intended to produce $Rb_3Li_{10}Ge_{23}$, the Li/Ge analogue of the known $A_3Na_{10}Sn_{23}$ (A = K, Rb, Cs).[8] After the structure and the exact stoichiometry of the compound were determined from single-crystal X-ray diffraction data, $RbLi_7Ge_8$ was synthesized from the corresponding stoichiometric mixture of elements by heating at 1000 °C for 4 h and then cooling down to room temperature at a rate of 20 °C h^{-1}. All reactions were carried out in tubular niobium containers that were sealed at the two ends by arc-welding. These containers are then placed in fused-silica ampoules, and the latter are evacuated (below discharge) and sealed. Attempts to synthesize the corresponding K and Cs analogues have been unsuccessful so far. Nevertheless, these reactions yielded K_3LiGe_4 (*Pnma*, $a = 7.758(9)$, $b = 9.931(8)$, $c = 12.400(9)$ Å) and Cs_3LiGe_4 (*Cmcm* $a = 6.944(4)$, $b = 15.510(8)$, $c = 9.88(1)$ Å) isostructural with the known K_3LiSi_4 and Cs_3LiSi_4,[14] respectively. However, both reactions yielded traces of other, yet unidentified phases, and currently under way is a search for optimal compositions and reaction conditions.

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[16] Structure determination: Crystals selected from the initial reaction were sealed in capillaries and checked for singularity. For the best one (barlike shape, $0.12 \times 0.10 \times 0.08$ mm) a hemisphere of data was collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, ω-2θ scans, $2\theta_{max} = 60°$, RT). The data were corrected for absorption with the aid of the average of 3 Ψ scans at different θ angles. The structure was solved by direct methods and refined on F^2 with the SHELXTL-V5.1 software package. Crystal data: hexagonal, $P6_3mc$ (no. 186), $a = 9.8946(7)$, $c = 16.269(3)$ Å; $V = 1379.4(3)$ Å^3; $Z = 4$; $\mu = 206.34$ cm^{-1}; $\rho_{calcd} = 3.442$ g cm^{-3}. The refinement of all but two lithium atoms with anisotropic thermal parameters converged to $R1/wR2$ ($I > 2\sigma(I)$) = 0.0362/0.0755 and $R1/wR2$ (all data) = 0.0491/0.0804 for 1270 independent reflections (4475 total number of reflections) and 62 variables. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411606.

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[18] Magnetic measurements: The magnetization of 14 mg of selected crystals of $RbLi_7Ge_8$ was measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T over the temperature range 10–280 K. The data were corrected for the holder and for ion-core diamagnetism. The susceptibility is negative and temperature independent in the range $-(1.63-1.82) \times 10^{-4}$ emu mol^{-1}. This is consistent with a diamagnetic compound.

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[20] Similar truncated tetrahedra made of aluminum and capped by magnesium may exist in the metallic alloy "$Mg_{17}Al_{12}$" (powder diffraction work: P. Schobinger-Papamantellos, P. Fischer, *Naturwissenschaften* **1970**, *57*, 128). Nevertheless, this can not be established unequivocally by powder diffraction for two elements that differ by one electron only.

[21] This "violation" for the tetracapped truncated tetrahedron is very similar to that observed for the simple tetrahedron which also due to the T_d symmetry requires $2n+4$ electrons.

Controlled Synthesis of Cross-Linked Ultrathin Polymer Films by Using Surface-Initiated Atom Transfer Radical Polymerization**

Wenxi Huang, Gregory L. Baker,* and Merlin L. Bruening*

Covalent attachment of polymer chains to solid substrates by surface-initiated polymerization is an effective method for tailoring surface properties such as wetting, adhesion, and biocompatibility. Following Rühe and Prucker's successful work on free radical polymerization from surfaces,[1a] several research groups recently reported the use of controlled/living polymerization techniques[1b–h] to grow polymer chains from a surface in a well-defined manner. Several research groups also used surface-initiated polymerizations to generate patterned polymers on surfaces for lithographic applications.[1c,e, 2, 3] The grafted polymer layers have higher resistance to wet chemical etchants than the patterned monolayers from which they are grown.

Cross-linked polymer films, compared to linear polymer brush analogues, should yield even better mechanical and chemical stability and provide new pathways to functionalized surfaces for molecular recognition. However, the preparation of cross-linked thin films is an experimental challenge. Direct polymerization of cross-linkable monomers in solution usually results in an insoluble three-dimensional polymeric gel that cannot be deposited as a uniform thin coating. Cross-linked films can be prepared by deposition of a cross-linkable polymer precursor followed by a cross-linking reaction; however, the method is not straightforward and it usually is difficult to control film thickness and the curing reaction. Herein we report direct polymerization of ethylene glycol dimethacrylate (EGDMA) from a surface to form cross-linked polymer films (Figure 1).

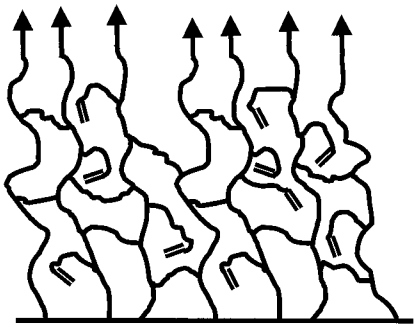

Figure 1. Schematic illustration of a cross-linked film growing from a gold substrate.

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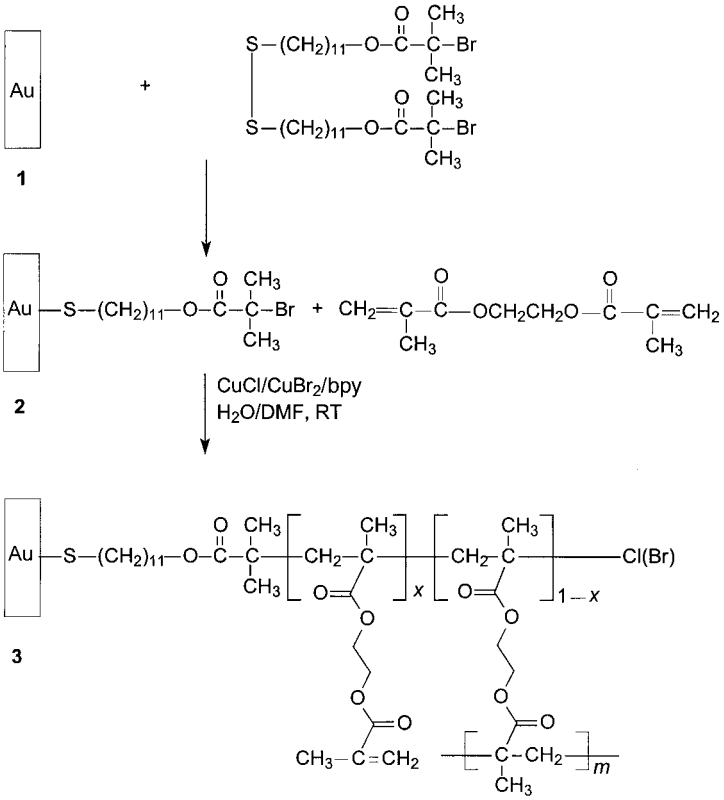
Preparation of a well-defined cross-linked thin film by polymerization from a surface requires that there be minimal parallel formation of polymer in solution. Side reactions that cause formation of polymer in solution will result in gelation, or in the case of polymers insoluble in the polymerization medium, cross-linked polymer will precipitate onto the substrate, creating a heterogeneous film. Low-temperature polymerization is essential to insure that thermal autopolymerization will be negligible. Low-temperature processes are also compatible with substrates such as Au-thiolates that are unstable at elevated temperatures.[4]

Scheme 1 outlines the synthetic pathway we used to prepare cross-linked, ultrathin polymer films on gold surfaces by surface-initiated atom transfer radical polymerization (ATRP). Immersion of gold-coated wafers in a 1 mM ethanolic solution of the disufide initiator for 24 h led to the formation of substrate **2**. The ellipsometric thickness of the initiator monolayer (1.8 ± 0.1 nm) and the appearance of a carbonyl peak at 1739 cm^{-1} in the reflectance FTIR spectrum of the film (Figure 2, spectrum a) confirmed monolayer formation. For surface grafting polymerization, we immersed the substrate in an EGDMA/water/dimethylformamide (DMF) mixture containing the CuCl/2,2′-bipyridine (bpy) catalyst. Addition of water is necessary for rapid ATRP at room temperature. Armes et al. recently showed that water accelerates ATRP, probably because it changes the nature of the active catalyst.[5] To extend this interesting scheme to water-immiscible, hydrophobic monomers, we added DMF to afford a homogeneous solution.



Scheme 1. Synthetic outline for the preparation of cross-linked, ultrathin poly(EGDMA) (PEGDMA) films on gold surfaces.

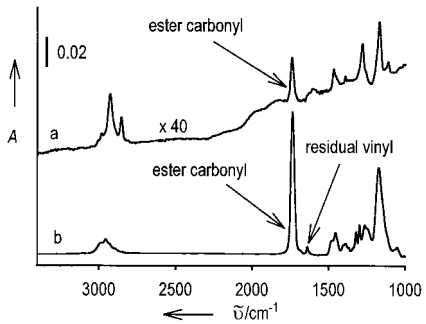


Figure 2. Reflectance FTIR spectra of a) an initiator monolayer, and b) a grafted PEGDMA layer (50 nm thick). A = absorbance.

The presence of a deactivating Cu^{II} complex in solution is necessary for control of ATRP. In solution ATRP, reaction of Cu^{I} with initiator produces the Cu^{II} complex. Because of the small amount of initiator at a substrate, however, the concentration of the deactivating Cu^{II} complex is too low to control polymerization from a surface. To overcome this problem, several research groups added free initiator to the polymerization solution.[2g,h, 3] When we employed this procedure to synthesize cross-linked films by using ethyl 2-bromoisobutyrate (0.01M) as a free initiator in solution, polymerization in solution resulted in an insoluble gel in 30 min. The gel could not be redissolved in any solvent. This experiment clearly demonstrates the need to restrict polymerization to the surface in the preparation of homogeneous, cross-linked films.

To ensure a sufficient concentration of deactivating Cu^{II} species in the solution, we added 30 mol% of $CuBr_2$ (with respect to CuCl) to the solution.[6] The use of mixed-halide initiation systems also allows better control of ATRP.[7] No gelation of the solution or precipitation of polymer was observed during film growth, indicating minimal polymerization in solution.[8] After completion of the polymerization, the substrate was cleaned by sonication in DMF for 20 min, and dried under a flow of nitrogen. A large increase in the carbonyl peak at 1736 cm^{-1} in the reflectance FTIR spectrum (Figure 2, spectrum b) confirmed the formation of the polymer layer. In addition, a peak at 1639 cm^{-1} (C=C stretching) indicates some unpolymerized EGDMA vinyl groups in the film. Residual monomer is unlikely because the film is ultrathin and was carefully cleaned with DMF. Surface Raman spectroscopy showed the presence of carbonyl and C=C bond peaks at 1730 and 1640 cm^{-1}, respectively. The combination of reflectance FTIR and Raman spectroscopy demonstrated the successful growth of the poly(EGDMA)(PEGDMA) layer.

To demonstrate the "living" character of surface-initiated ATRP, we used a 60-nm PEGDMA-coated wafer as a macroinitiator in a fresh EGDMA/catalyst solution. Ellipsometry measurements showed an increase in film thickness to 300 nm after an additional reaction time of 60 h. A large increase in the carbonyl peak in the reflectance FTIR spectrum also confirmed extension of the polymer layer.

Ellipsometric measurements reveal that the cross-linked films are very uniform. The variation in thickness for a 200-nm

thick polymer film over a $1.3 \times 2.5\ cm^2$ sample was as low as 1 nm. Atomic force microscopy (AFM) images showed that this film was also microscopically homogeneous (RMS roughness of 2 nm). As the polymer chains cross-link to neighboring chains during propagation, surface reorganization after polymerization is unlikely, and the uniformity of the film suggests the polymerization is homogeneous throughout the sample.

Figure 3 shows the thickness of PEGDMA films and the absorbance ratio for the C=C ($1639\ cm^{-1}$) and C=O ($1736\ cm^{-1}$) stretches as a function of polymerization time. We observed a linear increase in thickness with time, consistent

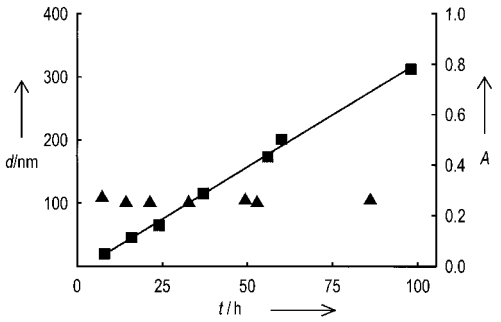


Figure 3. Time-dependence of the thicknesses (d) of grafted PEGDMA films (squares) and the integrated absorbances A (triangles) of the residual vinyl peak ($1639\ cm^{-1}$) in reflectance FTIR spectra of grafted PEGDMA layers. The absorbance of the vinyl peaks was normalized to the carbonyl peak at $1736\ cm^{-1}$.

with controlled chain growth from the surface with some degree of "living" character. We can obtain predictable film thickness up to 300 nm. The constant C=C/C=O ratio during polymerization further suggests that the polymer film is homogeneous. By comparing the normalized IR absorbance of vinyl groups in PEGDMA films with that of the monomer, we estimate that 25 % of the vinyl groups remain unpolymerized in films. This suggests that coatings are about 50 % cross-linked.

The results of swelling experiments are consistent with highly cross-linked PEGDMA films. In situ ellipsometry showed that a 220-nm thick PEGDMA film increased in thickness to 280 nm when swollen in THF, while a 140-nm thick poly(methyl methacrylate) (PMMA) brush increased to 340 nm under identical conditions. The films were cycled between the swollen and dried state two times with no apparent difference in thickness values. The minimal swelling of the PEGDMA film relative to the control PMMA film is presumably due to the highly cross-linked polymer network.

In conclusion, ambient temperature ATRP in water-containing solutions enables the controlled synthesis of cross-linked PEGDMA films from gold surfaces. The product polymer films are uniform over large areas, presumably because polymerization is limited to the surface, and minimal polymer is formed in solution. This feature is crucial for avoiding physisorption of cross-linked polymers. Both swelling experiments and FTIR spectroscopy indicate that the PEGDMA films are highly cross-linked, and the "living" character of ATRP allows the growth of an additional polymer layer. The use of low polymerization temperatures and aqueous media is compatible with various substrates and should allow engineering of a variety of surfaces.

Experimental Section

EGDMA was passed through a basic alumina column, and distilled under reduced pressure before polymerizations. Gold-coated wafers (sputter coating of 200 nm of Au on 20 nm of Cr on Si(100) wafers) were cleaned in a UV/O_3 chamber for 15 min before use. Ellipsometric measurements of dried films were obtained with a rotating analyzer ellipsometer (model M-44, J. A. Woollam) at a 75° angle of incidence. Ellipsometric swelling experiments were carried out with a computer-controlled null ellipsometer (Rudolph Auto-EL II) with a He–Ne laser (632.8 nm) light source and a 70.0° angle of incidence. In situ measurements were made with a specially built trapezoidal cell containing glass windows fixed at an angle of 20.0° from the surface normal. Thickness measurements were made before and after filling the cell with purified THF. Refractive index and thickness values for all the films were calculated simultaneously from the experimental Ψ and Δ values (n values for swollen films were 1.43 (PMMA) and 1.49 (PEGDMA)). Reflectance FTIR spectroscopy was performed using a Nicolet Magna-IR 560 spectrometer containing a PIKE grazing angle (80°) attachment. AFM images were obtained in the tapping mode with a Nanoscope IIIa instrument (Digital Instruments).

The disulfide initiator ($BrC(CH_3)_2COO(CH_2)_{11}S)_2$ (Scheme 1) was synthesized according to a literature procedure.[3]

Polymerizations: To a solution of degassed monomer (42 mL; EGDMA/H_2O/DMF, 3:3:8, v:v:v), CuCl (180 mg, 1.8 mmol), $CuBr_2$ (120 mg, 0.54 mmol), and bpy (731 mg, 2.34 mmol) were added under an argon atmosphere. The solution mixture was degassed by using three freeze–pump–thaw cycles, and warmed to room temperature with continuous stirring until a homogeneous dark brown solution formed. The monomer/catalyst solution was transferred by cannula into a degassed vial containing substrate **2**, and the reactor was kept at room temperature without stirring during polymerization.

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