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Influence of the solvent viscosity on surface graft-polymerization reactions

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Abstract

Solvent viscosity was found to be a predominant parameter to control free-radical surface graft polymerization. Poly(ethylene-*alt*-tetrafluoroethylene) foils were lithographically exposed to 92 eV photons in order to create patterns of radicals at their surface, which react with the oxygen of the ambient air to produce peroxides. Glycidyl methacrylate was then radically polymerized from these peroxide initiators. We discovered that increasing the viscosity of the grafting solution by addition of polyethylene glycol boosts the grafting reaction, leading to an order of magnitude increase in the height of the grafted layer. Further increasing the viscosity leads to thinner layers of grafted material. The increase of the grafted layer thickness in the low viscosity range is interpreted to be due to a diminution of the termination rate while for higher viscosity, the reduction of the initiation rate causes the observed decrease of the grafted thickness. This interpretation is in agreement with observed morphological and structural differences of nanostructures grafted at different viscosities. We conclude that viscosity is an essential and very easily controllable parameter for surface graft-reactions.

Keywords: Polymer brushes; Nanostructures; Radiation grafting

1. Introduction

Interest in grafting of polymers brushes onto surfaces has been growing in the last two decades for its high versatility in tailoring surfaces [1,2]. Polymer brushes are end-tethered polymers, which stretch away from the surface when densely grafted. Inorganic oxide surfaces, such as oxidized silicon wafers or mica, are used as hard flat surfaces, whereas polymer foils are used as flexible substrates for the grafting reactions. In the case of oxides, initiators are usually bound to surface hydroxyl groups for further grafting reactions. For grafting onto polymer substrates, the surface can be either treated chemically to attach initiators or exposed to radiation (photons or e-beams) or plasma in order to create radicals, which serve as initiators for free-radical graft polymerizations [3].

Since many years, the work in polymer grafting is concentrated on irradiated polyethylene (PE), polypropylene (PP), and various types of fluoropolymers [4]. The latter polymer family is appreciated for its high melting point, low thermal degradation, and high strain and shear stress resistances as well as for its low surface energy. Radiation grafting of hydrophobic fluoropolymer base films can, for example, convert fluoropolymer surfaces into highly hydrophilic surfaces or functional surfaces [5]. Such chemical modifications have been traced by contact angle measurements, X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) spectroscopy. Numerous publications have demonstrated the great advantage of surface grafted polymers, for example, for sorption of heavy ions [6,7], to bind specific sites for protein immobilization [8,9] or as building blocks for smart materials [10] or for biomedical applications [11].

For solution polymerization, the choice of the appropriate solvent is crucial as the final product characteristics depend on the solvent viscosity and polarity as well as on its ability

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to solubilize the monomer, the initiator, and the synthesized polymer. A well-known example for the importance of solvent viscosity in solution polymerization reactions is the Trommsdorff effect [12], an auto-acceleration effect induced by increasing viscosity due to polymer chain growth. This effect is explained by the lower mobility of the propagating chains in viscous media, resulting in lower termination rates.

Surface graft polymerization differs substantially from solution polymerization as the growth takes place at solid–liquid interfaces, where diffusion and mobility play an even more important role. As for solution polymerization, a comparable solvent evaluation has to be performed in order to obtain reproducible chain growth. In radiation grafting, radiation penetration and the deposited dose have to be considered for the upstream process to optimize the number and the depth distribution of initiating sites. Monomer concentration, solvent, reaction time, and temperature are downstream process parameters to control the growth of graft polymers.

EUV interference lithography based radiation grafting is a newly developed polymer patterning technique, which is suitable to study fundamental aspects of graft polymerization [13]. In the EUV exposure step performed at the Swiss Light Source (SLS), various radical patterns are produced on polymer foils. The radicals react with ambient oxygen to form peroxides and hydroperoxides, which serve as initiators for the subsequent graft polymerization to form structured polymer brushes. On each sample, defined fields can be written, i.e. microstructures to study the dose–height dependence and nanoscale interference patterns to study the resolution and morphological changes with the dose. The low penetration depth of the 92 eV photons used for exposure (<100 nm) limits the formation of radicals to near-surface region of the film. In this study, the influence of EUV exposure dose and of solvent viscosity for grafting of glycidyl methacrylate onto ETFE foils was investigated by varying the concentration of the polyethylene glycol (PEG) added to the initial monomer solution.

2. Materials and methods

Extruded 100 μm thick films of ETFE (poly(ethylene-*alt*-tetrafluoroethylene)), Nowoflon ET-6235 (Nowofol GmbH, Siegsdorf, Germany), were placed between two polished 4'' silicon wafers and heated for 5 min at 230 °C in a hot press under a pressure of 200 N/cm^2 in order to obtain flat surfaces with a roughness below 5 nm.

Glycidyl methacrylate (GMA, Fluka, p.a) was vacuum distilled before use. Methyl-ethyl-ketone (MEK, Merck), isopropanol (Fischer), acetone (Fischer), toluene (Fischer), dioxane (Merck), polyethylene glycol (~400 g/mol, PEG, Fluka), ethylene glycol (EG, Fluka), 2-hydroxyethly methacrylate (HEMA, Fluka), Methyl methacrylate (MMA, Fluka) were used as received.

2.1. Exposure

EUV exposures were done in vacuum ($<10^{-5}$ mbar) at the "X-ray Interference Lithography" beamline of the Swiss Light Source. The beamline uses undulator light with a central wavelength of 13.4 nm (92.5 eV) and ~3% spectral bandwidth. The incident EUV power on the sample was several mW/cm^2 and the delivered dose was controlled in the range of 1–360 mJ/cm^2 using a fast beam shutter. The samples were irradiated using interfering beams according to the methods described earlier [14]. Silicon nitride masks with gratings of various periods were used to create interference patterns with periods in the range of 100–1000 nm. The irradiated samples were stored in air in a deep freezer (−80 °C) until further processing.

2.2. Polymerization of GMA

Sample grafting was carried out under inert atmosphere in glass reactor tubes placed in an oil bath pre-heated to 70 °C. The used monomer solutions contained 10–30%$_{\mathrm{vol}}$ of GMA in PEG/solvent mixtures degassed with N_2. Typical reaction time was 30 min. The grafted samples were then washed for 30 min with acetone in an ultrasound bath.

2.3. Characterization

Atomic Force Microscopy (AFM) was performed using a Digital Instrument Nanoscope IV/Dimension 3100 in the tapping mode. Samples were mounted on glass slides without any prior treatments.

Viscosity measurements were done using a PHYSICA MCR 300 rheometer.

3. Results and discussion

3.1. Viscosities of GMA/PEG/solvent mixtures

The viscosity of mixtures depends on the temperature and concentration, as well as on viscosity and molecular interactions of the different components. During polymerization reactions an increase in viscosity due to chain growth is generally observed. In our systems, the monomer conversion in the bulk solution is low. It is therefore reasonable to assume little change in solvent viscosity during the reaction. However, the viscosity within the surface-grown polymer brush is expected to be higher than that of the solution.

Modelling of polymer–solvent mixture viscosities is one of the current challenges in physical property estimation of liquid mixtures [15]. Most theoretical, semi-theoretical or empirical models – as reviewed by Monnery et al. [16] – deal with mixtures of low molecular weight components and always require experimentally determined correction terms.

A simple approach is to estimate the viscosity from the mole fractions of the liquids forming the mixtures through:

$$\eta_{\mathrm{mix}} = x_1\eta_1 + x_2\eta_2 + x_3\eta_3 \tag{1}$$

where η_i is the viscosity of the component and x_i is their mole fraction. As an alternative, the logarithmic model, as proposed by Eyring and coworkers for "not too imperfect solutions" [17] could be adapted for ternary mixtures:

$$\ln \eta_{\text{mix}} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_3 \ln \eta_3 \tag{2}$$

The comparison of these models with our experimentally determined values for the system PEG/dioxane/GMA with varying PEG content is displayed in Fig. 1a for 20 °C and in Fig. 1b for 70 °C. The calculations according to Eqs. (1) and (2) were based on experimentally determined values for the pure components. Note that for the range of 0–90% vol PEG, the GMA content was set to 10% vol, which corresponds to the content used in the polymerization experiments, while for 90–100% vol PEG the GMA content was 10–0% vol. It was found that the calculation based on mole fractions in general underestimates the influence of low viscosity components, while the logarithmic calculation overestimates it.

As none of these simple calculations yields satisfying data, we used experimentally determined dynamic viscosities for all the mixtures and components in this study. Data of these measurements are displayed in Fig. 1c and d. Viscosities of GMA/PEG mixtures with toluene and MEK as the third component are very similar to the dioxane mixtures discussed above, despite the very different chemical structure and polarity of the molecules. For the PEG/EG/GMA system, the higher viscosity of EG compared to dioxane, toluene or MEK results in general in higher viscosity values in the low PEG concentration range, while at high concentration of PEG, the influence of the GMA content is predominant over the influence of EG.

In summary, a broad range of viscosities of GMA solutions can be covered by PEG addition to low viscosity solvents. The temperature dependence of the viscosity is high in the investigated range. This means that temperature has to be controlled carefully to allow conclusions on the influence of the viscosity on the graft polymerization.

3.2. Grafting in PEG/dioxane solutions

The exposure process with the EUV interference lithography setup enables to determine the height–dose relation of grafted microstructures in direct exposed areas, where the dose is very precisely defined [18]. We previously investigated the dose–height dependence of poly-glycidyl methacrylate (pGMA) grafted onto ETFE films in different alcoholic solvents and observed two different ranges. First, at low dose, the height increases with the square root of the dose caused by the increased coverage density, forcing the polymer chains to stretch away from the surface to form polymer brushes. Second, at high dose, the grafting height decreases with the dose, assigned to high termination rates of polymer chains growing in close vicinity and radiation damage in the base polymer film [19]. In the present study, we concentrated on the low dose range where the influence of radiation damage is minimized. In low viscosity solvents (isopropanol, ethanol, MEK,

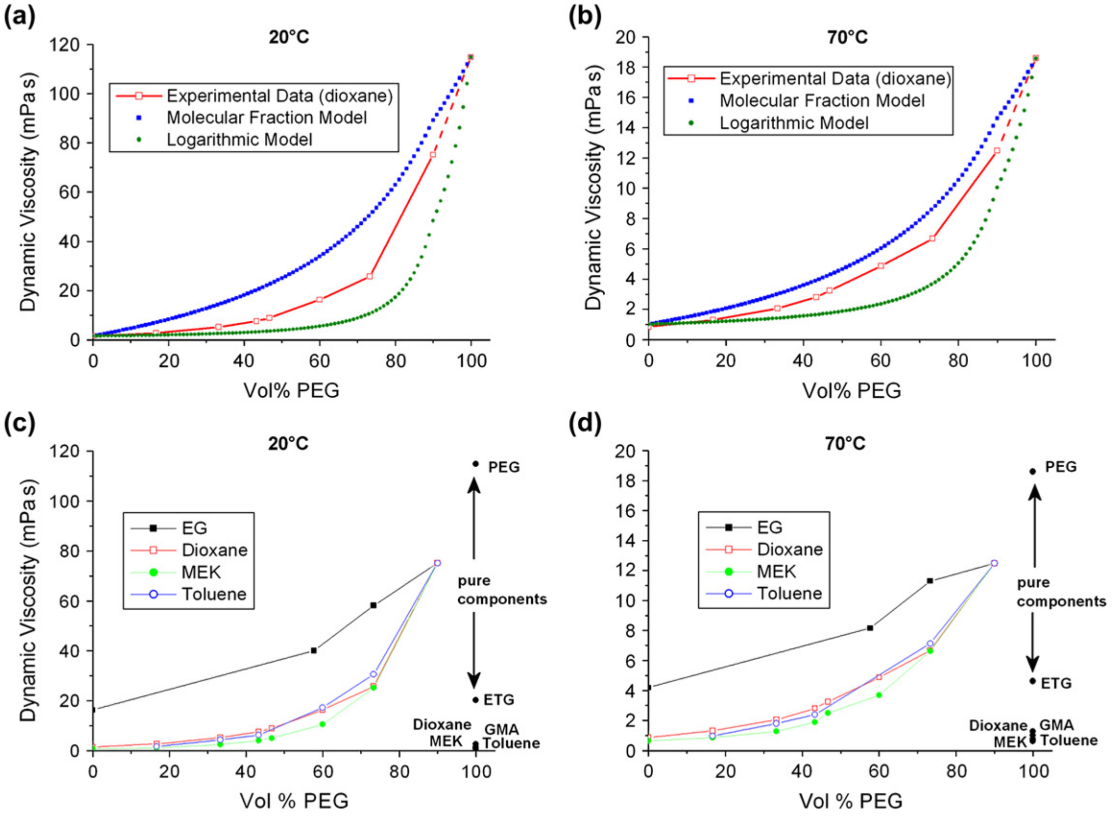

Fig. 1. Measured (□) and calculated dynamic viscosity of PEG/dioxane/GMA (10% vol) solutions for different PEG ratios. For (a) 20 °C and (b) 70 °C; for two different models: (■) the molecular fraction model; (●) the logarithmic model. Measured dynamic viscosity of PEG/solvent/GMA (10% vol) solutions for different PEG ratios. For (c) 20 °C and (d) 70 °C; for different solvents: (■) ethylene glycol; (□) dioxane; (●) methyl-ethyl-ketone; (○) toluene.

tetrahydrofuran, dimethylformamide, toluene and dioxane) and low monomer concentration (~10%), we generally observed poor reproducibility of the grafting reaction. A minimum concentration of monomer (~30%) is needed to obtain reproducible grafting for those low viscosity solvents. Furthermore, no gradual increase of the grafting height with GMA concentration was observed below 30% of concentration. In contrast, when GMA was grafted in more viscous media such as EG and PEG, we obtained well defined structures and reproducible results even for low GMA concentration (<10% vol), as well as gradually increasing polymer growth with increasing monomer concentration. We deduced that viscosity might be the key parameter for a good polymer growth. We therefore investigated GMA grafted in various dioxane/PEG mixtures with viscosities adjusted between 1 and 12 mPa s.

Two different types of dose dependency were found for the low and high viscosity ranges, respectively (Fig. 2). For clarity, the data of the whole viscosity range are displayed in two different charts.

In a solution of 10% GMA in pure dioxane, grafting was achieved only for the highest doses included in this study. By addition of 17% vol of PEG, the viscosity increases by ~50%, which boost grafting reaction such that a dose dependence typical for a brush regime is reached, where grafted height increases proportionally with the square root of the dose. The grafting height further increases with the same dose dependence with increasing PEG load, until a maximum is reached for ~50% vol PEG (viscosity: 3.3 mPa s) (Fig. 2, curves b–e).

Further increasing the PEG load (>50% vol) results in lower grafting heights (Fig. 2, curves f–h). Surprisingly, very low dose dependence was obtained in the investigated range, i.e. the height is now hardly affected by a dose difference of one order of magnitude.

3.3. Solvent dependence

The effect of dynamic viscosity on the grafted height was explored for different solvent types (MEK, toluene, dioxane, and EG) mixed with PEG and 10% vol of GMA. The chosen solvents had to be soluble in PEG for any dilution ratio, and had to have lower dynamic viscosity than PEG in order to allow the tuning of the viscosity with the addition of PEG. Note that for EG/PEG mixtures, dynamic viscosity lower than 4 mPa s could not be obtained as the initial value of 10% GMA in pure EG at 70 °C was 4.19 mPa s. Charts representing the evolution of the graft-height with the dynamic viscosity for all exposure doses are shown in Fig. 3. For toluene/PEG (Fig. 3b) and MEK/PEG (Fig. 3c) mixtures, two ranges similar to the dioxane mixtures (Fig. 3a) discussed above were observed.

First, a steep increase of the grafted height with increasing viscosity was noticed for all solvent mixtures, demonstrating that a slight increase of the dynamic viscosity favored the grafting reaction. Furthermore, increase of the graft-height with the square root of exposure dose was again observed for all solvent mixtures in this viscosity range. A maximum of the grafting height was found in all the curves showing viscosity dependence, for dioxane at ~3 mPa s, for toluene at ~2.8 mPa s and for MEK at ~2 mPa s.

Second, in the higher viscosity range, a decay of the grafting height with viscosity was detected for all PEG/solvent mixtures, including PEG/EG. In this viscosity range, the curves show no increase of grafted height with exposure dose; the solvent could be chosen arbitrarily.

Parallel experiments were carried out using HEMA and MMA instead of GMA using the MEK/PEG solvent system. A similar strong increase of graft layer thickness was observed for all these monomers when 50% PEG was added to a 10% monomer solution. These results indicate that the chemical reaction of the epoxy group of GMA with the hydroxyl function of PEG molecules is the reason for the found effects.

3.4. Nanostructures

In the performed EUV exposures, nanopatterns of radicals are formed by interference of beams diffracted by the gratings in the mask. In this region the average dose cannot be directly measured, but it is estimated as 1/10 of the dose deposited in the directly exposed area.

Effects of viscosity for the growth of nanostructured GMA brushes were investigated with the AFM in the dry state. Fig. 4

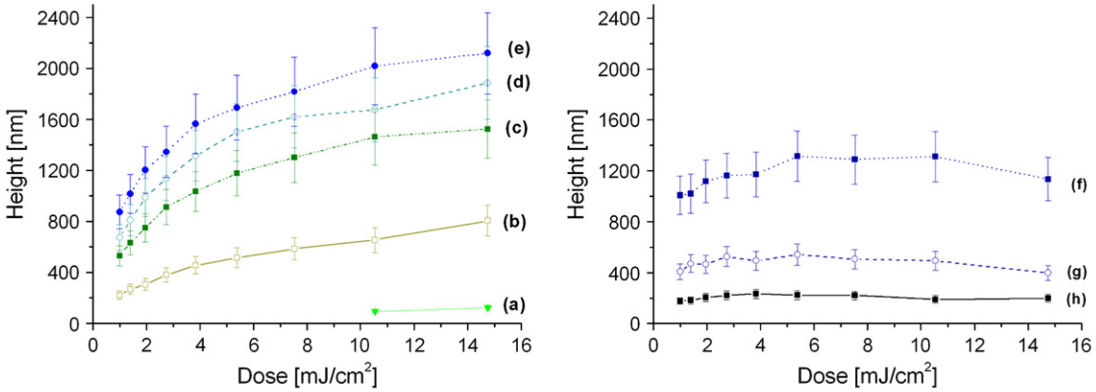

Fig. 2. Dose–height curves for different PEG fractions in dioxane/GMA solution. Curves: (a) 0%; (b) 17%; (c) 33%; (d) 43%; (e) 47%; (f) 60%; (g) 73%; (h) 90%. Grafting conditions: 30 min at 70 °C in GMA (10% vol)/dioxane/PEG solutions.

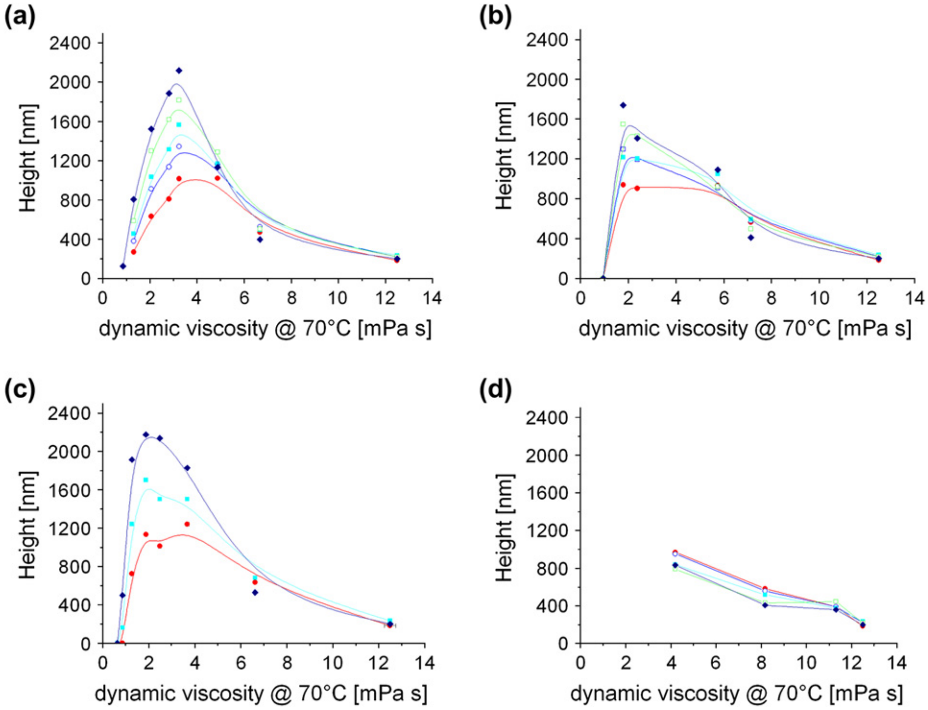

Fig. 3. Viscosity–height dependence for different solvents mixed with 10% vol of GMA: (a) dioxane; (b) toluene; (c) methyl-ethyl-ketone; (d) ethylene glycol and at different doses: ● 1.4 mJ/cm^2; ○ 2.74 mJ/cm^2; ■ 3.84 mJ/cm^2; □ 7.53 mJ/cm^2; ◆ 14.76 mJ/cm^2. Grafting conditions: 30 min at 70 °C.

shows AFM height pictures and average profiles of 200 nm period line nanostructures of poly-GMA grafted in PEG/dioxane mixtures for low, medium and high dynamic viscosities. At low dynamic viscosity (Fig. 4a) small dots are observed, which can be assigned to coiling of polymer chains in a mushroom-like configuration when the packing density is not sufficiently high to get into the brush regime. For medium viscosity (Fig. 4b) much more material is grafted, assigned to a good initiation and rapid chain growth. However, the grafted material showed irregular growth and high polydispersity resulting in domains of varying thickness. For high viscosity, the best pattern definition was found for 90% of PEG (Fig. 4c). The hairy structure of the grafted material indicates that long polymer chains are grafted.

4. Discussion

Viscosity is a parameter that evolves during polymerization in solution, which influences dynamically the growth rate. In solution or bulk polymerization, the viscosity changes with the conversion or with the polymer growth, respectively. In our system, due to low conversion in the bulk solution, the viscosity is assumed to be constant during the grafting reaction at the value determined by the composition of the grafting solution. For the interpretation of the results of this heterogenous system, we will distinguish two different time periods for the grafting reaction:

(a) $t \approx 0$, initially the reaction rates are supposed to be similar to solution polymerization reaction rates at low conversion. Peroxide initiators and short growing chains are not affected by each other and are only surrounded by polymerization mixtures.

(b) $t \gg 0$, the reaction rate is no longer comparable with solution polymerization reaction rate. Each polymer chain influences its neighbours and therefore changes the surrounding viscosity for the remaining initiators and the growing chains.

4.1. Initiation

Due to the strong absorption of 92 eV photons, peroxide initiators are formed in about the top 100 nm of the polymer films, with concentration decreasing exponentially with depth. It is necessary to distinguish the surface peroxides, which are in direct contact with the polymerization solution and the subsurface peroxides which come in contact with the monomer only after its diffusion into the polymer film. Kulik et al. [20] demonstrated that molecules can scarcely penetrate the polymer network and get access to the peroxides embedded in the sub-surface due to the hydrophobicity of the base polymer. Once the properties near the surface of the base film are modified by the grafting, sub-surface peroxides become more likely to react with the monomer.

Due to the low concentration of peroxides at the accessible surface of the substrate, a good initiation is a key issue to obtain high and dense growth of grafted polymers. The importance of the initial phase of the reaction is nicely illustrated by the fact that we were not able to graft even in a highly concentrated monomer solution, in an experiment where we

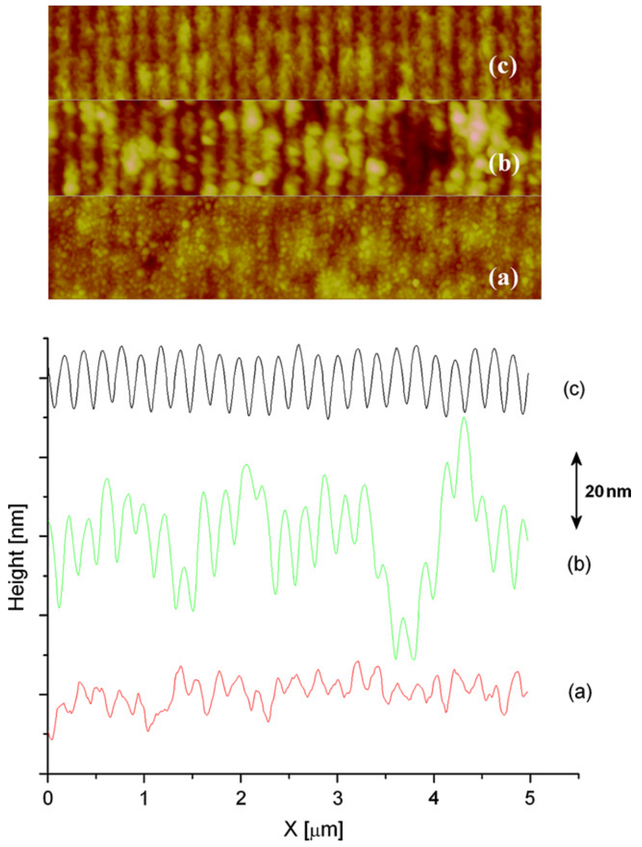

Fig. 4. AFM micrographs and average profiles of 200 nm period line structures exposed to 2.74 mJ/cm^2, grafted for 30 min in dioxane/GMA (10% vol) solutions with (a) 17% PEG (dynamic viscosity: 1.31 mPa s), (b) 46.7% PEG (dynamic viscosity 3.24 mPa s) and (c) 90% PEG (dynamic viscosity 12.49 mPa s).

pre-heated the exposed ETFE film in a monomer-free solvent mixtures for 15 min, meaning that thermal treatment destroys most of the surface peroxides within that period of time. This observation is in good agreement with the results of Kulik et al. [20], who revealed that the surface concentration of peroxides decreases by an order of magnitude within 15 min at 65 °C, independent of the nature of the polymer.

In solution polymerization, initiation rates are characterized by two parameters, which are k_d and f, the dissociation constant of the initiator and the initiator efficiency. The decomposition of initiators in solution produces a pair of radicals in a solvent cage, which can recombine or separate by diffusion. The radicals react then with the monomer to form polymer chains. The initiation as a combination of these two processes is characterized by the product $k_d f$, which is highly dependent on the conversion or viscosity of the system, respectively. The higher the viscosity is, the higher is the geminate radical recombination (cage effect) [21–24] and the lower is the probability to initiate a polymer chain. The initiation parameter $k_d f$ is almost constant for low viscosity, but it is strongly decreasing at high viscosity [25–27].

In our grafting reaction, for $t \approx 0$, similar assumptions as for solution polymerization at low conversion can be made: with higher viscosity the overall initiation rates are lowered due to the caging effect. For $t \gg 0$, the close vicinity of grafted polymer chains locally increases the viscosity near the remaining initiation sites, leading to a diminishment of initiation rates due to a decrease of k_d. The diffusion of the geminate radical out of the cage as well as the probability to match with a monomer diffusing into the polymer brushes then controls the initiation. Therefore, the number of initiating chains further diminishes with the reaction time and with the viscosity, leading to less dense structures in viscous solutions.

4.2. Propagation

We assume that in the initial phase, the living ends of the grafted polymers stay in direct contact with the solution and that no diffusion controlled state is reached. However, the reaction of subsequently dissociated peroxides is controlled by the diffusion-limited feed of monomers to their growing ends embedded in the bulk.

Propagation rates of solution polymerization are characterized by their propagation constant k_p, which is known to be constant at low monomer conversion and drastically decreases at high conversion (>70%) or at high viscosity, respectively [28–30]. In our system, the conversion in the bulk solution is assumed to be very low and therefore the temporal change in propagation rates is low for surface grafting.

For $t \approx 0$, k_p of the heterogenous system is similar to the one in solution, i.e. lower at high viscosity. The same assumption is valid for $t \gg 0$, as we suppose that propagation mainly occurs at the interface between the growing ends of the chains and the liquid solution. Only for chains growing either from sub-surface peroxides or in a late state of the reaction inside a densely packed brush, k_p decreases with time, due to restricted chain mobility.

4.3. Termination

Main termination reactions in radical polymerizations are radical–radical recombinations and disproportionations, which are both diffusion controlled processes. The termination constant k_t is highly dependent on conversion or viscosity, respectively [27–29,31,32]. As a consequence of lower mobility of longer polymer chains in the system, k_t steadily diminishes during polymerization in solution.

Also for surface graft polymerization, for $t \approx 0$, k_t is lower at higher viscosity. The polymer chains should therefore grow longer at higher viscosity. However, we need to consider that at high exposure dose polymer chains are growing in close vicinity; therefore radical–radical termination is more probable than for solution polymerization, which results in a higher k_t than in solution polymerization.

For $t \gg 0$, k_t decreases with the solution viscosity and with the grafting height (mobility).

In summary, for $t \approx 0$, $k_d f$ and k_t can be assumed to be lower at high viscosity, whereas k_p is independent of the viscosity in a wide range and only decreases at very high viscosity. For $t \gg 0$, $k_d f$ and k_t decrease drastically with increasing viscosity in the system, whereas k_p stays constant during the reaction.

With these considerations, the experimental data are interpreted as follows: the prominent increase of the grafting height with the viscosity in the range below 4 mPa s for all PEG/solvent mixtures (Fig. 3) is assigned to a decrease of the termination rates of the graft reaction, whereas the decrease of the grafting height for viscosities higher than 4 mPa s is correlated to the decrease of the initiations rates. The overall reaction is given by a balance of these two opposite effects: in one hand, the addition of PEG in the system avoids quick recombination of the growing chains. On the other hand, the increase of the solution viscosity diminishes the grafted density.

For viscosity below 4 mPa s, the height is proportional to the square root of dose, due to increasing numbers of grafting sites. This coverage increase forces the grafted polymer to form a polymer brush. In highly viscose media (>4 mPa s), the height is more or less dose independent, due to accidental balance of the anyway low initiation and termination rates.

As a general rule, we deduced that short and dense brushes are grown in the low viscosity range, whereas long polymer chains with low grafting density are grown in viscose media.

This interpretation of the influence of viscosity on surface grafting is supported by the observed effect on the formation of nanostructures (Fig. 4). The structures grown at low viscosity (1.3 mPa s) show the formation of small dots (Fig. 4a), which indicate that most of the growing chains died within few monomer additions due to high termination rates. The few longer grown polymer chains organize in bundles or collapse due to affinity interactions. By increasing the viscosity (3.2 mPa s; Fig. 4b) termination rates are lowered and denser brush-like structures are formed. Due to the high growth rates, local variations in viscosities are provoked resulting in domains of slower and faster growth (“local Trommsdorff effect”) and with that to poor structure definition. For the highest viscosity (12.5 mPa s), lines are better defined because of lower initiation and termination rates, leading to a limited number of relatively long chains. Due to generally high viscosities, local viscosity variations have very little influence, resulting in a more homogenous appearance of the structures.

5. Conclusion and outlook

Viscosity is an important parameter to control surface graft polymerization. By increasing the viscosity of the initial polymerization solution, it is possible to sequentially lower, first, the rate of termination and, second, the rate of initiation of the graft reaction. In the intermediate viscosity range, these reaction determining rates are balanced such that the highest polymer growth is reached. The change in initiation and termination rates with solvent viscosity furthermore influences the morphology of grafted micro- and nanostructures. From the same exposure dose, polymer layers with different chain length distributions and with morphologies ranging from mushroom to brush-like configurations are obtained by grafting in media of different viscosities. The influence of viscosity is basically independent of the chemical properties of the solvent and, as first experiments demonstrated, transferable to other monomers used for radical graft polymerizations. The influence of viscosity on polymerizations from initiators bound to oxide surfaces is currently under investigation.

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