

Preparation of Micro- and Nanopatterns of Polymer Chains Grafted onto Flexible Polymer Substrates

Hans-Peter Brack,^{*,†} Celestino Padeste,[‡] Michal Slaski,[†] Selmiye Alkan,[†] and Harun H. Solak[‡]

Electrochemistry Laboratory and Laboratory for Micro- and Nanotechnology, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

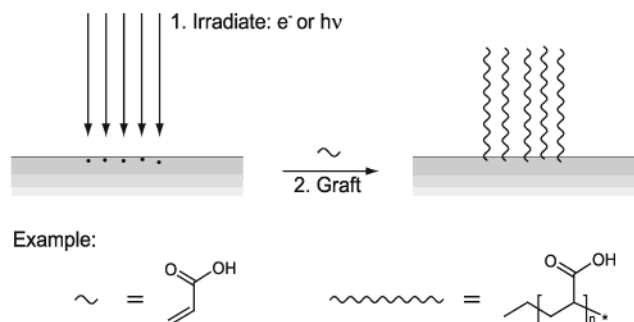
Received August 18, 2003; E-mail: hans-peter.brack@hispeed.ch

We present some first results concerning a new method based on radiation grafting to create polymer structures with lateral dimensions as small as 100 nm on the surface of polymer films. In radiation grafting, reactive radical species are generated first in a polymer substrate through electromagnetic or particle (e.g., electron beam) irradiation, and the grafting is carried out in a separate subsequent step.^{1,2} This method has been known for over forty years, and it has found some niche applications and is the continued subject of research in the areas of membranes, chromatography, textile fiber modification, polymer surface modification, and biomedicine.^{1–3} It is especially useful when the combination of the desirable properties of two dissimilar polymers in one new material is required. In some cases radiation grafting has been used to graft only on the surface of materials, for example, to improve adhesion,² or only on certain macroscopic areas of samples through the use of masks.¹ In our present work, lateral definition of the structures is achieved by localized creation of radicals using a focused electron beam (e-beam) or synchrotron radiation in an X-ray interference setup (Scheme 1).

Polymer chains are typically covalently attached to a substrate surface by means of either the “grafting-to” or “grafting-from” techniques.² Preformed polymer chains are reacted with a surface in the grafting-to method, but this method usually only leads to low grafting densities. In the grafting-from technique, initiator species on substrate surfaces are used to initiate polymerization upon exposure to a monomer under appropriate conditions. Using the grafting-from technique, high enough grafting densities can be achieved so that the grafted chains are forced into elongated conformations characteristic of the “brush” regime. Such materials are of considerable interest because their surface properties can be tailored by the brush composition and structure, and this capability is leading to the emergence of numerous potential applications for these novel materials in the area of “smart surfaces”, biological compatibility, and drug delivery.⁴

Grafting of polymers on specially prepared reactive surfaces has been described recently.^{4,5} Lateral resolution in the 50 nm range has been achieved by selective activation or deactivation of surface functional groups using e-beams.⁵ Nonetheless, there are significant limitations in these methods. Special gold or silicon substrates are generally used. Such surfaces require several preparative steps before the actual grafting reaction, for example, for the preparation of self-assembled monolayers, functionalization, and derivatization of surface functional groups to give surface-bound initiators. Therefore, it would be desirable to have simpler methods for the preparation of initiating sites for the polymerization of the grafted chains. Ideally such methods should involve fewer preparation steps, typical lithography equipment, and use common and inexpensive reagents, reactions, and substrates. In particular, it would be

Scheme 1. Preparation of Micro- or Nanografted Surfaces. Radicals Are First Created in a Polymer. The Subsequent Grafting Polymerization Represents a Chemical Amplification Step



desirable to be able to use common flexible and extrudable, moldable, or castable polymers as substrates.

In this study we employed films of poly(tetrafluoroethylene-co-ethylene), or ETFE, as flexible substrates for surface modification. Line patterns with varying exposure dose and line width were written with a LION-LV1 e-beam system (Leica Microsystems, Jena) operating at 2.5 keV beam energy. High spatial resolution X-ray exposures were carried out at a beam energy of 92 eV at the “X-ray Interference Lithography” beamline of the Swiss Light Source (Villigen PSI, Switzerland).⁶ Lower resolution patterns were created by using a TEM-grid with features in the 10–50 μm range as a shadow mask at the same X-ray beamline.

Grafting of the irradiated pieces of ETFE films was carried out under inert atmosphere at 50–60 $^{\circ}\text{C}$ in a reactor filled with an aqueous solution of 3–10% acrylic acid. After a 15–20 min reaction time the samples were washed with distilled water and dried in a stream of dry nitrogen. The samples were characterized using a mechanical profilometer and atomic force microscopy.

Figure 1 shows a typical AFM image of a line structure produced by e-beam irradiation and grafting in a 10% acrylic acid solution. Control measurements on samples with the same e-beam exposure dose but without grafting showed no significant change in surface texture. Increasing the e-beam dose led to broadening of the features, due to the increased influence of the tails in the e-beam profile. Irradiation with even higher doses led to degradation of the polymer substrate. A typical exposure dose for grafting was 100 $\mu\text{C}/\text{cm}^2$, but the degradation became apparent only at doses of about 10⁴ $\mu\text{C}/\text{cm}^2$.

To quantitatively study the effect of exposure dose on grafting height, ETFE films were exposed to various doses of X-rays through a shadow mask. After grafting with 5% acrylic acid, the structures ($\geq 10 \mu\text{m}$) were visible with an optical microscope. The structure height increased linearly with low doses but then quickly reached a saturation level, depending on the concentration of monomer or temperature used (Figure 2). The exposure doses at our saturation levels are similar to those required for chemically amplified resists

[†] Electrochemistry Laboratory.

[‡] Laboratory for Micro- and Nanotechnology.

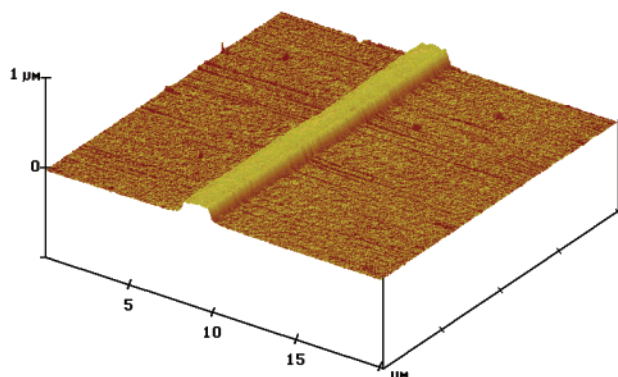


Figure 1. AFM image of a 1.7 μm wide, 150 nm high line structure generated by e-beam irradiation of an ETFE film followed by grafting with acrylic acid.

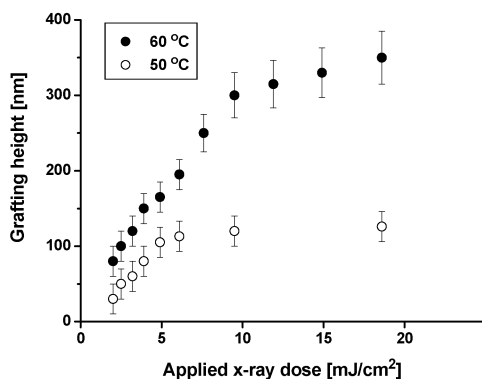


Figure 2. Profilometer measurement of the dose dependence of the height of poly(acrylic acid) structures grafted onto ETFE irradiated with X-rays through a shadow mask.

used in advanced lithography.⁷ This is because the grafting technique itself incorporates chemical amplification, in which a single created radical on the substrate initiates a chain of reactions. The dependence of thickness on dose seen in Figure 2 should be due to an increase in grafting density with dose as the length of the grafted chains should depend on the polymerization conditions and be the same for all the exposure doses. Since thickness variation with grafting density is a signature of the brush regime,⁸ we conclude that the films were in the brush form for the whole range where the thickness measurements were made. The saturation of the grafting thickness at high doses may be due the attainment of the maximum possible grafting density, after which creation of additional radicals does not lead to creation of additional grafted chains. The grafting conditions that gave a height of about 100 nm were chosen for application in our first nanoscale patterning experiments.

AFM images of a sample, which was irradiated with different X-ray interference patterns and then grafted with 5% acrylic acid for 15 min. at 50 °C, are shown in Figure 3. Large area structuring in the form of dots, holes, or line patterns was achieved with periods down to 200 nm. The observed roughness in the grafted areas may be due to a number of reasons including statistical variations in the radical density or particular conformations of the grafted polymer chains. Remarkably, the resolution obtained in these first experiments is comparable to that of other well-developed polymer-based lithography processes.

Using e-beam structuring we demonstrated the ability to create arbitrary polymeric structures in the micrometer range. Due to the

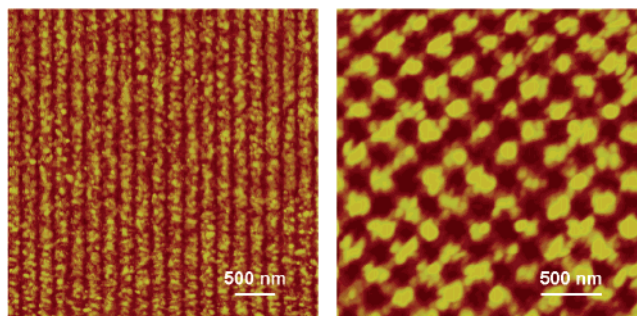


Figure 3. AFM image of periodic structures of poly(acrylic acid) grafted onto ETFE substrates irradiated with X-ray interference patterns. The total image contrast represents a height scale of 50 nm.

sequential writing of patterns, this method is slow compared to X-ray interference-based patterning. The latter technique allows us to generate large area periodic structures with resolution on the hundred nanometer scale. It should be possible to further improve the resolution by optimization of the sample irradiation and grafting conditions. For example, we intend to use living polymerization, which should allow us to more easily control thickness, reduce roughness of the grafted features, and graft block copolymers. In addition, the use of other substrate/monomer pairs and UV irradiation sources in projection or proximity imaging techniques will be explored. We also plan to use more penetrating irradiation in order to create micro- and nanopatterned membranes that are modified throughout their thickness.

Micro- and nanolithography techniques using various forms of radiation and polymer-based photoresist materials are behind the tremendous achievements in the semiconductor industry, and their applications are quickly spreading to other areas. The ability to graft polymer films with submicron scale resolution using these well-established exposure techniques introduces a new way of forming patterned materials with potential advantages.

Supporting Information Available: Experimental details and characterization of grafted surfaces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Chapiró, A. In *Radiation Chemistry of Polymeric Systems*; Mark, H., Marvel, C. S., Melville, H. W., Eds.; High Polymers Vol. XV; Interscience: London, 1962.
- (2) (a) Bhattacharya *Prog. Polym. Sci.* **2000**, *25*, 371. (b) Clough, R. L. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2001**, *185*, 8.
- (3) (a) Kawai, T.; Saito, K.; Lee, W. J. *Chromatogr. B* **2003**, *790*, 131. (b) Huslage, J.; Rager, T.; Schnyder, B.; Tsukada, A. *Electrochim. Acta* **2002**, *48*, 247. (c) Yang, B.; Yang, W. J. *Macromol. Sci., Pure Appl. Chem.* **2003**, *A40* (3), 309. (d) Xing, C.-M.; Deng, J.-P.; Yang, W.-T. *Polym. J.* **2003**, *35* (8), 613. (e) Taniguchi, M.; Pieracci, J.; Samsonoff, W. A.; Belfort, G. *Chem. Mater.* **2003**, *15*, 3805.
- (4) (a) Currie, E. P. K.; Norde, W.; Stuart, M. A. C. *Adv. Collect. Int. Sci.* **2003**, *100–102*, 205. (b) Netz, R. R.; Andelman, D. *Phys. Rep.-Rev. Sect. Phys. Lett.* **2003**, *380*, 1. (c) Freemantle M. *Chem. Eng. News* **2003**, *April 14*, 41. (e) Gutowski, W. S. *J. Adhes.* **2003**, *79*, 445.
- (5) (a) Schmelmer, U.; Jordan, R.; Geyer, W.; Eck, W.; Götzhäuser, A.; Grunze, M.; Ulman, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 559. (b) Henderson, C. L.; Barstow, S.; Jeyakumar, A.; McCoy, K.; Hess, D. W.; Tolbert, L. M. *Mater. Res. Soc. Symp. Proc.* **2002**, *705*, 3.
- (6) Solak, H.; David, C.; Gobrecht, J.; Golovkina, V.; Cerrina, F.; Kim, S. O.; Nealey P. F. *Microelectron. Eng.* **2003**, *67–68*, 56–62.
- (7) He, D.; Solak, H. H.; Li, W.; Cerrina, F. *J. Vac. Sci. Technol. B* **1999**, *17*, 3379.
- (8) Wu, T.; Efimenko, K.; Vlcek, P.; Subr, V.; Genzer, J. *Macromolecules* **2003**, *36*, 2448–2453.

JA0379870