Preparation of Thin Surface Layers by Grafting of PEO

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SUMMARY: We have developed a two-stage process to graft poly(ethylene oxide) (PEO) onto a silica surface. In the first stage the adsorption of an anchor reactive polymer to the surface is carried out, and in the second stage the grafting of compatibilizing macromolecular tails is performed via the reactions of functional groups of the polymer anchored. Random copolymers of styrene and maleic anhydride (SM) were chosen as reactive anchoring polymers. The kinetics of adsorption of SM from dilute solutions onto the silica surface as well as the grafting of PEO to SM macromolecules adsorbed was experimentally investigated by null ellipsometry. A model of the structure at the surface is proposed.

Introduction

Formation of thin polymer layers with well defined structure on solid mineral surfaces has not only great theoretical but also very important practical value, first of all for the development of new materials for electronics, medicine, chromatography, and so on. There are many approaches to the problem of attaching polymer macromolecules to the interface. The major ones developed recently are adsorption of block copolymers, functionalization of the surface by introducing azo-, peroxide or other groups, and graft polymerisation of vinyl monomers initiated via the treatment of surface with high energy, i.e. X-ray, UV-light, etc(1).

In the last decade we have developed a new approach to tailoring compatibilizing polymer layers immobilized at the interface of different polymer systems(2). This is a two-stage modification process, when at the first stage the adsorption of an anchor reactive polymer on the surface is carried out, and then at the second stage grafting of compatibilizing macromolecular tails is performed through the reactions of functional groups. The main advantage of such approach is that the functionalization of surfaces is achieved due to adsorption of reactive polymers. When compared with the immobilization of reactive groups on a surface via the chemical reaction of low molecular weight organic compounds, immobilization through polymer adsorption is less sensitive to the nature of surface. Therefore, the latter is much more universal. Taking into consideration that among polymers used for surface modification poly(ethylene oxide) is one of the most attractive because the

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surfaces covered with PEO demonstrate notable properties, such as reduced dynamic surface tension, low surface viscosity, high steric stabilization, preventing protein and cell adsorption, etc [3,4], the aim of the present work was to graft poly(ethylene oxide) chains to a mineral surface, e.g. to silica surface, through reactive polymers adsorbed on this surface.

Experimental

Copolymers of styrene with maleic anhydride with different molecular weight (1 600, 16 000, 40 000, and 100 000) have been employed as reactive anchor polymers. They were synthesized in acetone solution according to the procedure reported elsewhere [2,5]. PEO with molecular weight of 5 000 and 10 000 were obtained from Riedel-de-Hain and used without further purification. The solvents (acetone and 1,4-dioxane) both of reactive grade were purified by distillation over sodium metal and following filtration through a microfilter with 0.2μm sieve. Diethylene glycol (DEG) and succinic anhydride (SA) were obtained from Riedel-de-Hain. N,N-dimethylformamide (DMFA) and triethylamine (TEA) (Fluka) were purified according to custom procedure[6,7].

Silicon wafers from Wacker Chemie with a mirror surface were chemically oxidized to obtain SiO_2 layer of about 150 nm thickness [8]. These wafers were then cleaned in an ultrasonic bath with chloroform for 15 minutes, further oxidized by a mixture of perhydrol with ammonia (1:1 w/w), rinsed with distilled water and dried in a dust free nitrogen medium.

Adsorption was explored by means of null ellipsometry using the set-up at Max-Plank Institute for Polymer Research, wherein a pair of ellipsometric angles of the He-Ne laser beams with wavelength $\lambda = 632.8$ nm reflected from the substrate surface were taken with time[9]. All the experiments were performed at 22 °C and a wide variation of polymer concentrations in solution. Null-elipsometry was also applied for investigation of PEO grafting to SM adsorbed on the silicon wafers.

Acylation of diethylene glycol with succinic anhydride was studied in DMFA using triethylamine as a catalyst. Reaction was carried out in a two-necked reactor under continuous stirring at 60 °C. All reagents were anhydrous and purified before use. Probes of reactive mixture were drawn at intervals of one hour and precipitated into different solvents. All samples were purified by double reprecipitation and dried under vacuum. The structure of resulting esters was confirmed by means of H^1 NMR spectroscopy in DMSO-d_5 (Riedel-de-Hain) on a 200 MHz Bruker AM-200 spectrometer.

Results and discussion

Surface modification method

Anchor polymer adsorption. 1st stage. In the first stage SM was adsorbed on a solid surface from dilute solution in a polar organic solvent such as acetone or 1,4-dioxane. In this manner immobilization of reactive anhydride groups on a solid surface is achieved.

Grafting of PEO tails. 2nd stage. In the second stage grafting of PEO macromolecules onto the surface is achieved by applying the reactions of terminated hydroxyl groups of PEO with anhydride groups of SM adsorbed.

Adsorption kinetics

Typical kinetics of SM copolymer adsorption from dilute solutions in acetone, i.e. time dependence of adsorbed amount, are shown in Fig. 1. It is apparent that the curves converge at large times to a plateau value of the adsorbed amount *A*. This value is taken to be the equilibrium adsorbed amount, A_{eq} for the given concentration of polymer in solution. Adsorption isotherms shown in Fig.2 were plotted from the different A_{eq} values.

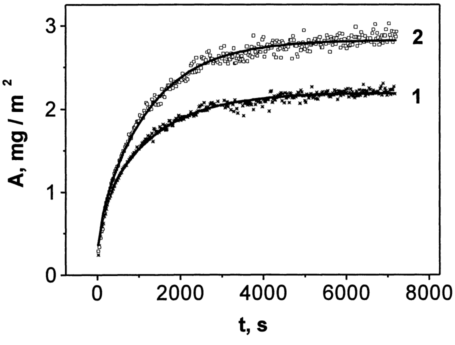

Fig.1: Experimental (points) and calculated (from Eq. 3, line) kinetics of SM-16 000 copolymer adsorption from acetone solution at concentration: 1 - c_0 = 0.05 mg/ml; 2 - c_0 = 0.1 mg/ml.

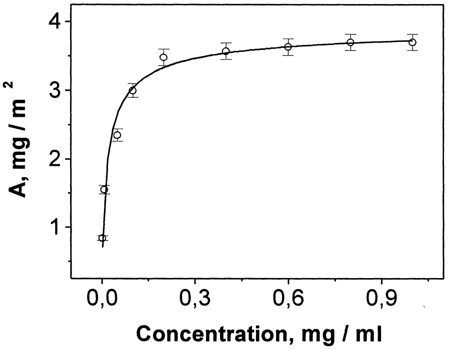

Fig.2: Experimental (points) and calculated (from Eq. 4, line) adsorption isotherm of SM-16 000 copolymer from acetone solution.

To interpret the kinetic curves of adsorption a model of the process with two sharply distinct characteristic times was applied [10,11]. According to this model polymer adsorption on the bare surface leading to the formation of isolated adsorbed macromolecules is a rapid process and is limited only by the transport of molecules to the surface by diffusion. If each polymer molecule reaching the surface is then immediately adsorbed, the process would be defined by the Fick's law [10)]:

$$A = \frac{2}{\sqrt{\pi}} c_0 \sqrt{Dt} \qquad (1)$$

where t is time, D – the polymer diffusion coefficient, and c_0 – its initial concentration in the solution at time $t = 0$. It can be seen from Fig. 3 that the initial parts of the kinetic curves are well linearized in the coordinates of Eq. 1, permitting to estimate the D values from the slope.

Upon complete covering of bare surface with polymer molecules the stage of slow adsorption commences. This period is characterized by the penetration of polymer molecules through the adsorption layer formed what is accompanied by compression and reconstruction of the adsorption layer. During this slow stage the process is suggested [12)] to be characterized by a characteristic time τ in accordance with the following equation:

$$A = A_{eq}(1 - \exp(-t/\tau)) \qquad (2)$$

Interpretation of the kinetic data corresponding to the linear form of Eq. 2 $ln(A_{eq} - A_t) = f(t)$ is shown in Fig. 4. It can be seen that the final parts of the kinetic curves are fairly linearized in the semi-logarithmic coordinates what gives an opportunity to estimate the characteristic time of the slow process.

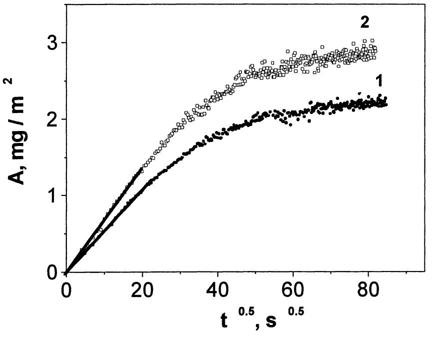

Fig.3: Adsorbed amount of SM-16 000 as a function of adsorption time **t** at the initial stages. Acetone, T= 22°C. SM concentration: 1 – c_0 = 0.05mg/ml, 2 – c_0 = 0.1mg/ml.

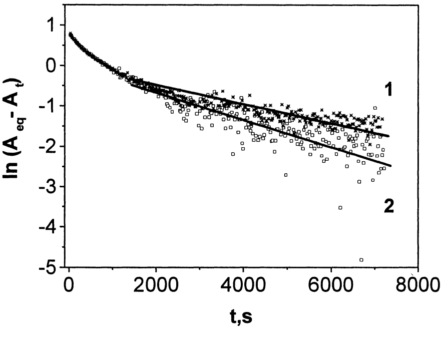

Fig.4: Interpretation of the experimental data by Eq. 2. Adsorption from acetone solution at concentration: 1 - c_0 = 0.05 mg/ml; 2 - c_0 = 0.1 mg/ml.

However, analysis of the obtained kinetic parameters of Eqs. 1 and 2 permits to conclude that these equations taken together describe the process of SM copolymer adsorption unsatisfactorily. For instance, the estimated values of D are strongly affected by the initial polymer concentration even in the case of very diluted solutions. In our opinion this is because both rapid and slow adsorption processes cannot be considered separately from each other. Therefore, retaining this model by which polymer adsorption on a bare surface is rapid, while further adsorption of polymer occurring after the complete coverage of the bare surface with isolated polymer molecules and resulting in the formation of a dense adsorption layer is slow, we combine both these stages by the following equation:

$$A = A_{1eq} \frac{\tau_2}{\tau_2 - \tau_1}\left(e^{-\frac{t}{\tau_2}} - e^{-\frac{t}{\tau_1}}\right) + A_{2eq}\left(1 + \frac{\tau_1}{\tau_2 - \tau_1} e^{-\frac{t}{\tau_1}} - \frac{\tau_2}{\tau_2 - \tau_1} e^{-\frac{t}{\tau_{21}}}\right) \qquad (3)$$

On comparing Eq. 3 with experimental kinetic curves, the parameters $A_{l\mathrm{eq}}$, $A_{2\mathrm{eq}}$, τ_1 and τ_2 were considered as unknown and their numerical value were found via solving the inverse problems exploiting the optimization method. A good correlation between the values of A calculated with the use of Eq. 3 and the experimental kinetic data is shown in Fig. 1.

The concentration behavior is indicative of a Langmuir-type adsorption, where equilibrium between adsorbed and desorbed chains is achieved at a given concentration. This data can be fitted by the equation:

$$A_{eq} = A_{2eq} = \frac{A_{2m}(Kc)^{\gamma}}{1 + (Kc)^{\gamma}} \qquad (4)$$

where A_{2m} is the plateau adsorption value for a dense layer, K - the constant of adsorption/desorption equilibrium, and γ the exponent. A good agreement has been found between experimental and calculated isotherm of SM adsorption (Fig. 2) for the parameters of Eq. 4 as $A_{2\mathrm{m}} = 3.8$ mg/m^2, $K = 56$ ml/mg, and $\gamma = 0.7$.

Grafting of PEO on top of adsorbed SM

Kinetics of grafting of PEO to SM adsorbed on the silicon wafers was investigated by means of null-ellipsometry clearly indicating changes in the thickness of adsorbed polymer layer with time. We established that in the absence of a catalyst PEO replaces SM adsorbed from the silicon wafer surface, evidently due to its high affinity towards the SiO_2 surface[13]. A perceptible decrease in the adsorption layer thickness was observed when the wafers with adsorbed SM were placed into the PEO solution. Moreover, the polymer adsorbed amounts were equal in both cases of PEO adsorption - on bare silicon wafer and on pre-adsorbed SM, clearly indicating the replacement of SM macromolecules with PEO.

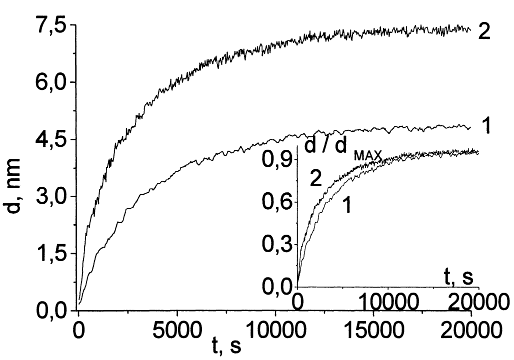

Fig.5: Grafting kinetics of PEO to SM-16 000 adsorbed on silicon wafers. 1,4-dioxan, T = 60 °C, [TEA] = 0.5 mg/ml, for PEO samples:
1 – M_w = 5 000, 2 - M_w = 10 000.

In the presence of a catalyst at elevated temperatures the thickness of adsorbed layer increases substantially (Fig.5). The amount of PEO grafted is dependent on its concentration, amount of catalyst, temperature, and the nature of solvent. The grafted amount at plateau is different for the samples of PEO with various molecular weights and increases with increasing molecular weight of PEO, whereas the velocity of grafting process does not depend on the molecular weight. An interesting effect has been discovered when grafting is performed as a multistage process. In this case the wafers with adsorbed SM were successively treated with solutions of catalyst and PEO several times. An essential increase in the adsorbed amount has been found after every circle, hence the grafted amount reaches a plateau at every stage. We suppose that conformational inversion of the adsorbed graft-copolymer occurs which involves the replacement of the anchor SM part of the macromolecules, previously in direct contact with the surface, by PEO parts of the same macromolecules. The reason for such rearrangements of the grafted adsorbed polymer is the aforementioned high affinity of PEO chains towards SiO_2.

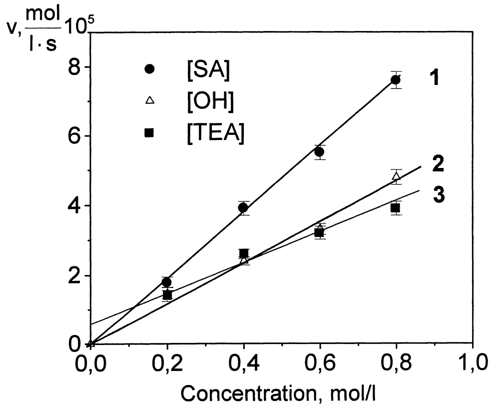

Fig.6: Initial reaction rate (v) vs. reactants concentration: 1- SA (at [OH] = 0.4 mol/l, [TEA]= 0.8 mol/l); 2 - DEG (at [SA] = 0.4 mol/l, [TEA]= 0.4 mol/l); 3 - TEA (at [OH]= 0.4 mol/l, [SA] = 0.4 mol/l); in DMFA as solvent at 60 °C.

In order to clarify the mechanism of grafting of PEO to SM the reaction with model compounds of low molecular weight, namely succinic anhydride and diethylene glycol, was investigated by means of NMR. Initial reaction rates as a function of reagent concentrations for SA, DEG and TEA are presented in Fig. 6. It was established that the order of this reaction is of first order with respect to both SA and DEG concentrations and depends on TEA concentration almost linearly. The extrapolation of the initial reaction rate to zero concentration of TEA (line 3 in Fig.6) permits to estimate the non-catalyzed reaction rate. This rate was found to be $0,65 \cdot 10^{-5}$ mol·l/s which is in good agreement with the value of $0.68 \cdot 10^{-5}$ mol·l/s obtained experimentally. It follows from the experimental data presented in Fig. 5 that in the presence of equimolar amounts of catalyst to SA and DEG the acylation rate is accelerated 30 fold as compared to the non-catalyzed reaction. This gives a clear explanation for the observed features of PEO interaction with SM adsorbed on the SiO_2 surface. In the presence of catalyst grafting of PEO chains onto macromolecules of SM occurs and brings about an increase in the adsorbed polymer layer thickness, while in the absent of catalyst the PEO macromolecules rather replace pre-adsorbed macromolecules of SM because of the very low rate of the grafting reaction.

An essential alteration in the surface properties of silicon wafers caused by formation of thin polymer layers has been found. The wetting angles for water using the contact angle technique were for bare surface $\theta_{SiO2} = 42°$, after SM adsorption $\theta_{SM} = 65°$, and after PEO grafting $\theta_{PEO} = 10°$. These results constitute a strong argument that reactions of polymers immobilized on the solid surface can be successfully applied for the design of polymer coverage with desired structure and properties.

Concluding remarks

It can be concluded that the proposed method permits the construction of dense and compatibilizing layers via the formation of graft polymers directly on a solid surface. This process consists of two successive stages namely adsorption of linear chains (i.e. MA copolymer) and grafting of brush-like tails (i.e. PEO). Transformations induced by the polymerization directly at the solid surface proceed via chemical interactions of PEO, i.e. hydroxylic groups with anhydride groups of the anchor polymer yield an ester bond, and a brush-like macromolecular coverage of a pre-assigned structure with predicted properties is formed. This thin layer can be used to modify the surface properties of the initial material, which has been shown to occur significantly with respect to wetting by water. Applications in various areas including the enhancement of bio-compatibility may be possible.

Acknowledgements

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