Macromolecules
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Step-and-Repeat Assembly of Molecularly Controlled Ultrathin Polyaramide Layers

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ABSTRACT: The preparation of polyaramide thin films on silicon wafers via stepwise layer buildup is described. Hydroxy- and amine-functionalized silicon wafers are reacted in step-and-repeat processes with aromatic dichlorides and diamines, which leads to a stepwise formation of a surface-attached polyamide layer. In the case of aromatic diamines and terephthaloyl dichloride the generation of an up to 115 nm thick polyaramide layer is described while the corresponding aliphatic compounds yield only very thin films. FTIR, ellipsometric measurements and atomic force microscopy (AFM) show a linear growth of the polyaramide layers for more than a thousand reaction cycles. The mechanism of the monomer-by-monomer layer formation process and the structure of the formed films are elucidated.

Introduction

Surfaces of inorganic materials can be tailored through the covalent attachment of monolayers of polymer chains.[1−4] Numerous synthetic approaches were developed to allow the preparation of such surface-attached monolayers. In order to establish a chemical bond between the polymer molecules and the surface to be modified essentially two different strategies have been developed: the "grafting to" technique where an (end-)functionalized polymer is reacted with appropriate surface sites[5−9] and the "grafting from" approach where initiator molecules are chemically bound to the surface and the polymers are then grown *in situ* on the substrates during a subsequent surface-initiated polymerization reaction.[10−13] The "grafting to" technique yields polymer layers which are for kinetic and thermodynamic reasons intrinsically limited to film thicknesses of typically less than 5 nm. In contrast to this, it has been shown that using the "grafting from" approach, monolayers can be generated where polymers with very high molecular weights (often more than 10^6 g mol^{-1}) are attached to surfaces at a high graft density, so that monolayers with thicknesses of up to 2 μm can be obtained.[14,15]

Different types of chain polymerization have been shown to be suitable for the creation of polymer monolayers: free radical polymerization,[13−15] controlled nitroxide mediated polymerization,[16] ATRP,[17−20] RAFT,[21] and ionic polymerizations.[22−24] As far as step polymerization reactions are concerned, polycondensation reactions have also been used for the preparation of monolayers consisting of terminally anchored polymer chains.[25−32] However, the layer thicknesses obtained from these polymers were quite limited for several reasons:

    (a)   Degrees of polymerization of the polymer chains obtained by polycondensation are frequently lower than those obtained by typical chain-polymerizations. One of the reasons is that polycondensation reactions are highly sensitive toward the stoichiometry, another that extremely high conversion is required to achieve a high molecular weight.

    (b)   Polycondensations are equilibrium reactions where monomer attachment and monomer detachment as well as transformation reactions such as transesterification or transamidation occur. At the beginning of monolayer growth, the enthalpy of the formation of new bonds drives the reaction and the polymer chains begin to grow both in solution and at the surface. However, as the graft density increases and the polymer chains overlap more and more, the chains start to stretch, which reduces the entropy of the system and the free energy of the surface-attached chains increases. This renders the attachment of further repeat units to the monolayer unfavorable and/or makes transformation reactions, which lead to the degrafting of longer surface-attached chains, energetically favorable. In other words, the higher the graft density, the more the reaction of short oligomers with surface-attached subchains, which leads to subchain detachment, becomes favored against further monomer addition.

As a consequence, monolayers created by polycondensation reactions are limited concerning film thickness. The film thickness which can be achieved is expected to depend strongly on the free energy of the polycondensation process and/or the activation energy of the reaction. The higher these energies ("irreversible reactions"), the more of an entropy loss can be tolerated before degrafting becomes dominant. This in turn will lead to higher molecular weight of the surface-attached polymer and accordingly to a higher film thickness of the layer.

An alternative solution for the preparation of surface-attached high molecular weight polymer chains by condensation reactions is a discontinuous process in which A−A and B−B monomers are added sequentially to form the polymer chains in a monomer-by-monomer assembly. The advantage here is that in each step the substrate with the growing reactive site may be exposed to an excess of monomer pushing the equilibrium at each step toward a complete reaction. Such an approach resembles the classical Merrifield peptide synthesis.[33]

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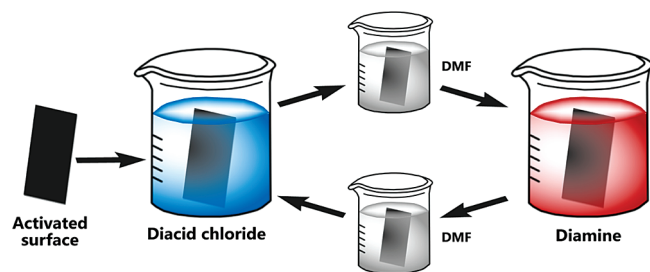
     Published on Web 10/08/2010

Figure 1. Monolayer preparation of polycondensates on silicon wafers by sequential addition of the monomers.

A similar strategy has been followed successfully by Blanchard and co-workers[34−36] who prepared multilayer films using a sequential covalent strategy. They investigated the alternate reaction of diisocyanates and diamines and found that up to seven bilayer cycles could be carried out without observing loss of reactivity of their surface. The thickness of the obtained layer grew linearly and was approximately 10 nm.

In the present work we follow such an approach for the formation of step-by-step polyaramide monolayers and study multistep condensation reactions for the formation of surface-attached high molecular weight polyaramide films.

Experimental Section

Materials. *p*-Phenylenediamine, terephtaloyl chloride, adipoyl chloride, hexamethylenediamine, *N*,*N*-dimethylformamide (DMF), hexamethylphosphoramide, 1-methyl-2-pyrrolidone (NMP), and toluene were purchased from Sigma-Aldrich and used without further purification. (Acetoxyethyl)dimethylchlorosilane and (3-aminopropyl)dimethylethoxy)silane were used as received from ABCR GmbH & Co, Germany. Triethylamine was dried over CaH$_2$ and distilled prior to use. As substrates for the deposition of the monolayers, silicon wafers with a 2.5 nm thick silicium oxide layer (Si-Mat; Germany) polished on both sides were used.

Preparation of *p*-Phenylenediamine−Terephthalamide Monolayers. The immobilization of acetoxyethyl dimethylchlorosilane at the surface of the silicon substrate was carried out in dry toluene (1:100 v/v) in the presence of catalytic amounts of triethylamine. The solution with the substrates was stored overnight at room temperature under nitrogen. The samples were then cleaned by rinsing with toluene and chloroform. Hydrolysis of the acetoxy groups was carried out in aqueous sodium carbonate solution (pH = 8) at 40 °C overnight. Samples were then acidified by immersion in aqueous HCl solution (pH = 3) for 1 h, washed several times with deionized water, and dried.

For immobilization of (3-aminopropyl)(dimethylethoxy)silane at the substrate surface, the wafers were cleaned first with piranha solution (H$_2$O$_2$/H$_2$SO$_4$, 1:2, v/v) and rinsed with large amounts of water. Then the clean wafers were immediately silanized according to a literature procedure.[37]

The OH- or NH$_2$-functionalized wafers were then sequentially dipped in a freshly prepared 10^{-3} M solution of diacid chloride in toluene (one drop of pyridine added) and a 10^{-3} M solution of diamine in DMF with intermediate rinsing steps with DMF (see Figure 1). Finally, the samples were washed with a mixture of NMP/hexamethylphosphoramide.

Characterization. Transmission FT-IR spectra of the attached polymer layers were recorded using a Bio-Rad Excalibur spectrometer. An atomic force microscope (Multi-Mode, Veeco Metrology Group) was used to characterize the morphology of the layers. Determination of the layer thickness of the monolayers was carried out using null ellipsometry on a Nanofilm EP3 imaging ellipsometer.

Results and Discussion

In order to create monolayer systems of a polycondensate we have chosen a polyaramide from terephtaloyl dichloride and *p*-phenylenediamine as an example as polyaramides are technologically very interesting compounds and because the amide formation is under the chosen reaction conditions an essentially irreversible process. A corresponding system which is based on aliphatic monomers (adipoyl dichloride and hexamethylenediamine) was chosen as a reference.

The procedure to the formation of polyaramide monolayers by multistep condensations is shown in Scheme 1, and the experimental procedure is depicted in Figure 1. The first step in the reaction cascade is the activation of the silicon wafer with appropriate reactive functionalities. In our case we have chosen the formation of layers with NH$_2$− groups (sample **Kev−Am**) and OH− groups (sample **Kev−OH**). Amine groups on silicon wafers are introduced by reaction of the substrate with 3-aminopropyldimethylethoxysilan at elevated temperatures. In the second system, the reaction with acetoxyethyl dimethyl chlorosilane is well-known[38] for the creation of surfaces which are densely grafted with acetyl-protected organic hydroxyl groups. Hydrolysis of the protection groups can then be carried out under mild conditions (40 °C, pH = 8, overnight) to yield the final hydroxyl functionalized surface.
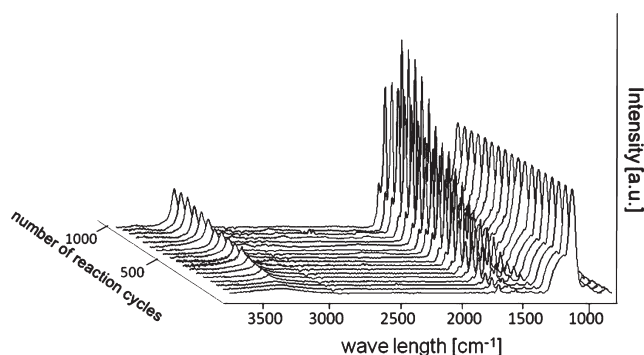
The thus obtained functionalized surfaces are then alternately dipped into two solutions containing the dichloride and the diamine. This way, functionalized surfaces are obtained which carry free acid chloride groups or amine groups, depending whether an even or uneven number of layers is viewed (Scheme 1).

After the addition of each monomer the wafer is thoroughly washed in DMF in order to ensure the complete elimination from traces of physically absorbed monomers or oligomers. Furthermore, after the last monomer addition step the surfaces are extracted for several hours with *N*-methylpyrrolidinone (NMP) and hexamethylphosphoramide (HMPA), which are good solvents for the polymer. In control experiments with a nonactivated surface, where polymer prepared in solution and which was cast as a thin film on an unmodified surface it was shown, that in contrast to the layer described in the following, polymer which is not firmly bound to the surface can be washed away in such an extraction process (Figure 5). An FTIR-spectrum of the formed layer is shown in Figure 2 together with the spectrum of a solution polymerized cast film, which proves the chemical identity of the polymer layer.

After every 50 reactions (i.e., attachment of 25 polyaramide units) an FTIR transmission spectrum of the wafer is recorded. In control experiments, in which no silane was deposited, no adsorption bands apart from those which can be assigned to Si−O vibrations at 1066 cm^{-1} are observed. If aliphatic diacidchloride and diamine were used, which would lead to formation of a polyamide 6−6, in contrast to the situation of the aromatic monomers no signals due to an organic layer are observed.

In the case of polyaramide formation the FTIR spectra changed significantly with increasing number of reaction cycles. The evolution of the obtained spectra as a function of the number of condensation steps is shown in Figure 3. It should be specifically noted that the spectra are shown as obtained and are *not* normalized to the reference band at 1066 cm^{-1} as the intensity of the Si−O bonds of the silicon wafer did not vary with the number of cycles.

After around 50 reaction cycles, the first small absorption bands due to the polymer formed on the silicon surface can be detected and assigned to the polyaramide structure. The band at 3320 cm^{-1} can be assigned to N−H stretching vibrations of an amide in trans form. The band at 1646 cm^{-1} is characteristic for an amide C=O stretching vibration for hydrogen-bonded amide groups (usually called amide I band) and at 1543 cm^{-1} for N−H deformation and C−N stretching coupled modes. Bands at 1608 and 1515 cm^{-1} can be assigned to C=C stretching vibrations of aromatic rings and 827 cm^{-1} to out-of-plane C−H vibrations of

Scheme 1. Synthesis of Polyaramide Monolayers Attached to the Surfaces of Silicon Wafers: (a) Activation Step To Generate Surface-Attached Monolayers with (I) Amine Groups and (II) Hydroxyl Groups; (b) Polymer Layer Formation
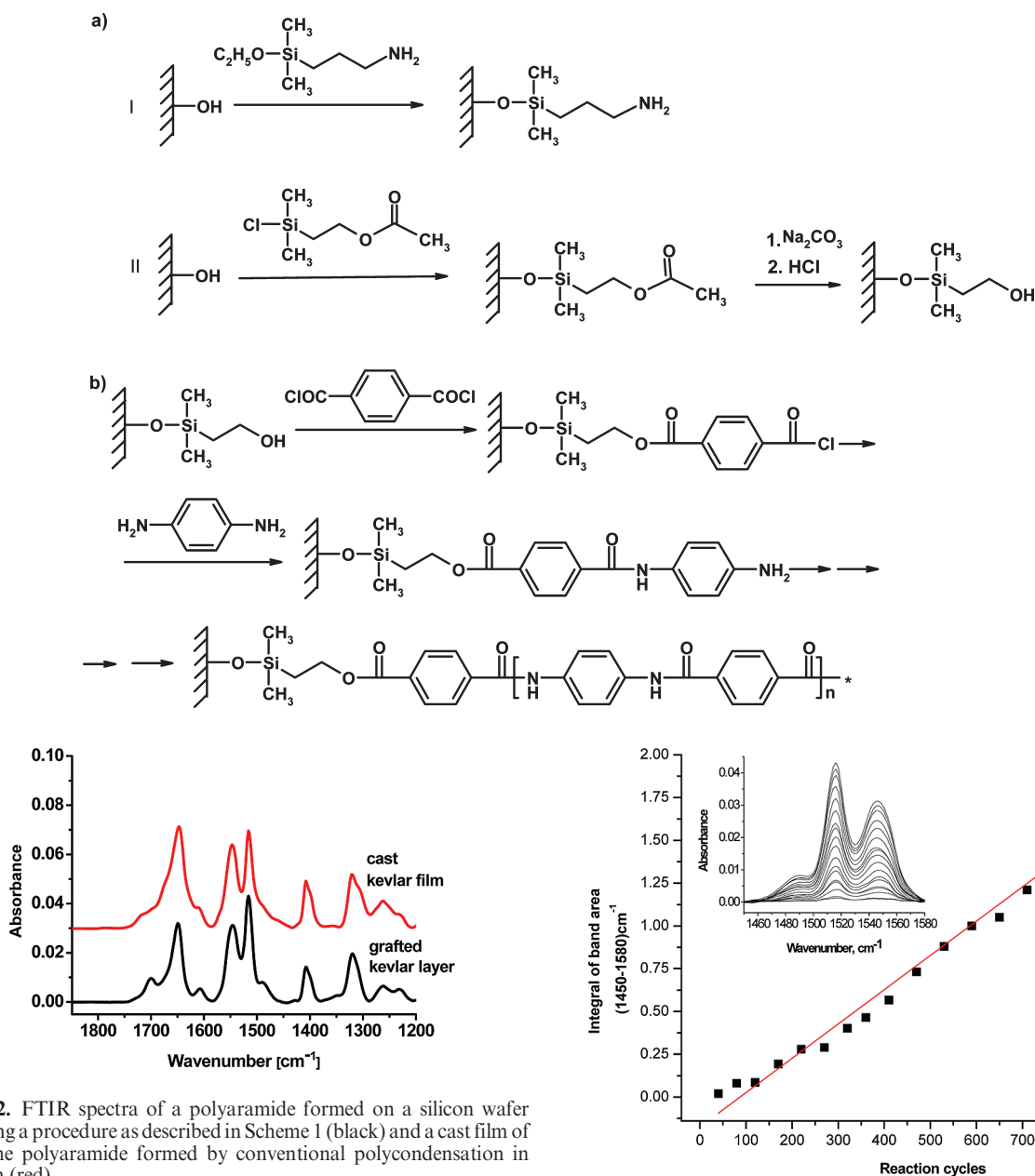
Figure 2. FTIR spectra of a polyaramide formed on a silicon wafer following a procedure as described in Scheme 1 (black) and a cast film of the same polyaramide formed by conventional polycondensation in solution (red).

Figure 4. FTIR band area of surface-attached polyaramide monolayers in the region from 1580 to 1450 cm^{-1} as a function of the number of reaction cycles.

In Figure 3, it can be seen that the bands corresponding to the growing polyaramide layer increase as a function of the number of reaction cycles. In order to quantify this behavior, the integral of the absorption band in the range between 1580 and 1450 cm^{-1} was determined and plotted as a function of the number of reactions (Figure 4). A linear relation over the whole range of cycles (up to 1000 reactions) is observed, indicating continuous growth of the polymeric layer. A similar behavior had been observed by Blanchard and co-workers[34−36] for the growth of surface-attached chains made from diamine and diisocyanate. In their work, seven reaction cycles had been carried out and a linear growth of the layer thickness had been described.

To investigate the layer growth further, the layer thickness of the growing polyaramide monolayers was additionally studied by AFM and ellipsometry. AFM (Figure 5a) shows that the

Figure 3. IR transmission spectra as a function of the number of sequential condensation reactions of a polyaramide assembly on a silicon support.

two adjacent hydrogen atoms in an aromatic ring (para substitution of the aromatic ring).
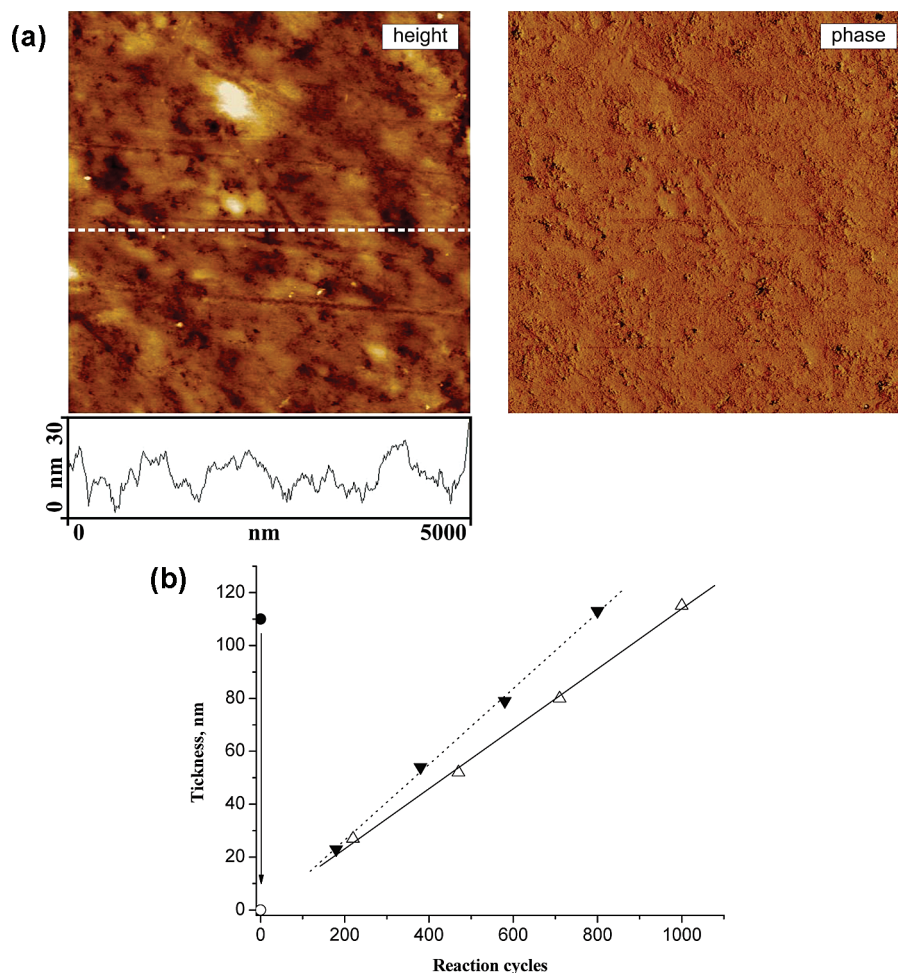
Figure 5. (a) AFM micrographs of polyaramide assemblies on a silicon wafer. (b) Thickness of polyaramide multilayer assemblies as a function of number of reaction cycles for **Kev−OH** (△, solid line) and **Kev−Am** (▼, dotted line): (●) layer thickness of *p*-phenylenediamine−terephtalamide film spin-casted from solution on a silicon waver; (○) layer thickness after washing of the wafer with NMP and hexamethylphosphoramide.

polyaramide monolayer has a rather flat topography with an rms- roughness of 4 nm when an area of 1 μm^2 is viewed. This is significantly higher than that of the unmodified silicon wafer, but still less than 5% of the layer thickness. Furthermore, the AFM images give evidence that layer growth is not patchy, but occurs in a homogeneous manner over the whole substrate. Whether a truly flat topography is obtained in an ultrathin layer has in most cases nothing to do with small scale variations in molecular weight or graft density, but depends most likely very strongly on the drying conditions of the film.

Figure 5b shows that also ellipsometry (a refractive index of $n = 1.55$ was assumed for the polyaramide layer) measurements confirm the linear dependence of the layer thickness with the number of reaction cycles found by transmission FTIR spectroscopy. From the slope of the straight lines a growth of the monolayers of 0.11 ± 0.02 nm (sample **Kev−OH**) and 0.14 (sample **Kev−Am**) per added monomer unit is calculated. In addition, the obtained layer thicknesses of the monolayers can be used to estimate the graft density Γ of the polyaramide chains on the silicon surface according to

$$\Gamma = d*\rho/M$$

Here d is the layer thickness, ρ the polymer density, and M the molecular weight of the polymer chains. In the case of activation with OH groups, after 1000 reactions, 500 polyaramide units with a molecular weight of 238 g/mol each are obtained. The total molecular weight of such a chain would be 119 000 g/mol and the

observed layer thickness was measured to 115 nm. With a density value of 1.44 g/cm^3 for polyaramide,[39] a graft density of 1.4 μmol/m^2 in the case of **Kev−OH** is obtained while a graft density of 1.7 μmol/m^2 is calculated for **Kev−Am**. Both values are close to the typical graft density of a silane monolayer on a silicon wafer, which is close to 1.9 μmol/m^2.[14] This close agreement indicates that almost every silane group initially present at the surface carries a polymer chain of full length. The slightly lower graft density in the case of **Kev−OH** is probably due to a smaller number of reactive molecules at the surface as two reactions had to be carried out for the creation of the activated sites.

It is highly likely that the condensation reaction of acetoxy-ethyl dimethylchlorosilane to the surface and/or the hydrolysis step did not occur with quantitative yield. This means that after 1000 reactions the overall yield of the monomer-by-monomer layer formation process is somewhere between 75 and 90%.

The fact that monomer-by-monomer formation of the polymer layers leads to continued growth of Kevlar chains,[40] even after a large number of reaction cycles, is favored by the huge excess of monomer present in each condensation step as the number of surface functional groups is several orders of magnitude smaller than that of the monomer in solution. Such an excess guarantees an efficient capping even without protecting groups. However, as all reactions are carried out under ambient conditions it seems likely that a certain percentage of acid chloride groups at the surface is hydrolyzed during each cycle.

However, this does not necessarily imply the end of polymer growth as the formed carboxylic acid can form a salt complex
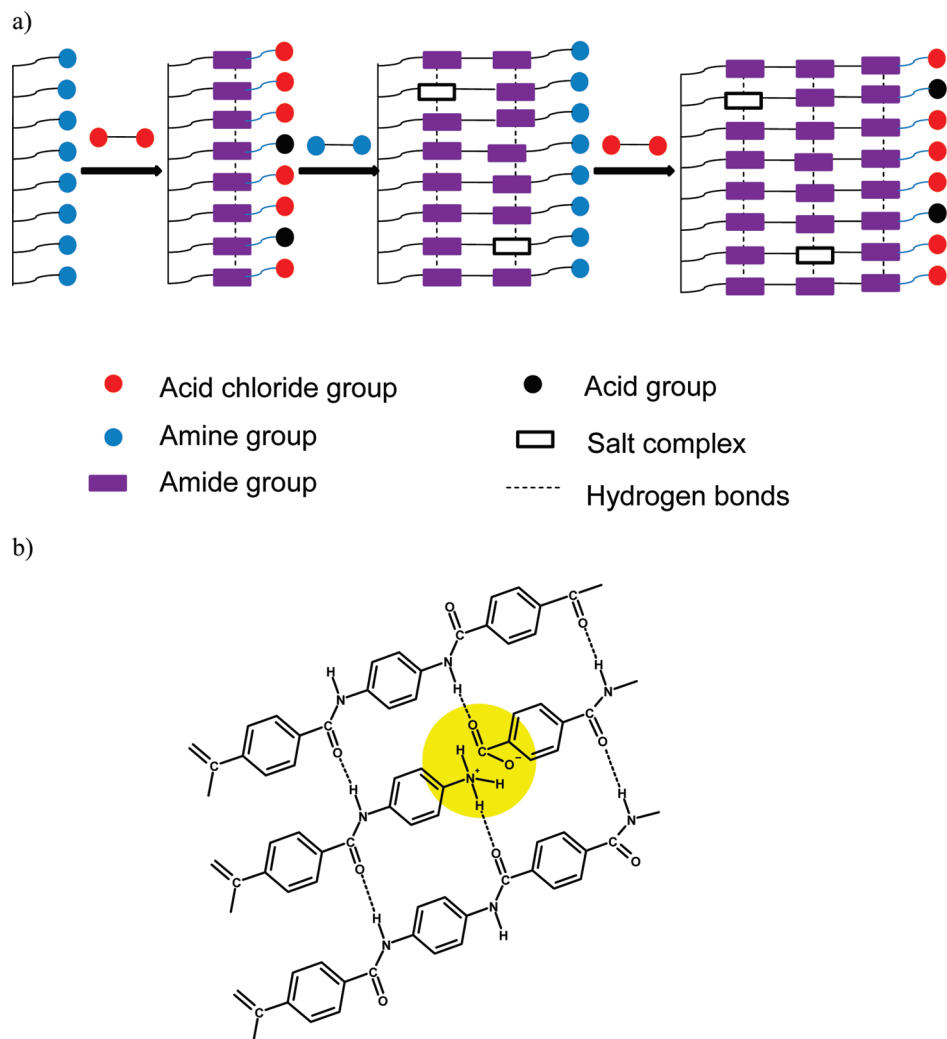
a)

b)

Figure 6. (a) Structure of a Kevlar assembly obtained by a step- and repeat procedure. (b) Stabilization of salt complexes in the Kevlar assembly.

with one of the amine groups of the next incoming diamine. The second amine group of this incoming monomer may then continue the chain growth through reaction with a diacid chloride in the next cycle so that a surface-attached polymer consisting of covalent and noncovalent bonds is formed. Control experiments with low molecular weight compounds show that the formed salt cannot be dissolved in DMF or typical solvents for the polymer. In the monolayer assembly hydrogen bridges may be formed to neighboring repeat units of the same layer. The proposed structure of the obtained Kevlar assembly is depicted in Figure 6.

To elucidate this aspect further, we have prepared a terephtalic acid/diamine polymer in solution and a corresponding salt complex and have recorded their IR spectra. In the FTIR spectra (Figure 7) of the surface-linked system a small adsorption band at around 1700 cm^{-1} is observed that corresponds very well to that of the carbonyl bond of the salt complex.

The presence of this band is a strong indication that the same kind of ionic links are also present in the surface linked Kevlar chains. Using a calibration curve, the ratio of covalent to ionic linkages in the monolayer can be estimated to around 20:1. The fact that the carbonyl band at 1700 cm^{-1} is slightly shifted (5 cm^{-1}) to lower energies with respect to that of the salt complex is due to the weakening of the C=O bond by the formation of hydrogen bonds to amide groups in their vicinity.

In the second experiment we have now attempted to break the ionic interactions in the monolayer and washed the surface linked polyaramide system with a mixture of NMP/HMPA containing
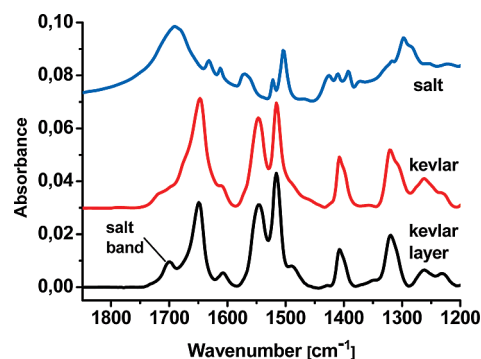

Figure 7. FTIR spectra of poly(terephtalic acid/phenylendiamine) complex (blue), a polyaramide formed on a silicon wafer following a procedure as described in Figure 2 (black) and the same polyaramide formed by conventional polycondensation in solution (red).

significant amounts of salt (LiCl). As the result of the breaking of the ionic interactions, the layer thickness of the system is reduced from 115 nm to only 5 nm (Kev−Am) and from 113 to 4 nm (Kev−OH), respectively. These layer decreases (−95%) are in agreement with the estimated amount of salt complex and thus strongly support the model that in the monomer-by-monomer layer growth process both covalent bond and ionic complexes are formed.

It has to be pointed out that hydrolysis of acid chloride groups could be strongly reduced if the reaction conditions were improved.
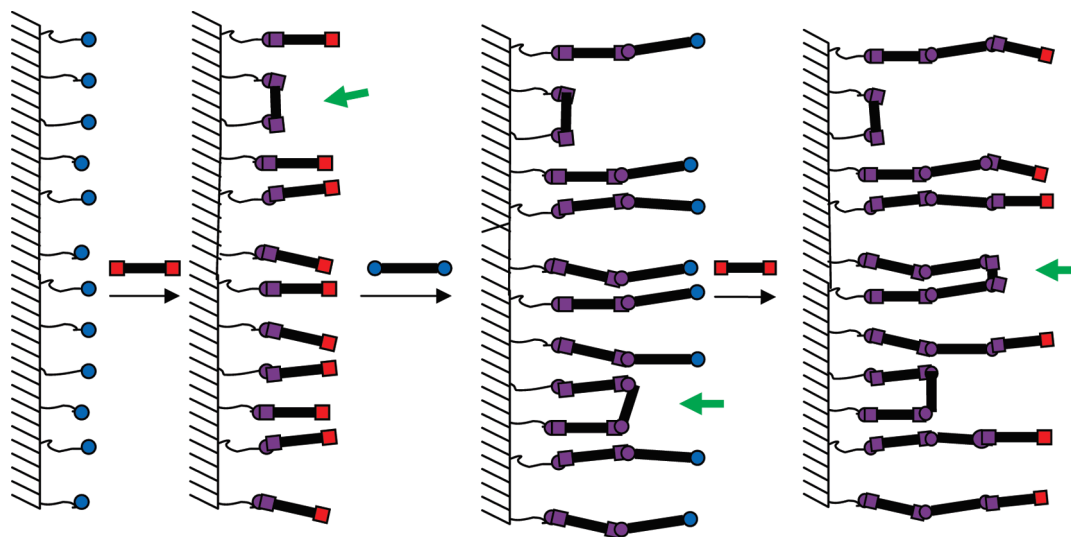
Figure 8. Schematic presentation of surface-attached polymer growth with possible macrocycle formation (green arrows). Key: blue symbols, amine groups; red symbols, acid chloride groups; violet symbols, amide groups.

In this way one would obtain layers with less defect concentrations and a higher percentage of covalent links. However, the aim of this work was to prepare such structures using an experimentally less demanding way (ambient conditions).

It is further interesting to note that when analogue concentrations of aliphatic amines and aliphatic acid chlorides are used, which are known to have an even higher reactivity toward each other than their aromatic counterparts, no significant chains can be grown. They obviously do not even reach the IR detection limit.

We could hypothesize that the strong difference between the aliphatic and the aromatic system might be due to a small, but significant difference in the yield of macrocycle formation in which the two ends of an incoming monomer react with two surface-attached chains. A critical situation is given once an incoming monomer has attached to the end of a surface-bound chain: now the other end of the monomer, which is still reactive, might bind to an already attached chain to form a macrocycle (Figure 8). In the case of stiff, aromatic polyamides the chain dynamics can be expected to be rather low, so that diffusion of the chain ends toward each other and accordingly reaction becomes unlikely. In flexible polycondensates, however, due to the higher chain dynamics, after each reaction cycle a certain percentage of the reactive groups closes a macrocycle so that the number of growing chains gets lower and lower with increasing number of reaction cycles and the monolayer growth stops more or less rapidly. A short calculation of the number of active chain ends as a function of the number of reaction cycles illustrates the situation: if we suppose that in each reaction step only 1% of the monomers reacts in such a way that a macrocycle is formed (which would deactivate two growing chains) this would mean, that after 50 cycles, there are only $0.98^{50} = 36.4\%$ active chains left. After 300 cycles, the yield would drop to 0.2%. Another explanation would be that in the aromatic compounds the π-stacking leads to additional interactions which decrease the solubility of the salt complexes (see Figure 6b).

Conclusions

The present study has shown that polyaramide assemblies of well-defined thickness and uniform topography can be synthesized on amine or hydroxy functionalized silicon wafers following a step and repeat approach. To this the substrate is alternately dipped in solutions containing aromatic diacid chloride and diamine monomers leading in a monomer-by-monomer layer formation process to well-defined surface-attached thin polyaramide films. IR, ellipsometry and AFM measurements demonstrate that the film thickness grows linearly with the number of dipping steps and that more than 1000 reaction cycles can be carried out without observing any decrease in film growth. This Merrifield-like approach of molecular assembly represents a very interesting mechanism of film growth as the layers consist of polymer chains in which the units are firmly attached to the surface and linked together either through covalent chemical links or through ionic interactions. This mechanism leads thus to a rather unusual form of formation of surface-attached thin films.

The described approach allows thus the preparation of molecularly designed assemblies of polyaramides with precisely controlled thicknesses. The synthetic effort required to generate these interesting systems is high, but might be lowered significantly through automatization of the dipping procedure.

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