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Growth kinetics of the adsorbed layer of poly(2-vinylpyridine) – an indirect observation of desorption of polymers from substrates†

Marcel Gawek, Hassan Omar, [iD] Paulina Szymoniak [iD] and Andreas Schönhals [iD] *

The growth kinetics of the adsorbed layer of poly(2-vinylpiridine) on silicon oxide is studied using a leaching technique which is based on the Guiselin brushes approach. The adsorbed layer is grown from a 200 nm thick P2VP film for several annealing time periods at different annealing temperatures. Then the film is solvent-leached, and the height of the remaining adsorbed layer is measured by atomic force microscopy. At the lowest annealing temperature only a linear growth regime is observed, followed by a plateau. Here, the molecular mobility of segments is too low to allow for a logarithmic growth. At higher annealing temperatures, both linear and logarithmic growth regimes are observed, followed by a plateau. At even higher annealing temperatures, the growth kinetics of the adsorbed layer changes. A linear growth followed by logarithmic growth kinetics is observed for short annealing time periods. For longer annealing time periods, an upturn of the growth kinetics is observed. At the highest annealing temperature, only a logarithmic growth regime is found. The change in the growth kinetics is discussed by an alteration in the structure of the adsorbed layer. Moreover, the interaction between the polymer segments and the substrate becomes weaker due to both enthalpic and entropic effects. Therefore, at high annealing temperatures the polymer segments might more easily desorb from the substrate.

Introduction

The performance of many innovative multiphase materials involving polymers like polymer-based nanocomposites and hybrid nanomaterials including also thin films with thicknesses of several nanometres is determined by the interaction of the macromolecules with inorganic substrates.[1–5] Especially, polymer films with thicknesses below 100 nm are important in materials protection, as functional layers in sensors, and in novel (opto-)electronic devices (see for instance ref. 6). For non-repulsive interactions of the polymer with the substrate, Granick *et al.* showed that an irreversible adsorbed layer with a nanometric thickness is expected to develop which is stabilized by the connectivity of the polymer chain.[1,7–11] The adsorbed polymer segments on the substrate surface can have a reduced molecular mobility or in some cases can even be immobilized.[12] Temperature modulated differential scanning calorimetry (TMDSC) experiments employing a high molecular weight poly(vinyl acetate) (PVAc) sample on a silica substrate demonstrated that the

Bundesanstalt für Materialforschung und -prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany. E-mail: Andreas.Schoenhals@bam.de; Fax: +49 30/8104-73384; Tel: +49 30/8104-3384

† Electronic supplementary information (ESI) available. See DOI: **https://doi.org/10.1039/d3sm00129f**

adsorbed polymer (which can be even grafted) show a thermal activity with three different regions corresponding to interfacial layers:[13,14] (I) a "Tightly bound" region, corresponding to segments directly located on the surface of the substrate. These segments undergo a glass transition located at higher temperatures (characterized by the glass transition temperature T_g) compared to bulk. (II) A "loosely bound" region which is related to polymer segments spatially arranged away from the substrate surface. (III) A "mobile region", where segments are located at the polymer/air interface, showing a decreased T_g compared to bulk. This decrease of T_g is due to missing segment/segment interactions.[13,14] Recently this effect was confirmed for thin films by dielectric measurements and molecular dynamic simulations.[15] Similar results were found for instance for poly(methyl methacrylate) (PMMA) on silica substrates. PMMA has a stronger interaction with silicon oxide, compared to PVAc, which is due to hydrogen bonding.[13]

Housmans *et al.*[11] unveiled the growth kinetics of a spatially heterogeneous structure within the adsorbed layer for high M_w atactic polystyrene (PS) employing a leaching approach. The growth kinetics of the adsorbed layer has a two-step adsorption regime. At short time periods, the time dependence of the thickness of the adsorbed layer is linear. Here the polymer chains pin as many segments as possible to the substrate, at an energy cost of $k_B T$ (k_B is Boltzmann's constant). This leads to a "strongly bound" layer,[16,17] with a higher density[10,18,19] and

reduced molecular mobility. Form the theoretical point of view, this could be understood by a first-order adsorption mechanism. In this approach, chains in contact with the surface pin onto the substrate *via* kinetics limited by the characteristic time for the attachment of one segment.[20,36] The number of adsorbed segments, and therefore the thickness of the adsorbed layer h_{ads}, increases linearly with time. Considering that the statistics of the chains obey a reflected random walk close to non-repulsive walls, at a given time, it holds $h_{ads} \sim N^{1/2} \sim$ radius of gyration (R_g). The structure of this part of the adsorbed layer consists mainly of trains.[10] However, at a certain time, a crowding of segments at the substrate prevents the first-order adsorption mechanism. Housmans *et al.* proposed a description of the irreversible adsorption mechanism including a crossover between linear and logarithmic growth.[11] For a more detailed discussion see ref. 36. In the logarithmic regime, the thickness of the adsorbed layer increases further by diffusion of segments and/or changing its conformation, through the already existing layer. This process will take place at the expense of their entropy. This yields a "loosely bound layer" with a different segment mobility, compared to that of the strongly bound one. At this stage of the growth of the adsorbed layer, loops and tails are formed. In addition, the growth kinetics of this layer also depends on other parameters, for instance, annealing time, molecular weight, packing frustration, and processing conditions.[21] For a detailed review of these parameters, the reader is referred to ref. 22. Earlier, it was shown that polymers can be adsorbed on metal oxide, glass or carbon surfaces (for instance see ref. 11, 23–35). Reviews about adsorbed layers in general are given in ref. 36 and 37 which also report the adsorption kinetics of the adsorbed layer for different polymers. Recently, in addition to the leaching approach, chip calorimetry has been employed to investigate the growth kinetics of the adsorbed layer.[38]

This work attempts to address the growth kinetics of the adsorbed layer of poly(2-vinylpiridine) (P2VP) on a flat silicon oxide substrate. Some results of the growth kinetics of P2VP have been published by Koga *et al.* considering only one temperature.[10] Here a series of different temperatures are employed here. To the best of our knowledge, no temperature-dependent data for the growth kinetics of the adsorbed layer have been reported. These temperature-dependent data lead to the conclusion of a possible desorption of P2VP segments from the substrate.

Materials and methods

P2VP was purchased from PSS Polymer Standards Service GmbH (M_w = 1020 kg mol^{-1}, M_n = 766 kg mol^{-1}, PDI = 1.33). The glass transition temperature was estimated to be 371 K (98 °C) by differential scanning calorimetry (heating rate: 10 K min^{-1}, second heating run).

A wafer with a size of 10 × 10 mm^2 was used as the substrate. The thickness of the native silicon oxide layer was about 1.7 nm as estimated by ellipsometry. The substrate was

cleaned with acetone to remove the protecting photoresist layer. A CO_2 snow jet gun was employed to further clean the surface of the substrate down to the microscale. Then it was placed in a plasma oven with an air atmosphere (60 watt) for 600 s to further clean the substrate and to activate the natural silica. A film with a thickness of *ca.* 200 nm was spin coated from a diluted solution of P2VP in chloroform (a rotational speed of 3000 rpm for 60 s). Then the polymer film was annealed at several temperatures (383 K, 403 K, 413 K and 433 K) for different time periods. These annealing temperatures correspond to T_g + 12 K, T_g + 32 K, T_g + 42 K and T_g + 62 K. The degradation temperature of P2VP was reported to be *ca.* 660 K.[39] The considered annealing temperatures are much lower. Therefore, degradation of P2VP during annealing is unlikely.

It is noteworthy that the question of how the thickness of the initial film influences adsorption was investigated in ref. 33 for poly(vinyl methyl ether) by some of the authors. It was found that the thickness of the resulting adsorbed layer is independent of the initial film down to *ca.* 120 nm. Then with decreasing initial film thickness the thickness of the adsorbed layer decreases. At a critical thickness of the initial film of *ca.* 30 nm no stable adsorbed layer is formed anymore.

After the annealing procedure of the 200 nm thick films, the solvent-leaching experiments (also called Guiselin brushes) were employed. An irreversibly adsorbed layer was obtained with this procedure. For this purpose, the samples were soaked in chloroform for 30 min. Since chloroform is a good solvent for P2VP it can be expected that all polymer chains which are not adsorbed to the substrate will be washed away. In that sense the leaching process is dissolution of the polymer which is not adsorbed. After the leaching process, the films were rinsed using chloroform and fast dried under a dry nitrogen stream. Finally, the samples were annealed for further 20 min at the chosen annealing temperature. For a more detailed discussion of the process, the reader is referred to ref. 11. In addition to a leaching time of 30 min, few experiments were carried out where the leaching time was varied to investigate its influence on the thickness of the adsorbed layer.

A Cypher atomic force microscope (AFM) (Asylum Research, Santa Barbara, CA, USA) equipped with a silicon cantilever with a reflective aluminum coating (AC160TS, Oxford Instruments) was employed to measure the thicknesses of the adsorbed layers. For this purpose, the resulting adsorbed layer was scratched using a sharp knife and the step height of the scratch was measured by the AFM. Three scratches were measured per sample and arithmetically averaged. The error of the obtained values was found to be around 1 nm. In addition, AFM measurements were employed to control film topography and to confirm that no dewetting occurred.

Results

Fig. 1 depicts an AFM image of the adsorbed layer leached from a 200 nm thick film annealed at 413 K (140 °C, T_g + 42 K) for 336 h as an example of how the thickness of the irreversible
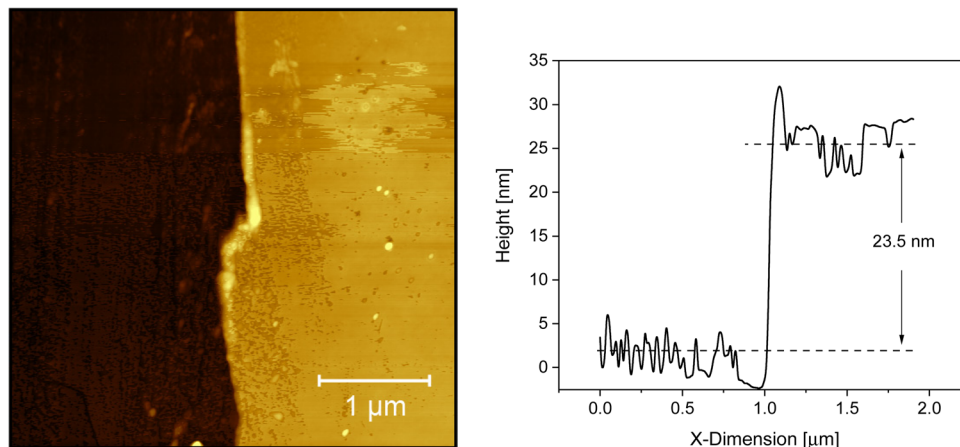
Fig. 1 AFM image for the adsorbed layer of P2VP solvent leached from a *ca.* 200 nm thick film which was annealed at 413 K (140 °C, T_g + 42 K) for 336 h. The right side of the figure shows the thickness profile of a scratch through the adsorbed layer.

adsorbed layer was estimated. The figure shows that the adsorbed layer has a relatively smooth surface and that no dewetting takes place even at relatively high temperatures. The phase/friction contrast image of the AFM image given in Fig. 1 is given in Fig. S1 in the ESI.† The figure evidences that really the scratch goes through the whole film thickness. Besides Fig. 1 the result shows that no dewetting was observed for all topographic AFM images in the considered temperature and annealing time range although dewetting is a common feature of thin polymer films (see for instance ref. 40–42). Moreover,

the thickness of the adsorbed layer could be estimated accurately.

Fig. 2 shows the time dependencies of the thickness of the irreversibly adsorbed layer h_{ads} leached from a 200 nm thick P2VP film, which were annealed at temperatures of 383, 403, 413 and 433 K (T_g + 12 K, T_g + 32 K, T_g + 42 K and T_g + 62 K). First, the thickness of the adsorbed layer is larger than previously reported.[10] This might be due to the different treatment of the substrate which leads to a different interaction of the polymer with the solid surface. Moreover, the molecular weight of P2VP employed here is much higher (1020 kg mol^{-1}) than that considered in ref. 10 (200 kg mol^{-1}). It is known that the thickness of the adsorbed layer depends also on the molecular weight of the studied polymer.[11] Second, the raw data in the figure reveal the differences in the growth kinetics of the adsorbed layer for the different annealing temperatures without employing a theoretical model. In ref. 10 the initial growth kinetics of the adsorbed layer of P2VP measured at one temperature was analyzed using a power law $\sim \left(\dfrac{t}{t_{growth}}\right)^{\sigma}$, where

t_{growth} is a time constant which characterizes the growth kinetics and σ is an exponent. In a first attempt, this approach is employed here also to analyze the growth kinetics of P2VP in the initial stages at different temperatures, although no theoretical basis is discussed for that approach in ref. 10. Fig. S2 (ESI†) depicts that the data at the annealing temperature of 383 K (T_g + 12 K) can be described using a power law with an exponent of one. This corresponds to a linear growth regime discussed in the introduction. The errors of the fit parameters are given in the caption of Fig. S2 (ESI†). At first glance at an annealing temperature of 403 K (T_g + 32 K) the growth kinetics can be approximated using a power law where the exponent is decreased to 0.49 (see Fig. S3a, ESI†). Fig. S3b (ESI†) shows an enlarged image of the growth kinetics at the initial time range. This figure shows that the fit with a power law has large systematical deviations from the data. These deviations are further proved by the residuals of the fit depicted in Fig. S3c (ESI†). The residual displays rather a structured pattern than a
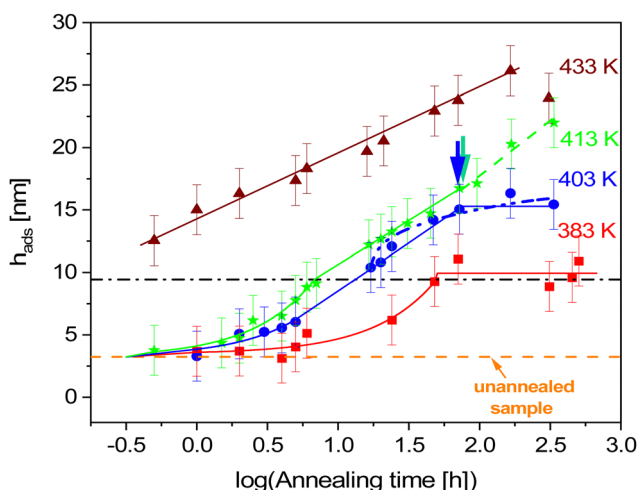

Fig. 2 Time dependence of the thickness of the adsorbed layer at different annealing temperatures: red squares – 383 K (110 °C, T_g + 12 K), blue circles – 403 K (130 °C, T_g + 32 K), green asterisks – 413 K (140 °C, T_g + 42 K) and brown triangles – 433 K (160 °C, T_g + 62 K). The error bars are estimated from measurements of three different scratches. The orange dashed line represents the thickness of the unannealed sample. Colored solid lines are fits of linear and logarithmic growth to the data in the corresponding regions of the data. The dashed-dotted-dotted line is a fit of eqn (2c) to the data of the sample annealed at 413 K in the logarithmic growth regime. The green dashed line indicates the time dependence in the logarithmic growth regime at longest times for 413 K.

statistical distribution of the data points around the zero line. This pattern indicates that the power law is not a perfect description of the data. Fig. S3b (ESI†) shows that a linear fit provides a better description of the initial stages of the growth kinetics. Fig. S4a (ESI†) depicts that the time dependence of growth kinetics at an annealing temperature of 433 (T_g + 42 K) might also follow a power law with a further decrease in exponent to 0.32. Fig. S4b (ESI†) provides the residual plot of the power law fit to the growth kinetic data obtained at an annealing temperature of 413 K. Like for 403 K, this plot shows that a power law fit probably does not provide the best analysis of the data. The growth kinetics at an annealing temperature of 413 K (T_g + 62 K) cannot be described using a power law. Fig. S5 (ESI†) shows that the exponent of the power law decreases approximately linearly with the annealing temperature. As currently the power law approach to the growth kinetics has no theoretical basis the temperature dependence of the exponent cannot be discussed further. Besides the exponent σ, the time constant t_{growth} can be extracted from the fits and is plotted *versus* inverse temperature as shown in Fig. 3. The data can be approximated using the Arrhenius equation which reads

$$t_{growth}, t_c = t_\infty \exp\left(\frac{E_a}{RT}\right). \tag{1}$$

Here, t_∞ is the crossover time for infinite temperatures, E_a is an (apparent) activation energy and R is the general gas constant. The meaning of t_c is given below. The fit of the Arrhenius equation yields an activation of *ca.* 602 kJ mol^{-1}. This value is much too high for a truly activated process and cannot be interpreted on a sound physical basis. This experimental observation makes the physical meaning of the power law approach questionable. Moreover, the time constant estimated at an

Fig. 3 Time constant t_{growth} (solid squares) and crossover time t_c (solid circles) *versus* the reciprocal temperature in the Arrhenius diagram at temperatures of 383 K, 403 K and 413 K. The dashed line is the fit of the Arrhenius equation to t_{growth}. The errors of t_{growth} are smaller than the sizes of the symbols and given in the ESI.† The solid line is the fit of the Arrhenius equation to t_c. The red asterisk is the extrapolated crossover time to the thickness of the adsorbed layer at an annealing temperature of 433 K (see text for more details).

annealing temperature of 413 K is much lower than the shortest covered experimental time which also makes such a kind of analysis doubtful.

In a second approach the growth kinetics of the adsorbed layer of P2VP will be discussed in the frame of the two adsorption regimes proposed in ref. 11 and for other polymers discussed elsewhere[36] which has a theoretical justification. As discussed above, for theoretical reasons, the growth kinetics of the adsorbed layer should follow time dependence with two different regimes:

$$h_{ads}(t) = h_{t=0} + vt \text{ for } t < t_c \tag{2a}$$

$$h_{ads}(t) = h_c + \Pi \log\left(\frac{t}{t_c}\right) \quad \text{for} \quad t > t_c. \tag{2b}$$

In eqn (2), t_c is the crossover time from the linear growth regime to the logarithmic one. $h_{t=0}$ and h_c are the thicknesses of the adsorbed layer at $t = 0$ and $t = t_c$, respectively. v is the growth rate in the linear regime and Π is related to the growth rate in the logarithmic regime. The physical basis of these equations is discussed in detail in ref. 1. Eqn (2a) (the first mechanism) results from the direct pinning of the segments onto the substrate, whereas the second mechanism (eqn (2b)) is due to the growth of the adsorbed layer by diffusion of segments through the already adsorbed layer. This takes place at a cost of entropy. One must note that for soft matter systems transitions between the different regimes are not that sharp like that for crystals. For soft matter systems gradients are involved which is already discussed in the three-layer model for thin films. Eqn (2b) predicts unlimited growth of the adsorbed layer which is physically not possible. Therefore, an alternative approach was developed which considers this issue. These considerations result in[43]

$$h_{ads}(t) = h^\infty + \ln\left[1 - A \cdot \exp\left(-\frac{t - t_c}{\tau}\right)\right] \quad \text{for} \quad t > t_c. \tag{2c}$$

A is a parameter related to the adsorbed amount of polymer segments at t_c where τ is a time constant related to the equilibrium value of the adsorbed amount and to the equivalent loop adsorption rate.

At first glance, the estimated growth kinetics of the adsorbed layer of P2VP seems to be in agreement with the two regimes proposed in ref. 11 and for other polymers discussed elsewhere.[36]

At the lowest annealing temperature of 383 K (110 °C, T_g + 12 K) and for short times a linear growth regime of the adsorbed layer is observed. It is worth to note that also the power law approach to the growth kinetics at this temperature predicts a linear growth (see Fig. S2, ESI†). After an annealing time of *ca.* 40 h the thickness of the adsorbed layer becomes independent of time. The crossover time is estimated by a plot of the thickness of the adsorbed layer *versus* the linear time scale. The crossover time is taken as the time when the growth kinetics deviates from a linear one. A logarithmic growth regime of the adsorbed layer is not observed for this annealing temperature. This result is further proved in Fig. S2 in the ESI.† Likely the molecular
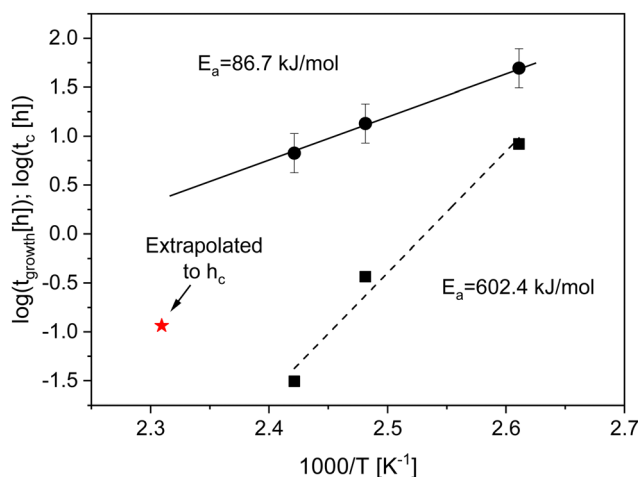
mobility of the segments and chains is too low at this temperature to allow for a logarithmic growth step. Hence the segments cannot diffuse though the already adsorbed layer.

At the annealing temperature of 403 K (130 °C, T_g + 32 K) also a linear growth kinetics is observed up to an annealing time t_c of 13.5 h. For longer times the linear growth regime is followed by a logarithmic one till a time of 73 h (indicated by a blue arrow in Fig. 2). The transition from the linear to the logarithmic growth becomes also clear in Fig. S6 (ESI†) where the thickness of the adsorbed layer is plotted versus time in the linear scale. This means that at this annealing temperature obviously the segments have enough molecular mobility to diffuse through the already formed tightly bound adsorbed layer. For annealing times longer than 73 h the thickness of the adsorbed layer becomes independent of time, showing a plateau. Thus, it is concluded that at an annealing temperature of 403 K and an annealing time of 73 h the thickness of the adsorbed layer reaches a maximum value and cannot increase further. Moreover, it was tried to fit eqn (2c) to the data. Fig. 2 shows that the fit of eqn (2c) did not work quite well.

When the annealing temperature is further increased to 413 K (140 °C, T_g + 42 K) again a linear growth regime is observed for short annealing times which changes to a logarithmic growth at a t_c of 7.1 h. Surprisingly no change of the logarithmic growth to a plateau is observed for the covered annealing times. This is not expected because the annealing temperature is only slightly increased compared to the lower annealing temperature of 403 K, where a plateau is observed. Instead of a plateau, a turn-up of the growth kinetics is observed which is indicated by a green arrow in Fig. 2. This might imply that at this annealing temperature and time the structure of the adsorbed layer is changed, showing an eased diffusion of the segments through the already adsorbed ones.

At an annealing temperature of 433 K (160 °C, T_g + 62 K) only a logarithmic growth regime of the adsorbed layer is observed. No linear growth regime of the adsorbed layer is found. This means that the linear growth regime at this annealing temperature is probably too fast to be observed in the experimentally accessible time window. In general, compared to the other annealing temperatures, the adsorption kinetics measured for 433 K seems to be different.

At annealing temperatures of 383 K, 403 K and 413 K the thickness of the adsorbed layer h_c at the crossover time seems to be independent of temperature having a value of ca. 9.5 nm. It should be noted that the error of h_c is the same as that of the measured data which is ±2 nm. In the linear regime the adsorbed layer growth by a direct pinning of segments to the substrate. This process leads to a crowding at the substrate interface and the growth kinetics changes to the logarithmic one. The crowding at the interface is only due to the segment density at t_c which should be only weakly dependent on temperature. An annealing temperature independent thickness of the adsorbed layer is also reported in the literature.[11] Moreover, Fig. 2 shows further that there is a finite thickness of the absorbed layer at $t = 0$ of 3.3 nm. The segments forming that part of the adsorbed layer will be probably pinned to the surface by the spin coating process.

At annealing temperatures of 383 K, 403 K and 413 K the crossover time t_c could be experimentally estimated as the time when the growth kinetics deviates from a linear one as suggested in the literature (see Fig. S2 and S3a, ESI†).[11] t_c is plotted versus the annealing temperature in a kind of activation diagram (Fig. 3). The temperature dependence of t_c for these data points follows a straight line which can be described using an Arrhenius equation. The fit of eqn (1) to the data yields an activation energy of ca. 86.7 kJ mol^{-1} which is a reasonable physical value. This value is also comparable with the data from the literature. For instance, for polystyrene an activation energy of 80 kJ mol^{-1} is found.[1] It is worth to mention that the observed value for the activation energy for the crossover time corresponds to the activation energy found recently for an equilibration mechanism with a slow mode (SAP).[44] This agreement might indicate that such a slow process might be responsible for the adsorption of polymer segments on the substrates. To confirm this assumption further investigations are necessary.

At an annealing temperature of 433 K only the logarithmic growth regime is observed in the experimental time window as discussed above. Therefore, the crossover time t_c could not be directly extracted. As experimentally observed, the thickness of the adsorbed layer h_c at the crossover time is approximately independent of the annealing temperature. To estimate a crossover time at an annealing temperature of 433 K the time dependence of the adsorption kinetics is extrapolated to h_c. The value obtained by this procedure is added to Fig. 3. Obviously, the extrapolated data point does not fit to the Arrhenius-like dependence of t_c defined by the lowest annealing temperatures. This might indicate that the growth kinetics of the adsorbed layer formed at an annealing temperature of 433 K is different from that at lower annealing temperatures.

This conclusion is further supported by Fig. 4, where the thickness of the adsorbed layer for an annealing time of 316.2 h is depicted versus the annealing temperature. The temperature dependence shows a transition from a low temperature behavior to a high temperature one at around 410 K. This means
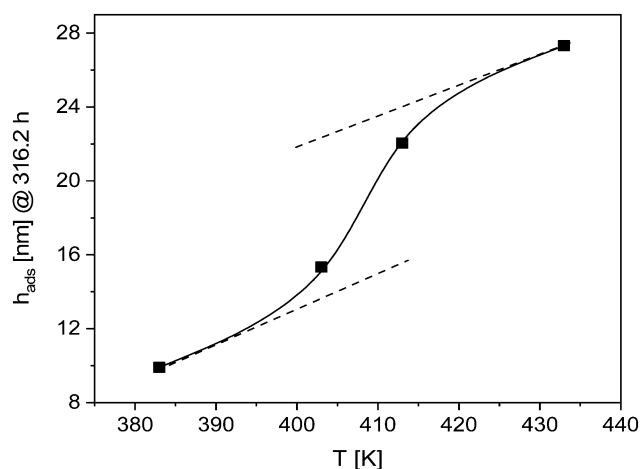
Fig. 4 Thickness of the adsorbed layer formed for an annealing time of 316.2 h versus temperature. The solid line is a guide to the eyes.

that the structure of the adsorbed layer depends on the annealing temperature. This can be discussed in the framework of weaker interactions of polymer segments at higher temperatures. This can be due to enthalpic and entropic effects. The latter contribution is discussed in ref. 20. Probably at higher annealing temperatures a more loosely adsorbed layer with a higher free volume is formed which eases the diffusion of segments. This might suggest that at higher temperatures the polymer segments can be desorbed from the substrate as discussed in ref. 20. The possible desorption of polymer segments can be also the reason that only a logarithmic growth regime is observed. Moreover, the upturn observed at an annealing temperature of 413 K in the logarithmic growth regime for longer annealing times might be also due to desorption effects. This seems to be realistic as the desorption of polymer segments depends not only on the annealing temperature but also on time.

Fig. 3 and 4 indicate a change in the mechanism of growth kinetics. Besides a possible desorption of the polymer chains from the substrate also a change of the growth kinetics to a growth regime assisted by the dynamic glass transition (α-relaxation) might be considered. To prove this hypothesis further investigations are necessary specially to study the growth of the adsorbed layer at higher annealing temperatures. Such investigations are planned.

Fig. 5 depicts the growth rate in the linear regime *versus* inverse temperature. In the considered temperature range the data seem to follow Arrhenius dependence with an activation energy of approximately 85.3 kJ mol^{-1}. This value corresponds to the activation energy estimated for the temperature dependence of the cross-over time t_c. This seems to be consistent because reaching the cross-overtime is determined by the growth rate in the linear regime.

Finally, the influence of the leaching time is considered. All results discussed above were obtained for a leaching time of 30 min. To investigate the influence of the leaching time at an
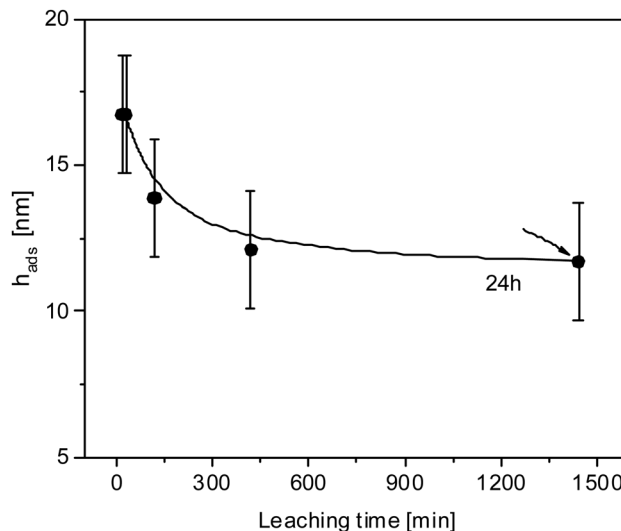
Fig. 6 Thickness of the adsorbed layer *versus* the leaching time for samples annealed at 413 K for 3 days. The line is a guide to the eyes.

annealing temperature of 413 K and an annealing time of 3 days (72 h) different leaching times have been considered in Fig. 6. With increasing leaching time, the thickness of the adsorbed layer decreases slightly and continuously decreases although absolute values are in the range of the experimental errors. The thickness of the adsorbed layer reaches a plateau value at a leaching time of 24 h. The maximal difference in the thickness of the adsorbed layer for a leaching time of 30 min and 24 h is around 5 nm for the selected annealing conditions which is close to the experimental error. In further studies different annealing temperatures will be considered to investigate the influence of leaching time in more detail.

Conclusions

The growth kinetics of the adsorbed layer of P2VP was investigated using a leaching approach where the thickness of the adsorbed layer was estimated *via* AFM measurements. In these experiments, the annealing temperature is varied in a broader range than previously reported in the literature.[10] At the lowest annealing temperature, only a linear growth regime is observed followed by a plateau at longer time periods. This is reasoned considering that at low annealing temperatures, the molecular mobility of the segments is too low to allow for diffusion through the already adsorbed layer formed in the linear growth regime. At the next higher annealing temperature, linear and logarithmic growth regimes as well as a plateau for the longest annealing time periods are observed. As expected, for annealing times long enough at intermediate annealing temperatures, the growth of the adsorbed layer saturates, and no further adsorption or desorption of segments takes place. Upon increasing the annealing temperatures, the growth kinetics differs from that at low and intermediate temperatures. At an annealing temperature of 413 K, first a linear as well as logarithmic growth regime is observed. Second, the logarithmic
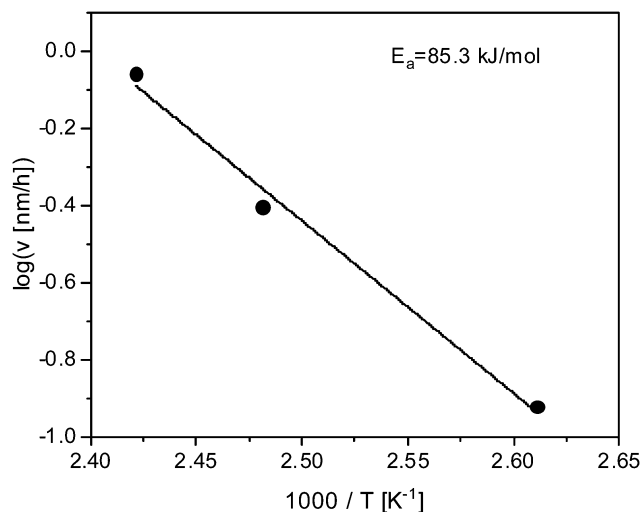
Fig. 5 Growth rate in the linear regime *versus* inverse temperature. The solid line is a fit of the Arrhenius equation to the data.

growth kinetics shows an upturn to a faster increase of the growth of the adsorbed layer. At an annealing temperature of 433 K, only a logarithmic growth regime is observed. Moreover, the cross-over time estimated by extrapolation does not agree with the temperature dependence obtained for the lower annealing temperatures. From these results it can be concluded that the structure of the adsorbed layer depends strongly on the annealing temperature. As a possible molecular interpretation, desorption of segments from the substrate is discussed.

Conflicts of interest

There are no conflicts of interest.

Acknowledgements

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