Surface-Catalyzed Growth of Polymethylene-Rich Copolymer Films on Gold

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Abstract: We report the preparation of a new class of copolymer films that consist of polymethylene (PM) with a low percentage (~1−4%) of randomly distributed ethyl ester side groups, consistent with poly-(methylene-*co*-ethyl acetate). The films are prepared through a surface-catalyzed polymerization on gold surfaces upon exposure to a dilute solution of diazomethane (DM) and ethyl diazoacetate (EDA) in ether at 0 °C. While EDA alone does not polymerize at gold surfaces but DM does decompose on gold to grow PM films, the combined presence of EDA and DM results in dramatic enhancements in film growth and promotes an alternative mechanism for propagation as compared with that for the PM homopolymerization. The rate of copolymer film growth is constant over a ~24 h period, consistent with a controlled polymerization in which chain terminations are minimized. Carefully controlled experiments indicate that chain propagation does not occur at the outer film−solvent interface, but more likely, at the film−metal interface, suggesting a catalyzed insertion mechanism that extends the chain and pushes the outer chain termini further away from the metal−polymer interface. The results also suggest that adsorbed intermediates of EDA function as co-catalysts to promote the propagation reaction. Of particular importance for materials modification is that the ester side chains of these copolymer films can be hydrolyzed to carboxylate groups that exhibit pH-dependent wettability.

Introduction

While polyethylene is produced abundantly and has many desirable properties, its use in thin films and coatings for advanced materials processing has been limited by its poor solubility,[1] which precludes spin coating and solution casting the polymer into films and its chemical stability, which creates challenges in surface functionalization.[2] The former problem could be greatly alleviated by recent solution-phase methods to grow polymethylene (PM) from metal surfaces[3−7] based on decomposition of diazomethane (DM) and subsequent polymerization. Allara, Tao, and co-workers demonstrated that mere exposure of gold to an ether solution of DM results in the spontaneous growth of PM films with thicknesses of up to 100 nm.[3] Our group has shown that atomic-level modification of gold surfaces with copper and silver layers greatly affects the kinetics of PM film growth.[6,7] The presence of copper dramatically enhances the polymerization and produces a linear growth of the film with time, whereas a dense monolayer of silver completely prevents polymerization.[6] We have used this re-markable surface selectivity to direct the growth of highly insulating PM films by first patterning copper and silver monolayers at discrete regions on a gold surface.[7] This prior work demonstrates that the surface-catalyzed growth of PM films is highly sensitive to the atomic-level details of the metal surface and that controlled growth can be achieved by appropriate engineering of surface composition.

Although the chemical inertness of PM is useful in many processes, it prevents straightforward functionalization, which could promote interactions with other materials and expand the applications of these surface-catalyzed films. Common methods to modify the surfaces of PM or PE include bromination[8] or oxygenation[9] with UV irradiation or treatment with strong acids[2] or oxygen plasma,[10] each of these occurring under harsh conditions that may be incompatible with other materials present on a particular surface. Synthetic methods, such as polyhomologation, have been pioneered by Shea and co-workers[11−16] to create uniquely end-functionalized PM, but this remarkable

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(a) CH_2N_2

(b) $N_2=CH-\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}-O-CH_2CH_3$

(c) $\left[CH_2\right]_A\left[\underset{\underset{\displaystyle O}{\displaystyle \|}}{\overset{\displaystyle CH}{\underset{\displaystyle C-O-CH_2CH_3}{|}}}\right]_B$
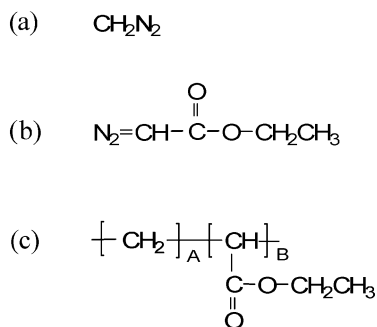
Figure 1. Chemical structures of (a) DM and (b) EDA. Structure (c) represents the likely polymer formed when gold is exposed to a solution of DM and EDA.

chemistry has not been extended into thin film processing. In general, well-controlled methods for preparing PM films with functionalized side chains could be useful in interfacing these cost-efficient and widely utilized materials with other components or in tuning their physical properties.

Here, we report a new approach to create functionalized PM thin films. We simply expose gold substrates to an ether solution containing both DM and ethyl diazoacetate (EDA) to produce a copolymer film containing PM segments with randomly distributed ethyl ester side groups (Figure 1). We demonstrate that these ester side groups can be hydrolyzed to produce pH-responsive carboxylic acid groups that are potentially useful for further film modification. We have varied the compositional ratio of DM to EDA to effect film composition and growth rates, as determined by reflectance absorption infrared spectroscopy (RAIRS) and spectroscopic ellipsometry, respectively. We have also used ellipsometry and RAIRS to characterize the kinetics of film growth and to track the film composition during growth. We have combined these tools with surface-sensitive wetting measurements to gain a greater understanding of the nature of copolymer film propagation. In particular, our results provide information on the location of the propagation site and on distinct mechanistic pathways for PM homopolymerization versus copolymerization.

Cationic,[17,18] free-radical,[3,19] and insertion[18,20] mechanisms have been proposed to describe the decomposition of DM to form PM in the presence of various catalysts. Seshadri et al. proposed a free-radical mechanism to describe the heterogeneous propagation of PM on gold from ethereal DM solutions.[3] Early results on homogeneous PM formation in the presence of a BF$_3$ catalyst have led researchers to propose an insertion mechanism where methylene adsorbs to the boron center and inserts into a B−halide or B−alkyl bond to increase the polymethylene chain length by one unit.[20] A similar insertion mechanism has been confirmed by Shea and co-workers[11] for the preparation of end-functionalized polymethylene using dimethylsulfoxonium methylide, a methylene-producing precursor similar to DM, in the presence of alkyl boranes. An insertion mechanism has also been proposed for the photochemical polymerization of DM on

hydrogen-terminated silicon[21] and for the propagation of alkyl chains on copper using methylene iodide at low pressures.[22] These insertion routes allow for the continual creation of carbon−carbon bonds at an appropriate catalytic surface and may enable the controlled preparation of polymer films with novel compositions.

This paper reports a unique type of polymerization and heterogeneous catalysis at evaporated gold surfaces to produce a new class of polymer films. We exploit the combination of two precursors in the polymerization to glean mechanistic insight into the catalyzed mechanism that is often not possible for homopolymerizations. The surface-initiated nature of this polymerization minimizes steric effects to enable nanometer-scale control over film thickness, is compatible with bottom-up processing to enable the directed growth of the films, and could be extended in a straightforward manner to surfaces of various geometries.

Experimental Section

Materials. Potassium hydroxide, hydroquinone, 4-*tert*-butylcatechol, Diazald (*N*-methyl-*N*-nitroso-*P*-toluenesulfonamide), ethyl diazoacetate (EDA), and poly(ethylene-*co*-ethyl acrylate) (PEEA) were used as received from Aldrich (Milwaukee, WI). Ethyl ether was obtained from EMD Chemicals (Gibbstown, NJ). Benzoic acid, toluene (HPLC grade), benzylamine, acetone, and isooctane (HPLC grade) were used as received from Fisher (Fair Lawn, NJ). Hydrochloric acid and sodium hydroxide were used as received from EM Science (Gibbstown, NJ). Styrene and isobutyl vinyl ether were used as received from Acros (Fair Lawn, NJ). Gold shot (99.99%) and chromium-coated tungsten filaments were obtained from J&J Materials (Neptune City, NJ) and R. D. Mathis (Signal Hill, CA), respectively. Silicon (100) wafers (Montco Silicon; Spring City, PA) were rinsed with ethanol and deionized water and dried with nitrogen. Ethanol (absolute) was used as received from AAPER (Shelbyville, KY). Nitrogen gas was obtained from J&M Cylinder Gas, Inc. (Decatur, AL). Deionized water (16.7 MΩ·cm) was purified with a Modu-Pure system (Continental Water Systems Corporation; San Antonio, TX) and used for rinsing.

Preparation of Gold Substrates. Gold substrates were prepared by evaporating chromium (100 Å) and gold (1250 Å) in sequence onto silicon (100) wafers at rates of 1−2 Å s^{-1} in a diffusion-pumped chamber with a base pressure of 4 × 10^{-6} Torr. After removal from the evaporation chamber, the wafers were typically cut into 1 × 4 cm pieces, rinsed with ethanol, and dried in a stream of N$_2$ gas.

Preparation of Diazomethane. DM was carefully prepared according to a literature procedure[23] and diluted with ether at 0 °C to prepare solutions of different concentration. CAUTION: Diazomethane is toxic and potentially explosive and should be handled carefully![23] The concentration of DM was determined by titration with benzoic acid.[24]

Preparation of Polymer Films. Polymer films were formed by exposure of gold-coated silicon substrates (ca. 4 × 1 cm) to ether solutions containing desired concentrations of DM or DM and EDA at 0 °C from a few minutes to several hours. Film growth was carried out in capped 20 mL vials, and only one substrate was placed in each vial. Upon removal, the samples were rinsed with ether, ethanol, and DI water, and dried in a stream of nitrogen.

Air Exposure and Solvent Switch Experiments. Gold-coated silicon substrates were immersed into a solution containing 4 mM DM and 40 mM EDA in ether at 0 °C for 1 h, and then removed, rinsed

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with ether, and placed into either 4 mM DM in ether, 40 mM EDA in ether, or the original solution for 8 h. After the 8 h exposure, the substrates were removed, rinsed with ether, and dried in a stream of N_2. The total time for air exposure and rinsing was ~15 s. Control samples that were exposed only to the original solution for 1 and 9 h or to the latter solution for 8 h were also prepared to compare film properties.

In a separate experiment, a gold-coated silicon substrate was placed into a solution containing 4 mM DM and 40 mM EDA in ether at 0 °C for 18 h, and then was removed, rinsed with ether, and placed into a different solution containing 1 mM DM and 80 mM EDA in ether at 0 °C for 6 h. Upon removal, the samples were rinsed with ether and dried in a stream of nitrogen. Control samples that were exposed only to the original solution for 18 h or to the latter solution for 6 h were also prepared to compare film properties.

Experiments with Additives. Hydroquinone, 4-*tert*-butylcatechol, styrene, isobutyl vinyl ether, or benzylamine was added to a solution containing 4 mM DM and 40 mM EDA in ether at 0 °C, such that the concentration of the additive was 20 mM. The gold-coated silicon substrates were then immersed into the solution for 24 h. Upon removal, the samples were rinsed with ether, ethanol, and DI water, and dried in a stream of nitrogen. Control samples were also prepared by exposing gold substrates to a solution of 4 mM DM and 40 mM EDA without additives for 24 h.

Hydrolysis. Hydrolysis of the copolymer films was carried out in a solution of 0.5 M KOH in ethanol at reflux for 4 h. The hydrolyzed samples were rinsed with ethanol and DI water and dried in a N_2 stream.

Characterization Methods. Polymer film properties were evaluated using the following methods. Reflectance absorption infrared spectroscopy (RAIRS) was performed using a Bio-Rad Excalibur FTS-3000 infrared spectrometer. The p-polarized light was incident at 80° from the surface normal. The instrument was run in single reflection mode and equipped with a Universal sampling accessory. A liquid-nitrogen-cooled, narrow-band MCT detector was used to detect reflected light. Spectral resolution was 2 cm^{-1} after triangular apodization. Each spectrum was accumulated over 1000 scans with a deuterated octadecanethiol-d_{37} self-assembled monolayer on gold as the background.

The molar ester contents of the surface-catalyzed copolymer films were determined from reflectance IR spectra using the integrated area ratios for the carbonyl stretching peak at 1735 cm^{-1} and the combined methylene stretching peaks (symmetric and asymmetric) at 2850 and 2920 cm^{-1}, respectively. The basis for the calculation of ester content was the peak area ratio obtained for a cast film of a commercially available random copolymer (poly(ethylene-*co*-ethyl acrylate) (PEEA)). The PEEA has a known 18 wt % ethyl acrylate content (2.9% (molar) ethyl ester; 97.1% $-CH_2-$) and exhibited a C=O:CH$_2$ peak area ratio of 0.26. This analysis assumes that the peak area ratio scales linearly with the molar ester content within the film.

Ellipsometry measurements were obtained on a J. A. Woollam Co. M-2000DI variable angle spectroscopic ellipsometer with WVASE32 software for modeling. Measurements at three spots per sample were taken with light incident at a 75° angle from the surface normal using wavelengths from 250 to 1000 nm. Optical constants for a bare gold substrate, cut from the same wafer as the samples to be characterized, were measured by ellipsometry and used as the baseline for all polymer film samples. Film thickness of the polymer layer on samples was determined using a Cauchy layer model. Since the copolymer films are PM-rich (ester content < 5%), we set the refractive index for the film to 1.5, consistent with the ranges measured for polyethylene.[25]

A Rame−Hart contact angle goniometer with a microliter syringe was used to measure advancing and receding contact angles on static drops of liquid on the polymer surfaces. The probe liquid consisted of deionized water in which the pH was unaltered or adjusted to pH 3 or
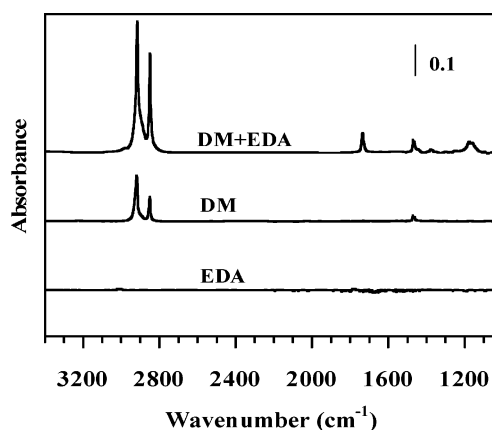

Figure 2. Reflectance absorption infrared spectra for gold surfaces after exposure to 4 mM DM, 40 mM EDA, or 4 mM DM and 40 mM EDA in ether at 0 °C for 24 h. There are several key regions of interest when evaluating the polymer film growth: C−H stretching, 2800−3000 cm^{-1}; C−H bending, 1460−1475 cm^{-1}; C=O stretching, 1730−1740 cm^{-1}; and C−O stretching 1000−1300 cm^{-1}.

11 by addition of HCl or NaOH, respectively. The needle tip of the syringe remained inside the liquid drop while measurements were taken on both sides of ~5 μL drops. All the contact angles were determined ~20 s after application of the drop. The humidity was maintained at 100% by placing the samples in a chamber saturated with deionized water. Reported values and ranges represent the averages and standard deviations of measurements obtained on at least five films prepared independently.

Results

Film Composition. To assess whether homopolymer and copolymer films could be grown from gold surfaces, we immersed gold-coated silicon substrates in solutions containing either 4 mM DM, 40 mM EDA, or 4 mM DM and 40 mM EDA in ether at 0 °C for 24 h and then obtained reflectance absorption IR spectra (Figure 2). For the gold substrate exposed to EDA, no peaks appear in the spectrum, indicating that EDA alone does not yield a polymer film on gold.[26] In contrast, gold exposed to DM results in a polymethylene (PM) film, as evidenced by the appearance of bands for CH$_2$ stretching (2800−3000 cm^{-1}) and CH$_2$ bending (1460−1475 cm^{-1}). The positions of the symmetric and asymmetric CH$_2$ stretching vibrational modes at 2851 and ~2921 cm^{-1}, respectively, suggest that the PM film is polycrystalline.[27] The absence of peaks at ~2960 and 2880 cm^{-1} indicates that the polymer does not contain a detectable amount of methyl groups ($-CH_3$), which could be introduced through branching or terminations.

When gold substrates are exposed to a mixture of DM and EDA in ether, the IR spectrum shows the additional appearance of C=O stretching at 1735 cm^{-1}, C−O stretching from 1000 to 1300 cm^{-1}, CH$_3$ bending at 1375 cm^{-1}, and CH$_3$ stretching

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(26) To verify that the absence of polymer film upon exposure to EDA is not related to solvent, other solvents, such as toluene and isooctane, were used, but no polymer was formed on the gold surface by EDA alone. However, copolymer films were formed in toluene and isooctane solvents upon exposure of gold to DM and EDA. In toluene, we obtained a film with nearly the same composition and thickness as that grown in ether, but in isooctane, the contribution of EDA toward the copolymerization is higher and the DM contribution is lower than that observed for the film grown in ether. PM films also formed on the gold surface by DM in both toluene and isooctane solvent, but no difference was observed among PM films from ether, toluene, and isooctane by IR analysis. A more detailed analysis of this solvent dependence will be discussed in a later manuscript.
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around 2960 cm^{-1}.[28] These IR results, combined with the lack of polymerization for EDA alone, are consistent with a random copolymer, similar to poly(methylene-*co*-ethyl acetate), as shown in Figure 1c. An important phenomenon observed during the copolymer growth is that the presence of EDA results in dramatically enhanced C−H absorbance bands, consistent with a much thicker film than PM. For the same DM concentration after 24 h of growth, the CH$_2$ stretching peaks of the copolymer film are nearly three times more intense than those of PM alone. This enhancement in C−H stretching cannot be accounted for based on the addition of ethyl ester side chains to the film since the C=O and C−O stretching peaks for the copolymer are very weak compared to the total C−H stretching peaks.

To estimate the molar ester content within the surface-catalyzed copolymer films, we cast a commercially available random copolymer (poly(ethylene-*co*-ethyl acrylate) (PEEA)) as a control film. The purchased PEEA has a known 18 wt % ethyl acrylate content and a chemical structure that is very similar to that of the studied copolymer. On the basis of the integrated ratio of CH$_2$ and C=O peak areas in the IR spectrum for the cast PEEA film, we have estimated that the ratio of methylene to ethyl ester units within the copolymer film of Figure 2 is ∼110:1 (molar ester content = 0.9%). The enhancement in growth, therefore, is not due to a stoichiometric complex derived from EDA and DM, but likely due to either faster or additional modes of utilizing DM in the film growth when EDA or an adsorbed intermediate is present.

Growth Kinetics. To investigate the kinetics of copolymerization, we have obtained thicknesses and IR spectra for gold substrates exposed to 4 mM DM and 40 mM EDA in ether at 0 °C for various times. On the basis of thickness measurements (Figure 3a), the copolymerization results in pronounced growth during the first ∼3 min (see inset) and a constant rate of growth thereafter for the entire 24 h. Since the rate of film growth should scale with the concentration of actively propagating chains, the initially decaying growth rate suggests a termination of polymer chains whereas the constant rate of growth over 24 h is consistent with a controlled polymerization in which the rate of chain termination is extremely slow.[29] We have previously shown that the PM homopolymer on gold exhibits a very rapid growth in the first few minutes but barely grows at all during longer exposures.[6] For comparison with the copolymer growth kinetics shown here, we also obtained thickness measurements for gold exposed to 4 mM DM in ether (not shown). While the PM thickness (∼45 nm) is similar to that of the copolymer (∼60 nm) after 1 h of film growth, the homopolymer film does not continue to show such rapid growth, exhibiting a thickness of only 97 nm after 24 h (as compared to ∼500 nm for the copolymer film). These results suggest that the initial, rapid growth shown in Figure 3a (inset) may be due to a PM homopolymerization that coexists with the copolymerization but becomes much less active at longer times.

To demonstrate the cooperation of both DM and EDA to form the copolymer, we have also plotted the time-dependence of the molar ester content (Figure 3b) as derived from IR spectra. We attribute the increase in ester content from 0.6 to 1.1% in the first 4 h to the steady growth of copolymer combined with
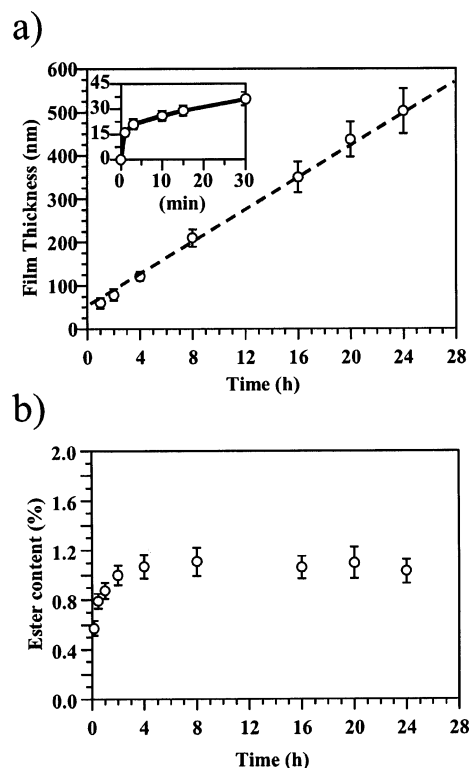
a)

b)

Figure 3. Time dependence of (a) copolymer film thickness and (b) ester content upon exposure of gold substrates to 4 mM DM and 40 mM EDA in ether at 0 °C. The inset in (a) shows the time-dependence of film thickness during the first 30 min of exposure. The data points and error bars represent the averages and standard deviations, respectively, of measurements obtained on at least three samples prepared independently. The dashed line serves as a guide to the eye.

the decay in PM homopolymer growth, consistent with the early exponential growth of film thickness shown in Figure 3a. The relatively constant ester content at long times reveals the dominance of the copolymerization and indicates that both DM and EDA (or their intermediates) continue to contribute to the copolymer growth at a constant ratio as film thickness increases. During film growth, the position of the asymmetric methylene band shifts from 2921 (1 h) to 2916 cm^{-1} (24 h), consistent with an improved chain crystallinity as film thickness is increased.[30]

Effect of Precursor Concentration. To study the effect of EDA concentration on copolymer growth, we fixed the DM concentration at 4 mM and varied EDA concentration from 10 to 80 mM. Figure 4a,b shows the film thickness and molar ester content as a function of EDA concentration after 24 h of film growth in ether at 0 °C. The case of 0 mM EDA provides a measure of the contribution of the PM homopolymer in the overall film growth (∼100 nm). The presence of EDA dramatically enhances PM growth, and the film thickness is directly proportional to the EDA concentration from 0 to 40 mM but becomes less sensitive as concentration is further increased. This linear behavior is suggestive of a first-order dependence of film growth rate on EDA concentration. The molar ester content increases sharply from 0.4 to 1.1% with EDA concentration from 10 to 20 mM but is constant from 40 to 80 mM. Therefore, the ester content in the copolymer does not scale in a general manner with the EDA to DM concentration ratio.

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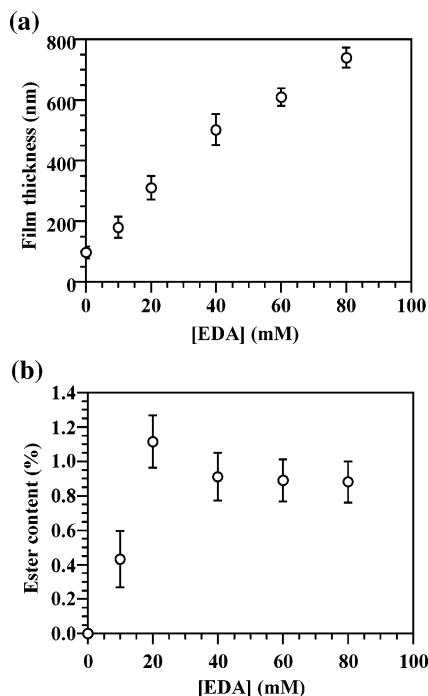
(a)

(b)

Figure 4. Effect of EDA concentration on (a) film thickness and (b) ester content. The films were prepared by placing gold-coated substrates into an ether solution at 0 °C for 24 h with DM concentration fixed at 4 mM and EDA concentration varied from 0 to 80 mM. The data points and error bars represent the averages and standard deviations, respectively, of measurements obtained on at least three samples prepared independently.

To study the effect of DM concentration on copolymer growth, we fixed the EDA concentration at 40 mM and varied DM concentration from 0 to 6 mM. Figure 5a,b shows the film thickness and the molar ester content of the copolymer film as a function of DM concentration. Consistent with Figure 2, when no DM is present, the polymerization does not occur. Film thickness increases nearly linearly with DM concentration from 0 to 2 mM, whereas the molar ester content is reduced from ~4 to ~1%, consistent with a competition between DM and EDA at the propagating site. When DM concentration is increased from 2 to 6 mM, film thickness and ester content do not respond, remaining at ~500 nm and 1%, respectively. This insensitivity in film thickness and composition at high DM concentration is consistent with surface saturation effects, where the rate-limiting step may be incorporation of an adsorbed intermediate into a propagating chain. Interestingly, for a DM concentration of 4 mM (in reference to Figure 4), an increase in EDA concentration from 40 to 60 or 80 mM would increase film thickness but would not alter the ester content. The insensitivity of film thickness to further DM addition coupled with the measurable change in film thickness upon further EDA addition suggests that an EDA-derived species can promote additional chain growth that utilizes methylene species to offset surface saturation effects. The results in Figures 4 and 5 provide clues as to the roles of DM and EDA in the copolymerization and demonstrate that, with judicious selection of DM and EDA concentrations, the ester content of the polymer can be varied from <1 to ~4%, enabling incremental control over film composition and properties.

Probing the Nature of the Copolymerization. Copolymers derived from exposure of gold surfaces to DM and EDA exhibit a strong linear growth with time after an early exponential stage,
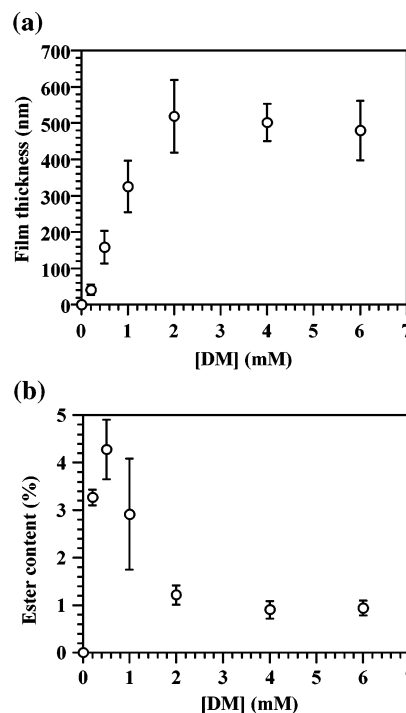
(a)

(b)

Figure 5. Effect of DM concentration on (a) film thickness and (b) ester content. The films were prepared by placing gold-coated substrates into an ether solution at 0 °C for 24 h with EDA concentration fixed at 40 mM and DM concentration varied from 0 to 6 mM. The data points and error bars represent the averages and standard deviations, respectively, of measurements obtained on at least three samples prepared independently.

suggesting that a significant concentration of chains remain active or exhibit "living" character. If the chains are truly living, then the film could be removed from solution, exposed to air, and replaced in solution without terminating chain growth. To obtain more insight into the mechanism of copolymer formation on gold, we have run carefully controlled experiments where growing chains were removed from solution and placed in other solutions. We have also spiked additives, such as quenchers, into the ethereal DM and EDA solution to investigate the effects on the growing chains and to help elucidate mechanistic aspects of chain propagation.

To test the effect of air exposure during copolymer formation, we have removed the samples from the DM and EDA solutions, rinsed them with ether, and then placed them back into the same solution for further film growth. This rinse procedure exposes the sample to air for ~15 s. We have observed that the film continues to grow after the rinsing and air exposure process. Figure 6 shows the C−H and C=O stretching regions of the IR spectra for copolymer samples exposed to 4 mM DM and 40 mM EDA in ether at 0 °C for 1 h (control), 1 h followed by rinsing and replacement in the same solution for another 8 h (denoted as 1 h + 8 h), and 9 h (control). When the spectrum for the rinsed sample is compared with those for the two controls, the results indicate that the copolymer continues to grow after the rinsing and air exposure, and that the ester content is the same as for the 9 h control. Ellipsometric measurements show that the thicknesses of the films are 62 (1 h), 206 (1 h + 8 h), and 230 (9 h) nm, which are consistent with IR intensities. In comparison with the 9 h control, the rinsed and air-exposed sample nearly achieves the same level of growth. This slight loss in thickness could be attributed to either a loss of some
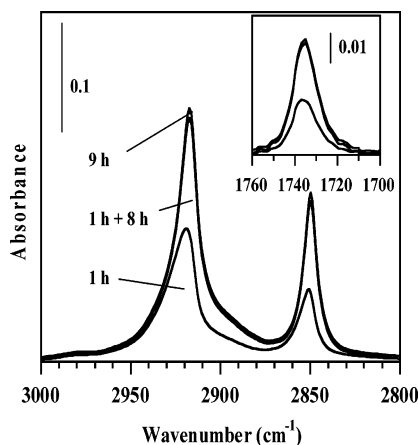
Figure 6. C−H and C=O (inset) stretching regions of IR spectra for copolymer samples exposed to 4 mM DM and 40 mM EDA solution for 1 h, 1 h followed by rinsing and replacement in the same solution for another 8 h, and 9 h. The least intense spectrum in the inset also corresponds to the 1 h control.

Figure 7. Reflectance absorption IR spectra for gold surfaces after exposure to 4 mM DM, 4 mM DM + 40 mM EDA + 20 mM BA, or 4 mM DM + 40 mM EDA in ether at 0 °C for 24 h.

active chains or a depletion of DM and EDA concentration within the film upon air exposure.

We also performed an experiment to determine the function of DM or EDA in copolymer growth. After exposure of samples to a solution containing 4 mM DM and 40 mM EDA for 1 h and subsequent rinsing, we immediately placed the samples in either 4 mM DM or 40 mM EDA solutions for another 8 h. The sample placed into the EDA solution stopped growing, while the sample placed in the DM solution grew slightly from 62 to 90 nm, although this sample was much thinner than the 9 h control (230 nm) continually exposed to 4 mM DM and 40 mM EDA. This experiment confirms that DM and EDA must both be present to propagate film growth at the normal rate observed during copolymerization.

A very important mechanistic consideration in a surface-initiated polymerization is whether the copolymer propagates from the chain ends at the metal surface or those near the film−solution interface. To address the site of propagation, we have used highly surface-sensitive contact angle measurements to determine if film surface composition is altered upon a step change in DM and EDA concentrations. As a basis for this experiment, copolymer films with different ester contents yield different water contact angles. For example, a copolymer film prepared from 1 mM DM and 80 mM EDA exhibits an ester content of 3.0% and an advancing contact angle of 90°, whereas a copolymer film prepared from 4 mM DM and 40 mM EDA exhibits a lower ester content (0.9%) and a higher contact angle 117°,[31] consistent with fewer oxygen-rich ester groups at the outer surface. To test whether the propagation site is at the outer film surface, we first placed a gold substrate into an ether solution containing 4 mM DM and 40 mM EDA for 18 h and then removed it, rinsed it with ether, and placed it into an ether solution containing 1 mM DM and 80 mM EDA for another 6 h. Comparison with a control sample exposed only to the original solution for 18 h revealed that the film grew an additional 35 nm during the latter 6 h exposure, and that the overall ester content of the film was measurably higher. However, the advancing contact angle of the film after the latter
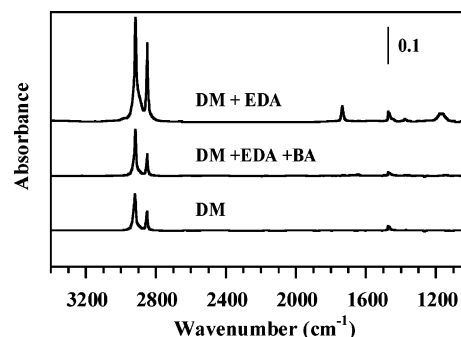
exposure was 117°, identical to that of the control film that did not undergo the latter 6 h exposure. Since water contact angles are sensitive to the outer half nanometer of film composition,[32] the latter 35 nm of film growth did not occur at the outer film−solution interface and most likely occurred at the gold−polymer interface where catalyzed intermediates are present to push the chains and film farther away from the metal surface.

To obtain additional information on the chemical nature of the active chains, we have added specific molecules that are known to either quench certain classes of propagating chains or become incorporated into the active chain. Both hydroquinone and 4-*tert*-butylcatechol are known to quench radical polymerizations,[17] but neither affected homopolymer or copolymer film growth on gold. Likewise, styrene and isobutyl vinyl ether are known to react and copolymerize with radicals and cationic chains,[33] respectively, but no inhibition of film growth was observed upon addition of these species and neither was detected in the films by RAIRS. These results suggest that the dominant mode of chain growth is not by radical or cationic propagation. However, primary amines, such as benzylamine (BA) and alkylamines, do inhibit copolymer growth. Figure 7 shows IR spectra of films formed upon exposure to 4 mM DM and 40 mM EDA (with and without 20 mM BA) or 4 mM DM. The presence of BA prevents copolymer growth, as evidenced by the weaker C−H stretching intensities and the absence of C=O stretching in the IR spectra. The ability of BA to prevent copolymerization, combined with the observation that copolymerization occurs from the metal surface, suggests an interaction between the nucleophilic amine and the propagating site at the metal surface. In contrast to the quenching behavior of BA for the copolymerization, it appears to slightly enhance PM homopolymer growth based on the ~5% increase in methylene stretching intensities as compared with those from the DM control. These results provide further evidence that two types of chain propagation routes exist: one for copolymerization and one for homopolymerization of PM.

Carboxylate Functionalization of Copolymer Films. An important advantage of the studied copolymer films is that the ester groups can be chemically modified to produce functionalized PM-rich films directly on gold. For example, the esters can be converted to carboxylate groups by hydrolysis in a basic solution. These carboxylate groups in the copolymer are

(31) For comparison, the advancing contact angle of water on the PM homopolymer is 125°. This high value is likely due to surface roughness as the contact angle hysteresis for the homopolymer is 55°.

(32) Laibinis, P. E.; Bain, C. D.; Nuzzo, R. G.; Whitesides, G. M. *J. Phys. Chem.* **1995**, *99*, 7663−7676.
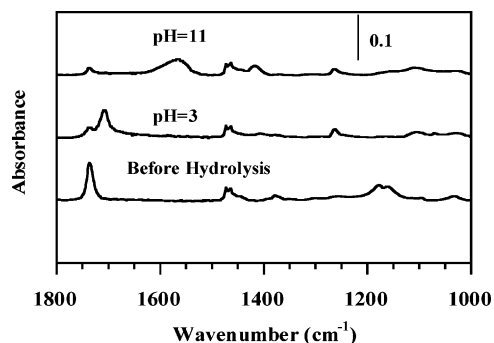(33) Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; John Wiley & Sons: New York, 1982.

Figure 8. Reflectance absorption IR spectra of copolymer films (3% ester content) before hydrolysis and after hydrolysis (4 h, 0.5 M KOH, ethanol, reflux) upon exposure to aqueous solutions at pH 3 and 11 for 30 min.

Table 1. Effect of pH on Advancing and Receding Contact Angles of Water on a 320 nm Copolymer Film (3% ester content)

		contact angle	
film state	pH	$\theta_{A,water}$	$\theta_{R,water}$
before hydrolysis	3	85 ± 2	60 ± 3
	11	85 ± 2	60 ± 4
after hydrolysis	3	84 ± 2	50 ± 3
	11	55 ± 3	33 ± 4

sensitive to pH, remaining ionized at high pH and becoming protonated at low pH, and can alter both the surface and the barrier properties of the film. Figure 8 shows the IR spectra of the copolymer before and after the hydrolysis process in a refluxed solution of 0.5 M KOH in ethanol. In this study, we have adjusted the DM:EDA concentration ratio to 0.5:80 mM to emphasize the copolymer structural changes from IR spectra. After 24 h of growth, the ester content within the copolymer film is 3.2%. During the 4 h hydrolysis, ~80% of the ester groups are converted to carboxylates.[34] For hydrolyzed films exposed to a solution at pH 11, Figure 8 (top) shows diminution of the C=O stretching peak at 1735 cm^{-1} and the CH$_3$ bending peak at ~1370 cm^{-1}, and the appearance of peaks at 1560 and 1420 cm^{-1}, which are characteristic of carboxylate ions within the polymer. If this hydrolyzed film is exposed to a pH 3 solution for 30 min, the carboxylate side groups are protonated to carboxylic acids, as evidenced by the disappearance of peaks at 1560 and 1420 cm^{-1} and by the appearance of a peak at 1710 cm^{-1} shown in Figure 8 (middle), consistent with the carbonyl stretching mode of an acid.

This reversible protonation/deprotonation of side groups also affects the surface properties of the copolymer films dramatically (Table 1). After the hydrolysis process, the advancing and receding contact angles were measured with humidity maintained at 100% by placing the samples in a chamber saturated with deionized water. Using a water drop at pH 3, the advancing water contact angle (84°) on the hydrolyzed film is nearly identical to that of the copolymer before hydrolysis (85°), but if using a drop at pH 11, the contact angle drops by ~30° due to the greater hydrophilicity of the charged carboxylate groups that are distributed along the surface. Therefore, the hydrolyzed copolymer film is sensitive to pH and exhibits strong potential for preparing surface-initiated, smart polymeric materials.

Discussion

PM Growth on Gold. Exposure of gold surfaces to DM in ether yields a PM film with a growth rate that slows with time.[6] Seshadri et al. have studied the decomposition of DM on both smooth[3] and rough[5] gold surfaces to form PM films and clusters. They used AFM to show that PM growth initiates at or near gold defect sites that likely provide enhanced stabilization for adsorbed methylidene species.[3] They postulated a free-radical mechanism to describe the growth of PM on gold.[3] In principle, a free-radical mechanism agrees with our previously reported kinetics for PM growth on gold where the growth rate slows with time,[6] consistent with chain terminations that limit the final thickness of the film. However, we have not been able to definitively prove the mechanism of chain propagation since the film growth is insensitive to the presence of various quenchers.

When the surface of gold is modified by a submonolayer of copper before exposure to DM, the kinetics of PM film growth is dramatically altered and much thicker PM films are formed, as we have recently demonstrated.[6,7] The growth rate for PM on Cu-modified gold is nearly constant with time,[6] exhibiting similar behavior as that observed for the copolymerization in this study. Another important commonality between PM homopolymer growth on Cu-modified gold and the copolymer growth on gold reported here is that primary amines quench both polymerizations. Since Cu adatoms have a partially positive charge,[35,36] we hypothesize that the nucleophilic amines adsorb and shut down propagation at these metallic sites. The altered growth in the presence of the copper monolayer illustrates the extreme sensitivity of surface charge and composition on surface-catalyzed polymerizations.

Copolymer Growth. Exposure of gold surfaces to ether containing both DM and EDA results in the growth of a copolymer film that contains a predominate methylene repeat structure with random ethyl ester side chains. The growth rate of this film, initially rapid, decays sharply in the first ~5 min and ultimately becomes constant for over many hours. These two distinct regimes of film growth suggest that two types of active chains contribute toward film growth. One chain appears to be a PM homopolymer and exhibits the characteristic decaying rate of film growth, while the other chain is largely immune to terminations and is a copolymer, containing both methylene and ester components. This two-chain model is supported by the fact that primary amines quench the copolymerization but not the homopolymerization of PM. These differences and the results described herein provide several clues regarding the mechanism of the copolymer chain growth. In the remainder of this section, we focus on the copolymerization, summarizing key results and offering interpretation as to the nature of film growth.

Chain propagation for the copolymer occurs at the metal surface and not at the solution–polymer interface. This observation implies that chain propagation is not due to common radical, cationic, or anionic growth where the active propagation site is at the outer chain terminus. Rather, the gold surface appears to catalyze carbon–carbon bond formation to push the outer chain termini further away from the metal–polymer interface, consistent with an insertion-type chain growth.[18,20–22]

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(34) The complete hydrolysis can occur but is slow and often causes damage to the film.

(35) Mishra, A. K. *J. Phys. Chem. B* **1999**, *103*, 1484–1498.
(36) Tadjeddine, A.; Guay, D.; Ladouceur, M.; Tourillon, G. *Phys. Rev. Lett.* **1991**, *66*, 2235–2238.

DM must be present to propagate the copolymerization, as no polymer was observed in the absence of DM and the copolymerization ceased when the film was transferred to a solution containing only EDA. This observation is consistent with a steric hindrance in the propagation reaction at the gold surface that prevents EDA-derived species from occupying consecutive links in the polymer chain. DM is also a more active participant in copolymer chain propagation, and a competition exists between DM and EDA at the propagating site. The more active participation of DM could be due to its enhanced reactivity[37] as compared with that of the larger and perhaps sterically hindered intermediate from EDA.

The presence of EDA with DM results in a greatly enhanced rate of overall film growth on the gold surface and produces linear increases of film thickness with time. On the basis of the growth enhancement and the low ester contents in the film, one might assume that an adsorbed intermediate of EDA functions to initiate an alternative chain growth and occasionally participates in the propagation. However, since transfer of a growing film to a solution without EDA dramatically slows polymerization, the role of EDA is far more significant than merely initiating the growth of a copolymer chain or occupying a small fraction of the film. Moreover, the presence of EDA is required to maintain the growth, even long after the polymerization has begun. The required presence of EDA suggests that the adsorbed ester intermediate has a prominent role in the propagation as a co-catalyst even though it is only a minor component in the copolymer.

Further insight into the roles of DM and EDA in the copolymerization is obtained by examining the concentration dependence of film growth shown in Figures 4 and 5. Increasing EDA concentration at constant DM results in nearly linear increases in film thickness without affecting the ester content within the film. This linear dependence of thickness on EDA concentration suggests that the growth rate of the film is directly influenced by the concentration of adsorbed ester intermediates. Also revealing is the fact that increasing DM concentration above 2 mM (at 40 mM EDA) does not affect film thickness, whereas increasing EDA concentration to 60 or 80 mM (at 4 mM DM) does indeed increase film thickness. These results imply a surface saturation of adsorbed methylene and a film growth that is limited by the propagation reaction. Thus, addition of DM in solution cannot increase the concentration of adsorbed methylene due to saturation effects so that the propagation rate remains constant. On the other hand, addition of EDA results in a higher concentration of active chains that can utilize the adsorbed methylene. These findings, combined with the requirement that EDA be present to promote the propagation, provide further evidence that an adsorbed intermediate of EDA functions as a co-catalyst in this copolymerization process.

While the exact mechanistic nature of the copolymerization, especially the initiation, is unclear at this time, we propose a candidate mechanism for chain propagation (Figure 9) that is consistent with recent literature[11,14,21] and the results obtained in this work. On the basis of other reports, we assume that both EDA[38−40] and DM[3,41,42] adsorb onto gold with loss of nitrogen to form carbene species. Once adsorbed, methylidenes may
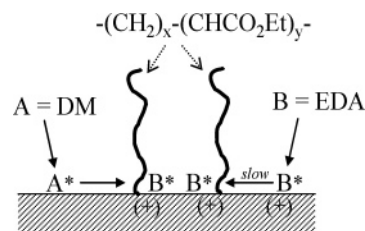

Figure 9. Proposed mechanism of copolymer growth on a gold surface. A* represents adsorbed methylene (Au=CH$_2$), and B* represents an adsorbed ethyl ester carbene (Au=CHCO$_2$Et). To grow copolymer, both types of carbenes may participate in an insertion reaction at the metal surface. The adsorbed ethyl ester carbene species pulls electron density away from the gold surface atoms toward the electronegative ester oxygens to create a partial positive charge across the metal surface and thereby alter the surface potential. These electron-deficient gold atoms may serve as the reactive center for an insertion chain growth polymerization.

collide to form a biradical species, as proposed by Seshadri et al.,[3] to initiate the growth of a PM homopolymer. To grow the copolymer, both types of carbenes may participate in a propagation reaction at the metal surface. We propose that the adsorbed ethyl ester carbene species pulls electron density away from the gold surface atoms toward the electronegative ester oxygens to create a partial positive charge across the metal surface and thereby alter the surface potential. Consistent with the behavior of copper adatoms on gold (vide supra), these electron-deficient gold atoms may serve as the reactive center for an insertion chain growth polymerization. Methylene and ethyl ester carbenes can then insert into a gold−carbon bond to propagate the chain by one unit and push the outer chain terminus away from the metal surface. Thus, we propose that two types of polymer chains exist on the surface: PM homopolymer chains, which participate in film growth early but eventually terminate, and copolymer chains that resist termination due to the controlled nature of the insertion reaction. Functioning as a co-catalyst, the ethyl ester carbene must be adsorbed on the metal surface to create a reactive center and to influence the propagation (Figure 9). The proposed mechanism is consistent with the fact that this type of polymerization cannot continue in the absence of EDA. If adsorbed ethyl ester carbenes are lost, the electron-deficient gold surface atoms revert to their neutral state and are no longer catalytic toward the insertion reaction. That this propagation is terminated upon exposure to nucleophilic amines is consistent with direct adsorption and deactivation at the electrophilic metal surface sites.

Carbenes of both EDA and DM are known to insert into metal−carbon bonds, although to our knowledge, EDA has not been used in heterogeneous catalysis. In studying homogeneous catalysis with Pt(II) complexes, Bergamini et al.[38] observed that the carbene intermediate of EDA inserts into Pt−CH$_3$ bonds through an alkyl to carbene migration and have proposed a cationic intermediate. A carbene intermediate of EDA is also known to insert into C−H bonds of alkanes, ethers, and various other hydrocarbons.[39,40] Across these studies, the metallocarbene intermediate is viewed as electrophilic, supported by its tendency to insert into electron-rich bonds. As for DM, McCrindle et al.[42]

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have shown that its addition to a solution containing a Pt complex resulted in continual insertion of methylene into the alkyl−Pt bond and have also proposed a cationic intermediate. This mechanism for homogeneous catalysis with DM is similar to that reported for the heterogeneous insertion of adsorbed methylene into Cu (100)−alkyl bonds for chain propagation in vacuum.[22]

The constant rate of copolymer film growth, as shown in Figure 3, in conjunction with propagation at the metal−polymer interface, implies that the propagation is limited by reaction rather than diffusion. If the process were limited by diffusion, the growing film would be expected to slow diffusion of DM or EDA to the metal surface, and the rate would decrease with increasing film thickness. On the basis of the growth rate of 20 nm/h from Figure 3, we have performed calculations that indicate a diffusion-limited propagation is unlikely when film thicknesses are in the submicron regime.[43] On the basis of a reaction-limited propagation from the gold surface, the constant rate of film growth further implies that the adsorbed polymer chains do not block access by adsorbed intermediates to active surface sites.

To our knowledge, the use of EDA in catalysis at gold surfaces has not been reported. In general, 2-D gold surfaces are typically thought to be poor catalysts, but a growing body of literature supports the fact that nanoscale gold particles, especially those on TiO_2 supports,[44,45] are effective catalysts for CO oxidation. Seshadri et al.,[3] who studied the decomposition of DM on 2-D gold to form PM films and clusters, have

speculated that the favorable catalytic properties of gold in this reaction stem from its relatively weak interaction with adsorbed methylene that enables facile surface diffusion. In the present work, the addition of an EDA co-catalyst appears to enhance the catalytic properties of the gold surface and promotes a unique heterogeneous polymer chemistry.

Conclusions

We have developed a novel approach to prepare ester-modified polymethylene films on gold surfaces by exposure to a solution containing DM and EDA. This methodology enables a high level of control over film properties. The film thickness can be controlled by time or by increasing EDA concentration. The molar ester content can be tuned between 0 and 5% by using appropriate solution ratios of EDA to DM, and this content is nearly constant throughout the depths of the film. Finally, the film can be further modified by hydrolysis to prepare carboxylate-modified PM that exhibits pH-responsive properties.

The results suggest that the films propagate from the metal−polymer interface, and that an adsorbed intermediate of EDA functions as a co-catalyst. The most likely mode of propagation is an insertion mechanism, in which adsorbed methylene and/or ethyl ester groups insert into a Au−C bond to push the chain away from the metal surface. That this unique film growth occurs directly from a gold surface, combined with the precise control over film properties and the ability to generate pH-responsive films by straightforward modification, implies that such an approach could be broadly applied to modify surfaces with well-defined, smart coatings.

(43) On the basis of the experimental conditions and results shown in Figure 3a (DM concentration (C) = 4 × 10^{-6} mol/cm³; growth rate (η) = 20 nm/h or 5.56 × 10^{-10} cm/s) and estimating film density (ρ) as 0.95 g/cm³ (same as that for HDPE) and diffusivity (D) of DM through the film as 1 × 10^{-8} cm²/s (based on values obtained for molecules of similar molecular weight (M) through HDPE), the film thickness (d) at which the growth becomes diffusion-limited is estimated as ∼30 μm via $d = (DC/\eta\rho)$. This analysis equates the known flux of the growing film (obtained from Figure 3a) to the diffusive flux of DM (the dominant contributor toward film growth) through the film. Since the typical film thicknesses in this study range from 100 to 500 nm (orders of magnitude below the critical thickness (d)), the film growth can be viewed as reaction-limited.
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