressures. Surface grafting may be achieved by activating the solid substrate with an inert gas plasma to generate radicals or peroxides prior to grafting[10~13] or exposing it directly to monomeric or other functional plasmas[13~16]. The main difficulty is to create a uniform plasma in small hollow spaces as would be encountered in small diameter pits and between substrate and mask[17] when grafting topographies or patterns of submicron dimensions. Also when using inert plasma for activation, surface etching of the substrate may occur.

Other alternatives are surface grafting initiated by UV-, γ- or electron beam (EB) irradiation which are also carried out in heterogeneous systems where the substrate could be exposed to monomer in a surrounding liquid[18~21] or vapour phase[22, 23]. In comparison to γ- and EB- irradiation UV has a much lower energy and thus in general the lowest damage potential to the substrate. For materials which are transparent to the UV irradiation inner as well as outer surfaces could be treated also when grafting surfaces within very small cavities.