555d Kinetic Characterization of Surface-Initiated Controlled-Radical Photopolymerizations

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Introduction

Modifying a surface with polymeric materials of specific chemistry and well-defined architecture is a facile method for tailoring interfacial properties such as biocompatibility, wetting, corrosion resistance and lubricity. In the current work, we have used a controlled free-radical photopolymerization technique based on a dithiocarbamate photoiniferter chemistry first discovered by Otsu et al.[1] to produce surface-tethered poly(methyl methacrylate) (PMMA) layers. Surface-initiated controlled radical photopolymerizations (si-CRPPs) are advantageous because they enable spatial and temporal control over polymerization by controlling the location, intensity and duration of light exposure. Hence, si-CRPPs can readily be used for micropatterning surfaces with polymer chains of defined molecular weights and thicknesses.

To synthesize well-defined polymer layers using si-CRPP, it is essential to understand its kinetics. In this study, kinetics of film growth were followed by measuring layer thickness as a function of reaction time, monomer concentration and light intensity using variable angle ellipsometry. Kinetic models were developed to predict the effect of various parameters on the growth of PMMA layers.

Experimental

A derivatized photoiniferter, N,N-(diethylaminodithiocarbamoylbenzyl-(trimethoxy)silane) (SBDC) was synthesized by coupling sodium diethyldithiocarbamate (Fluka) and p-chloromethylphenyltrimethoxysilane (Gelest Inc.). A self-assembled monolayer (SAM) of SBDC was deposited on a piranha-treated silicon wafer by standard protocols. Methyl methacrylate (MMA; Aldrich) was used in these studies and was distilled from CaH_2 prior to use. A solution of MMA in anhydrous toluene (Aldrich) was prepared in a Schlenk flask and degassed with four freeze-pump-thaw cycles. The solution was then transferred to a reaction vessel containing photoiniferter-modified silicon wafers. The reaction vessel was covered with a glass plate and sealed. The assembly of the reaction cell and transfer of degassed monomer solution were all carried out in a glove box where the oxygen level was kept below 1 ppm. The reaction cell was then exposed to collimated 365 nm light (EXFO 100W Acticure Ultraviolet/Visible Spot-Curing System with 365 nm bandpass filter) at fixed intensities.

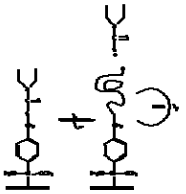
After polymerization, silicon wafers were taken out of the reaction vessel, sonicated for 30-45 minutes and dried with a stream of dry nitrogen. The dry layer thicknesses of the polymer layers were measured by variable angle ellipsometry. The polymer layers were also characterized by transmission-Fourier transform infrared spectroscopy and contact angle goniometry.

Results and Discussion

Kinetic Analysis of Polymer Layer Growth

Photoiniferter-mediated photopolymerization (**Scheme 1**) is often described as a “living” radical polymerization.[1] Upon irradiation with ultra-violet light, surface-tethered photoiniferter molecules yield one stable thiol radical and one highly reactive carbon radical. In the presence of monomer, the carbon radical initiates polymerization while the more stable thiol radical acts as a transfer or deactivating agent by reversibly reacting with propagating polymer chains. This chemistry allows one to achieve a photoinitiated “living” radical polymerization that propagates from the substrate surface in a controlled manner.

For a living-radical polymerization, irreversible termination reactions are absent so that the concentration of free radicals remains constant during the course of polymerization. In the case of a surface-initiated polymerization, the polymer chains adopt an upright and stretched configuration due to high grafting densities. Therefore, the rate of polymerization is proportional to the change in polymer layer thickness Additionally, the concentration of monomer remains constant because of low monomer conversion, which can be attributed to the fact that a very low number ($<10^{15}/cm^2$) of initiator molecules are present on the surface to initiate polymerization. Therefore, the absence of termination reactions should produce a linear increase in the thickness of the grafted polymer layer with time.



Scheme 1. Schematic of Surface-Initiated Controlled-Radical Photopolymerization (si-CRPP).

Figure 1 shows how the measured dry layer thicknesses of grafted PMMA layers vary with polymerization time for three different monomer concentrations. Arrows indicate the mushroom-to-brush transition of grafted PMMA layers. Also seen in **Figure 1**, the growth of the PMMA layer in the brush regime is nonlinear with exposure time indicating that si-CRPP of MMA under the described conditions does not proceed *via* a living free radical polymerization mechanism. These non-living characteristics arise due to the loss of radicals by various termination reactions that occur in the absence of a sufficient concentration of persistent deactivating radicals. Possible termination reactions that lead to the permanent loss of radicals include a) bimolecular termination and b) chain transfer to monomer.

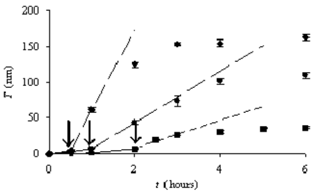


Figure 1. Dry poly(methyl methacrylate) layer thickness as a function of exposure time at a light intensity of $5mW/cm^2$. Methyl methacrylate concentrations in toluene were (■) 12.5, (●) 25, and (♦) 50% v/v.

Kinetic Analysis of Termination Mechanisms.

Figure 2 compares the PMMA thickness data with predictions of a bimolecular termination model. As can be seen from this figure, the model predictions provide a reasonably good fit to all experimental data sets including those obtained at 12.5 % v/v and 25 % v/v monomer concentrations. Additionally, bimolecular termination predicts that the initial growth rate and maximum layer thickness are functions of monomer concentration. The experimental data show similar features indicating that bimolecular termination is probably the dominant termination mechanism.

Comparison of model predictions with the thickness of PMMA layers as a function of light intensity (not presented in this preprint) also supports the conclusion that bimolecular termination is the dominant termination mechanism.

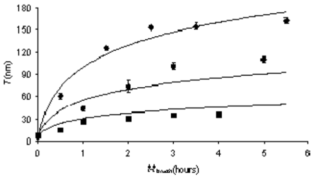


Figure 2. Comparison of the PMMA layer thicknesses measured using variable angle ellipsometry as a function of exposure time with model predictions (thin lines) for bimolecular termination. The light intensity was 5 mW/cm^2 and methyl methacrylate concentrations in toluene were (■)12.5, (●)25, and (♦)50% v/v.

Enhanced Control over Polymerization Mechanism

To control PMMA layer growth and minimize bimolecular termination, tetraethylthiuram disulfide (TED) was added to the polymerization solution as a source of stable, deactivating dithiocarbamyl radicals. The TED concentration affects both the initial and overall growth rate of surface-initiated PMMA layers as seen in **Figure 3**. The data show a slow initial increase in layer thickness followed by a rapid increase after the "mushroom-to-brush" transition (shown by the arrow) which occurs at approximately 0.5 hours for all TED concentrations.

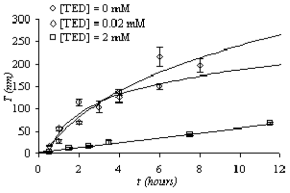


Figure 3. Dry PMMA layer thicknesses at TED concentrations of (a) 0 mM, (b) 0.02 mM and (c) 2 mM. The thin lines show the trends followed by the data. The data show that addition of TED enables "controlled" radical polymerization.

As seen in **Figure 3,** when no TED is added to the polymerization solution the thickness of the PMMA layer increases rapidly once it enters the brush regime followed by a sharp decline in the growth rate, indicating existence of bimolecular termination reactions. The initial growth rate decreases as [*TED*] is increased. Moreover, at the TED concentration of 0.02 mM, the thickness of PMMA layer exceeds the thickness for the case when TED was not added to polymerization solution which suggests that better "control" over SI-PMP is achieved by preaddition of TED. Finally, at the TED concentration of 2 mM, linear growth of the PMMA layer is observed over the entire 12 hours of polymerization indicating that a sufficient concentration of persistent deactivating radicals is present to maintain the reversible equilibrium between surface-tethered carbon radicals and dithiocarbamyl radicals. As a result, bimolecular termination reactions that reduce the concentration of surface-tethered radicals and lead to a limiting film thickness are suppressed. Conclusions

Poly(methyl methacrylate) layers were successfully synthesized on silicon substrates using surface-initiated photoiniferter-mediated photopolymerization. The initial rate of PMMA layer growth was observed to have first-order dependence on monomer concentration. The nonlinear growth of the PMMA layer with the exposure time indicated that irreversible termination reactions were present in the system, leading to the loss of active free radicals. Therefore, it was concluded that the photoiniferter-mediated surface-initiated photopolymerization was “pseudo-living”. It was hypothesized that irreversible termination of surface-tethered radicals occurred due to insufficient concentration of deactivating species (dithiocarbamyl radicals) at the surface. Application of a kinetic model indicated that bimolecular termination is the dominant termination mechanism for the range of reaction conditions investigated in this study.

To improve the “control” over SI-PMP of MMA, tetraethylthiuram disulfide was added to the polymerization solution. The experimental data and simulations of PMMA layer growth as a function of TED concentration suggest that preaddition of TED, which acts as a source of deactivating radicals enables “controlled” synthesis of PMMA brushes by si-CRPP.

References

(1) Otsu, T.; Yoshida, M.; Tazaki, T. *Macromol. Chem. Rapid Commun.* , 3, 127-132.