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POLYMERS GRAFTED FROM SOLID SURFACES

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Abstract: Monolayers of polymer molecules were generated at the surface of a solid substrate in situ by using self-assembled monolayers of initiator molecules. The layers were characterized by IR-spectroscopy, surface plasmon resonance measurements, ellipsometry, X-ray reflectometry, AFM and neutron reflectometry. Several novel techniques for the photolithographic patterning of the attached films are described. As a potential application for the attached layers the control of adhesion of biological cells to solid substrates is studied.

INTRODUCTION

To tailor the surface properties of a material several techniques have been developed in the past in which monolayers of polymer molecules are adsorbed or chemically bound to the solid substrate [1]. However, there are some rather strict limitations on the structures, which can be realized with the help of the established techniques limiting their general applicability. Firstly the use of reactive "anchor" groups used for the attachment of the polymers excludes the incorporation of many functional groups as they can either compete with the anchor moieties for surface sites or they can undergo side reactions with reactive groups present in the polymer or at the surface [2]. Furthermore it has to be considered, that by increasing the number of polymer chains attached to the surface a stronger concentration gradient is built up in close proximity to the surface. The polymer molecules have to diffuse uphill against this concentration gradient leading to a strong kinetic hindrance for further film growth. Therefore

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the thickness of the attached layers is intrinsically limited to thicknesses of 3-5 nm in the dried, collapsed state [3].

In this paper we report on the synthesis and characterization of molecularly thin polymer layers by using self-assembled monolayers (SAMs) of radical chain initiators (Fig. 1). We show that following this novel strategy films with well-defined chemical structure can be obtained in a wide range of film thicknesses and chemical compositions [4].

RESULTS AND DISCUSSIONS

The SAMs of the radical chain initiators were prepared through a base catalyzed condensation reaction between the hydroxyl groups of a SiO_2 surface (silicon wafer, glass substrates, evaporated SiO_x films) and the chlorosilane head group of an azo initiator (Fig. 1b).

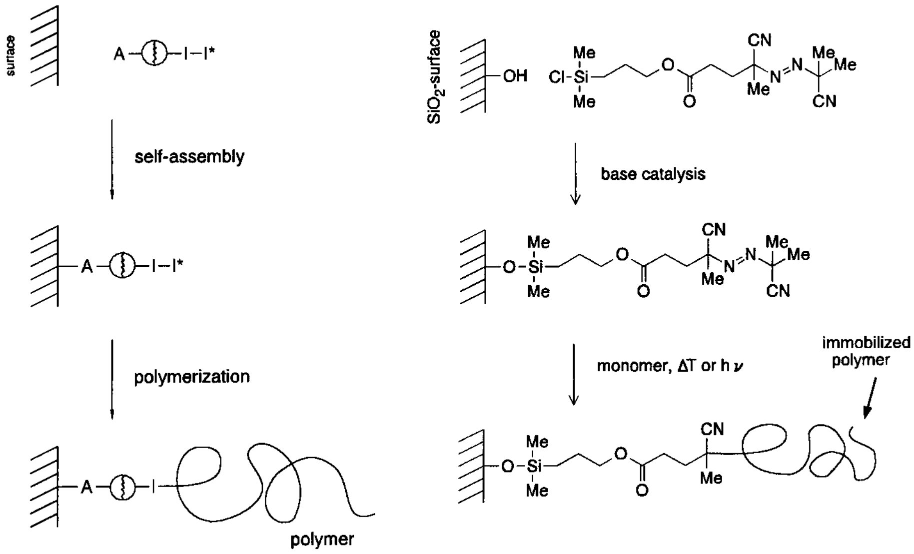
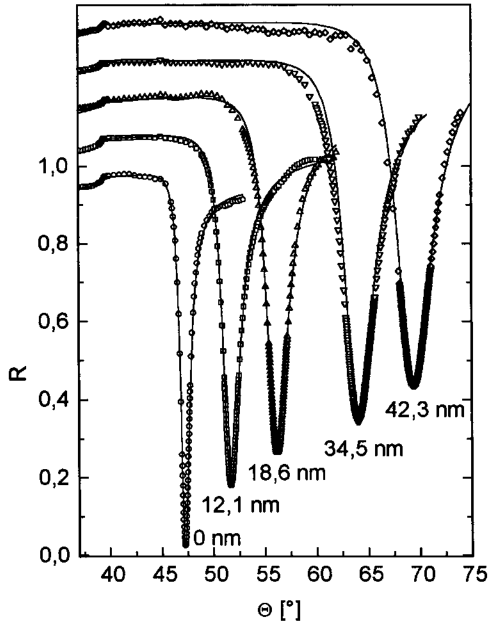


Fig. 1: Preparation of polymer monolayers by using self-assembled monolayers of an azo initiator containing a "break seal" group a) general concept, A = anchor group, I = initiator b) immobilization of an AIBN type initiator with a chlorosilane anchor group

After completion of the immobilization reaction the substrates were rinsed with various solvents, dried and placed in Schlenck-tubes, in which the polymerization reactions were carried out. The reaction vessels were charged with monomer and solvent and degassed through repeated freeze-thaw cycles to remove residual traces of oxygen. The initiators were activated with heat or light. After the polymerization reactions were stopped all non-attached polymer (physisorbed or entangled material) was removed during continuous extraction in a Soxleth extractor for at least 14 hours.

In Figure 2 it is shown, that monolayers with well defined thicknesses and good homogeneity can be obtained. The two factors which control the mass density of the attached material are the molecular weight and the graft density of the surface attached chains (i.e. number of polymer molecules per surface area).

a)



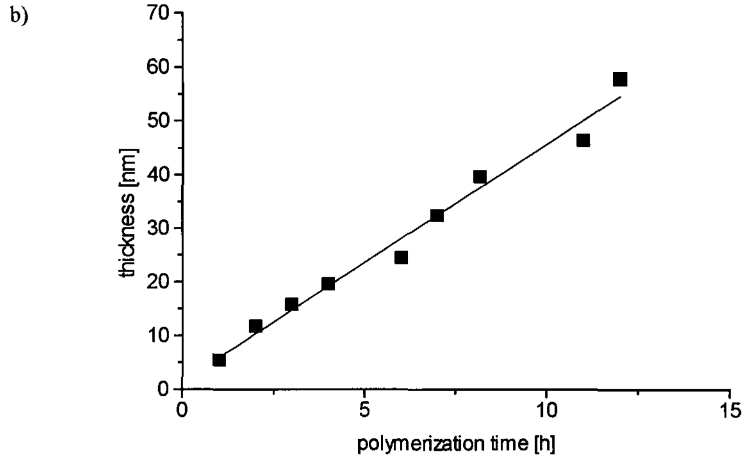


Fig. 2: a) reflectivity curves of polystyrene monolayers as a function of polymerization time (initiator conversion); substrate (glass, 50 nm Ag, 30 nm SiO_x), T = 60 °C; styrene: toluene 1:1, t = 0, 2,4,6 and 7 hours; the reflectivity curves are shifted by a constant additive factor for clarity; b) layer thickness of the obtained monolayers

Examples for parameters, which influence the thickness of the polymer film are polymerization time (i.e. conversion of the initiator), temperature (i.e. surface concentration of radicals), solvent quality and transfer properties of the solvent as well as monomer concentration (Fig. 3a) to name just a few. Polymer molecules with high molecular weights (up to several millions grams per mole; determined after degrafting of the polymer by transesterification) and high graft densities (average distance between attached chains 2-3 nm) can be attached leading to very thick layers of tethered molecules (Fig. 3b). The film thickness of the monolayers can be reduced by dilution of the initiator in the monolayer with inert compounds, partly statistical (thermal) deactivation or through addition of free initiator to the polymerization solution thus increasing the probability for termination of an attached growing chain with a chain growing in solution.

A large variety of polymer monolayers has been prepared through this route including water soluble and unpolar compounds, polyelectrolytes, statistical copolymers, polymers with crosslinkable or reactive groups and dye containing polymers. The attached polymers can be further modified by carrying out polymer analogous reactions. Examples are the transformation of uncharged tethered polymer molecules into a polyelectrolyte brush and the reaction of functional molecules with N-succinimide-ester groups which have been incorporated into the surface attached polymer layer by copolymerization.

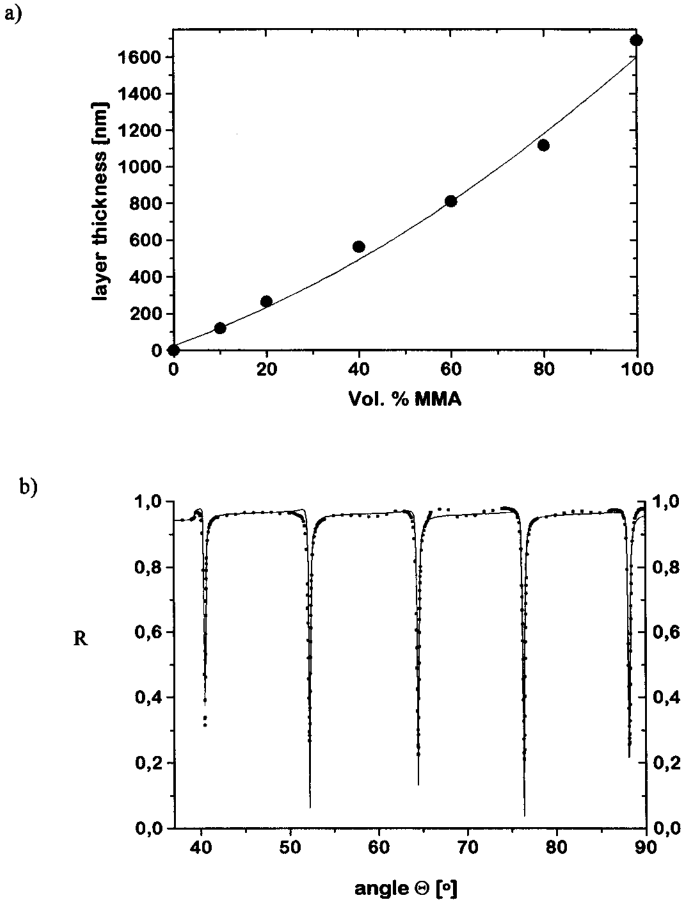


Fig. 3: a) film thickness of PMMA monolayers as a function of monomer concentration during the polymerization reaction (temperature 60°C, t = 18h); all samples have been extracted with toluene after stopping of the polymerization reaction for 20-48 hours; b) wave guide spectrum of a 1690 nm thick PMMA layer, solid line is a calculation according to Fresnel equations

Photolithographic patterning

The films can be patterned using appropriate masks and deep or near UV irradiation before, during or after polymer formation. Firstly, we performed conventional deep UV ablation experiments to pattern the attached molecularly thin films and carried out further surface reactions in the areas where the polymer has been removed by the photovolitalization. These procedures take advantage of the fact, that the polymer cannot be dissolved in further reaction steps due to the covalent linkage to the surface. A second approach uses light induced passivation of some areas of the self-assembled monolayer of the initiator (writing of a latent image) followed by polymer formation through thermally induced radical chain polymerization in the not irradiated areas (development) to yield a patterned, ultrathin polymer film. An even more promising technique is to photoactivate the initiator through a mask in the presence of monomer leading to formation of a film of tethered polymer molecules through photopolymerization. These three photolithographic procedures allow the chemical tailoring of surfaces with high spatial resolution. Step-and-repeat procedures, which take advantage of the covalent linking of the polymers to the surfaces, permit the preparation of multifunctional polymer patterns.

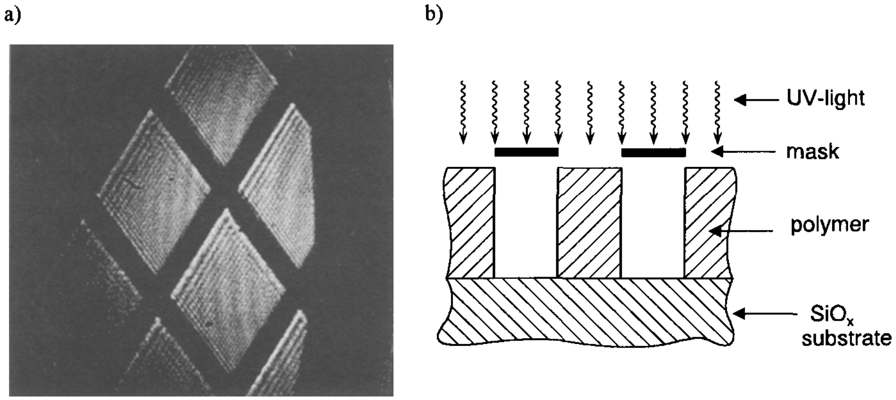


Fig. 4: Surface plasmon microscopy image of 21.5 nm thick polystyrene monolayer generated by photopolymerization; mask: electron microscope grid, stripe width 22 µm b) schematic depiction of the photopolymerization experiments

Biocompatibility studies

The attached monolayers can be used to improve the biocompatibility of materials. Through adjustment of the chemical composition of the attached layer the adhesion of biological cells can be either improved or decreased. Additionally, as shown above, the layers can be photolithographically structured and the obtained polymer patterns used for spatial control of the adhesion of cells to the substrate. In Fig. 5 the arrangement of biological cells (PC 12 cells) on a silicon chip, which has been modified by a patterned polystyrene layer is shown. The polystyrene layer (20 nm thickness) has been grown by photopolymerization where the initiator has been irradiated through a mask. It can be seen, that the cells follow closely the surface chemistry written in by the lithographic procedure.

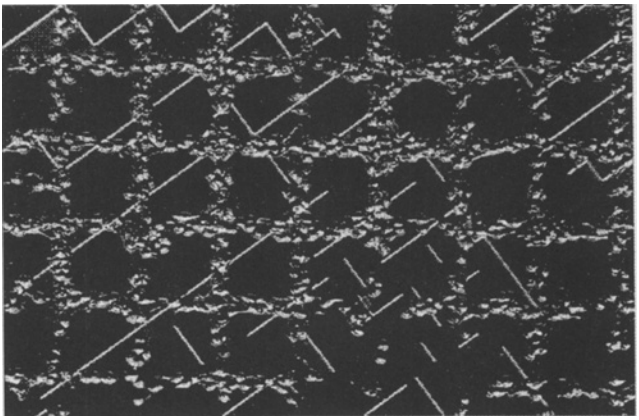


Fig. 5: Arrangement of biological cells (PC 12 cells) on a SiO_2 surface by using a photolithographically structured polystyrene monolayer

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REFERENCES:

(1) T. Cosgrove, B. Vincent, J.M.H.M. Scheutjens, G.J. Fleer and M.A. Cohen-Stuart, *'Polymers at Interfaces'* (Chapman & Hall, London, 1993)

(2) R. Zajac and A. Chakrabarti, *Phys. Rev. E*, **52**, 6536 (1995)

(3) a) J. Rühe, thesis (Habilitationsschrift), University of Bayreuth, 1995; b) J. Rühe, *Nachr. Chem. Tech. Lab.* **42** (1994) 1237

(4) G. Tovar, S. Paul, W. Knoll, O. Prucker and J. Rühe, *Supramol. Sci.* **2**, 89 (1995)