In-Situ Nonlinear Optical Studies of Photopolymerization of Gas Phase Acrolein onto Metallic Substrates

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ABSTRACT: The kinetics of the photopolymerization of gas phase acrolein onto gold surfaces were studied by monitoring the surface reaction dynamics and the gas phase kinetics *in-situ* and in real time. A technique based on surface second harmonic generation (SSHG), a second-order nonlinear optical process, was developed to monitor the surface second-order nonlinear susceptibility, which was related to the fraction of unreacted monomer coverage on the surface during ultraviolet (UV) irradiation. The adsorption of acrolein onto the gold surface was also monitored using SSHG. It was found that the second harmonic signal at the surface decreased as a result of adsorption of acrolein and that the adsorption was an irreversible process. Upon UV irradiation, the second harmonic signal was found to decrease immediately as a result of the decrease in the surface monomer coverage, while an induction period was observed in the gas phase by vapor pressure measurements. The surface reaction rate was found to be first-order in surface monomer concentration, one-half-order in light intensity, and independent of the gas pressure in the range of partial pressure studied (61−152 Torr). The results suggested that polymerization took place initially at the surface-adsorbed layer. The existence of a metal surface may enhance the formation of free radicals on the surface-adsorbed layer and result in the selective photopolymerization on the metal surface. After the formation of a polymer layer on the gold surface, the photopolymerization was found to take place mainly in the gas phase. The apparent rate of the gas phase polymerization was found to be first-order in the gas pressure and one-half-order in light intensity.

Introduction

"Solvent-free", gas phase photopolymerization of vinyl monomer onto metal surfaces shows potential for creating uniform, thin films with high physical integrity. Because it is a one-step process and the formation of free radicals can be spatially directed and temporally resolved by proper processing and light exposure procedures, photodeposition is useful for many applications. One promising application is the creation of surface passivation and protection, since the polymer film formed has high physical integrity, good homogeneity, and as will be shown below, excellent chemical stability in corrosive atmospheres. The reaction kinetics and processing during photodeposition, however, are poorly understood because of the complexity of the mechanism(s) governing the formation of polymer on the metal. The surface reaction and the gas phase reaction/deposition may both contribute, and neither process is well understood or characterized. It is important to begin to develop an understanding of the polymerization kinetics so that one can achieve better control of the polymer deposition when utilizing this process to develop thin polymer films for commercial applications.

Several vinyl monomers, including methyl methacrylate, butadiene, and acrolein, have been shown to readily photopolymerize under UV irradiation. In this study, acrolein was studied; acrolein forms a cross-linked or partially cross-linked polymer film on metal surfaces readily upon ultraviolet irradiation at low intensity and over a range of monomer partial pressures. The existence of a metallic substrate was found to (1) enable the polymerization of monomer that is not subjected to the conventional forms of polymerization, such as the monomer of hexachlorobutadiene at low temperature,[1] and (2) to enhance the rate of formation of principal gaseous phase products, such as the surface polymerization of perhalogenated adsorbates.[2−4] This early experimental evidence suggested that some of the enhanced reaction might be the result of photodecomposition of the adsorbate on the metal surface.[5−9] It was also reported that the presence of a metal surface during gas phase polymerization may affect the photoinitiation by inducing perturbations in the electronic levels within the adsorbate or introducing new electronic states that may be involved in UV absorption.[28] The interaction between the monomer and metal may influence the dynamics of the polymerization. Therefore, it is important to characterize the polymerization that occurs at the metal surface. Identifying the role of the metallic substrate on the deposition of polymer film can also aid in understanding the reaction mechanism.

There have been several papers that describe the photoinitiation mechanism of vinyl monomers in the presence of a metal surface by observing the gas phase photolysis or the mass change of the surface.[10−12] However, these techniques do not provide details on surface monomer concentration and the surface reaction dynamics that occurred during the polymerization. In recent years, a second-order nonlinear optical process, surface second harmonic generation (SSHG), has been found to be effective when studying surface dynamics with submonolayer sensitivity and high surface specificity in a continuous and real time manner. The second harmonic generation can be observed only in noncentrosymmetric media or at a discontinuity in the index of refraction such as an interface or surface. The second harmonic signal is related to the surface second-order nonlinear susceptibility, a characteristic constant of the interface. By monitoring the SH signal from a metal surface, information pertaining to surface symmetry, morphology, adsorption, and reaction may be determined.[22] This will enable us to study the reaction kinetics from another perspective and to achieve an

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accurate interpretation of the polymerization mechanism.

Surface second harmonic generation techniques have been shown to have advantages as compared to other methods. For a complete discussion of SSHG and the types of surface studies that may be performed using this technique, see the comprehensive review article by Shen.[22] The nonlinear signals exhibit a strong sensitivity to surface and interface properties on an atomic scale under the electric-dipole approximation.[13] One of the most important advantages of SSHG as compared to classic surface spectroscopy lies in the possibility of *in-situ* probing of surface processes in the absence of ultrahigh vacuum conditions.[14−16] It was found that certain surface processes can be identified and characterized through their effects on the interfacial nonlinear polarizability between various types of interfaces.[17a−f,18a−e] In this study, SSHG is employed to examine the monomer coverage on a metal surface during the photopolymerization and to determine the surface reaction dynamics in a nondestructive, real time, continuous fashion, since the reaction rate can be related to the temporal dependence of the optical signal, as shown below.

The experiments discussed in this paper examine the photopolymerization kinetics of gas phase acrolein on polycrystalline gold substrates using simultaneous measurements of the gas phase kinetics and the surface reaction dynamics. The overall reaction rate may be determined by monitoring the monomer concentration as a function of UV light intensity and the initial monomer concentration. In the gas phase, a macroscopic reaction rate was determined by monitoring the decay of the monomer pressure upon the irradiation. The macroscopic surface reaction rate was determined by monitoring the change in polarization that is related to the surface unreacted monomer coverage during the photopolymerization using surface second harmonic generation. A reasonable polymerization mechanism was established that is consistent with the experimental data to describe the deposition of polymer on the metal surface.

Background

The principles of surface second harmonic generation are briefly outlined. The theory of surface second harmonic generation has been well developed and is described elsewhere.[19,20] Light interacts with a medium through a polarization caused by the presence of the optical electromagnetic fields. The polarization can be written as

$$p = \epsilon_0 \chi E \tag{1}$$

where χ is a dimensionless constant known as the electric susceptibility and E is the external electric field. The amplitude and phase of the polarization is determined by a susceptibility which is a material property. When the field is weak, the interaction of light with matter gives rise to linear induced polarization of the medium, which is related to the dielectric constant, a complex quantity related to the refractive index and absorptivity. However, when intense radiation such as a laser beam interacts with the matter, the polarization may become nonlinear with respect to the incident electric field. In addition to the linear induced polarization, a second-order (and higher orders) induced polarization of the medium occurs. Surface second harmonic generation is the coupling of two photons at an energy of $h\nu$ to one photon at an energy of $2h\nu$, at a surface or an interface. The surface nonlinear polarization at 2ω, induced by the incident laser field is given by[21]

$$p_s^{R(2)}(2\omega) = \chi_{s,eff}^{T(2)} \cdot E_{(\omega)}^{R} E_{(\omega)}^{R} \tag{2}$$

where $E(\omega)$ is the electric field at frequency ω and $\chi_{s,eff}$ is the effective surface second-order nonlinear susceptibility. The surface second-order nonlinear susceptibility is a third rank tensor, which may be nonzero only where there is no center of symmetry. This demonstrates the basis of utilizing surface SHG to probe surface phenomena; i.e., when two centrosymmetric media are in contact, the second-order nonlinear susceptibility vanishes except at the surface. The nonlinear signals exhibit a strong sensitivity to surface and interface properties on an atomic scale. The surface second harmonic intensity, $I_{2\omega}$, in the reflected medium with nonlinear polarization $P^{(2)}(2\omega)$ as a source term, can be determined experimentally. The surface second harmonic intensity is proportional to the square of surface second-order nonlinear susceptibility,[21,22]

$$I_{2\omega} \propto |\chi_{s,eff}^{(2)}|^2 \tag{3}$$

Hence, the change of surface nonlinear susceptibility as a result of the surface/interface modification can be measured *in-situ* using SSHG.

The physical origin of the nonlinear polarizability arises from the structure discontinuity and the field discontinuity at the the interface.[23] Relative importance of the two contributions depends on the structure of the interface. The structural discontinuity may dominate the contributions to the interfacial nonlinear polarizability when a monolayer of polar molecules having a preferred orientation is adsorbed at the surface. The measurable second-order nonlinear susceptibility, $\chi_{s,eff}^{T(2)}$ can be related to the microscopic structure of the interface. A metal surface usually exhibits large interfacial nonlinear polarizability because of the delocalized free electron clouds.[24,25] In contrast to a metal, an organic system may consist of molecular units that have no net charge and weak intermolecular charge transfer. The optical nonlinearity of an organic system depends on the nonlinear optical properties of the molecular units.[13,22] Large nonlinearity arises in a system that possesses a highly deformable π-electron distribution such as a conjugated electronic system. The adsorption or reaction on the metal surface may result in the measurable interfacial nonlinear response due to the change in the electronegativity, nonlinear atomic polarizability, work function, or the metal response of the interface.[30]

Experimental SHG studies of the adsorption or reaction at a surface or interface are made possible by the comparison of the SHG intensity of the interface before and after the adsorption or reaction. During the adsorption, the resultant $\chi^{(2)}$ of the whole interface at any level of adsorbate coverage can be interpreted as a combination of one fractional area of perturbed surface with the remaining fractional area of uncovered surface.[26,27] The polymerization results in the change of the interfacial nonlinear polarizabilty from a metal surface because of the difference in polarity and dielectric properties between the monomer and polymer as a result of the change in the density of the π-electrons due to the opening of C═C and formation of σ bonds. It

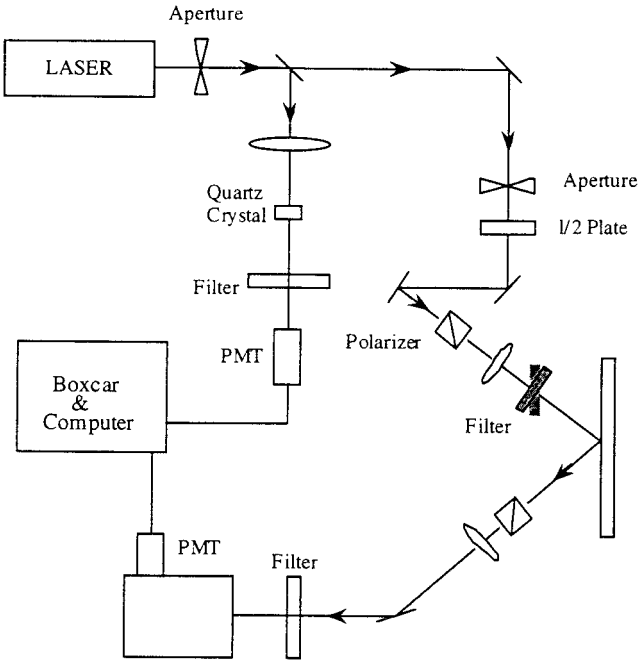

Figure 1. Schematic for the surface second harmonic generation apparatus testbed. The laser beam is split into sample and reference beams. Details are described in the text.

is possible to deduce the fraction of the unreacted monomer coverage during the polymerization and to monitor the polymerization dynamics *in-situ*. The change of surface SHG signal can be considered to be dominated by the depletion of monomer and the formation of polymer as follows:

$$I^{1/2} \propto \chi^{(2)}_{s,eff} = \theta\chi^{(2)}_{m/s} + (1 - \theta)\chi^{(2)}_{p} \qquad (4)$$

where $\chi^{(2)}_{m/s}$ and $\chi^{(2)}_{p}$ are the second-order nonlinear susceptibilities of the monomer-covered metallic substrate and the polymer-covered metallic substrate. In eq 4, the fraction of surface monomer coverage is the only contribution to the change of the measurable SSHG signal. The difference in the interfacial nonlinear polarizability from the metal/monomer interface and metal/polymer interface is the prerequisite for applying SSHG to study surface reaction dynamics.

Experimental Techniques

This section describes the experimental protocols employed to investigate the surface reaction dynamics of the gas phase acrolein monomer on the polycrystalline gold surface.

Surface Second Harmonic Generation Apparatus and Experiments. Figure 1 shows a schematic of the experimental apparatus. The SSHG setup consisted of a laser source and a detection system including a monochromator, a photomultiplier tube, and a boxcar averager. The polarized laser beam generated from a Q-switched Nd:YAG laser (pulse width $\sim$ 7 ns, intensity < 2 mJ/pulse, 10 Hz, λ = 1064 nm) was used as the fundamental. The emitted beam was split into reference and signal beams. This reference signal was observed in tandem with the sample signal to monitor and correct variations of sample signal potentially caused by laser power fluctuations. Two mirrors each at 45° to the normal of the laser table were used to raise the beam several inches above the table so that a 70° angle of incidence to the sample surface normal was acheivable at the sample cell. A polarizer was used to ensure proper polarization. A longpass filter (RG 610) was used to absorb any extraneous second harmonic signal that might have been generated by the optical components in the light path. The laser light at the 70° incident angle was reflected off the metal surface situated inside the reactor. The generated SSHG signal passed through a second polarizer and was reflected off a custom-coated mirror (reflection at wavelength 532 nm) into the slit of a triple grating monochromator/spectrograph (λ/4). Two shortpass filters (KG-3) were placed before the monochromator to keep the fundamental light from reaching the detector. Both SHG signals (sample and reference) were detected and amplified by photomultipliers, averaged, and digitized by a gated integrator and boxcar averager.

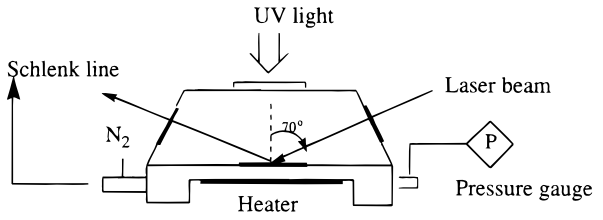

Figure 2. Schematic diagram of the photopolymerization cell. Details of the cell are described in the text. It was connected to a Schlenk line, nitrogen inlet, and a pressure sensor.

The intensity and wavelength of the fundamental and second harmonic beams were chosen so as not to excite monomer molecules in the study of monomer adsorption and polymerization on metal surfaces. The UV−vis absorbance of acrolein monomer at 22 ± 1 °C was studied. Acrolein has two absorbance peaks, with the first at a maximum wavelength of 310 nm and the second at 340 nm. However, acrolein has zero absorbance at the fundamental laser (1064 nm) and the SH (532 nm) wavelengths, which indicated that the fundamental light and the generated SHG beam will not photochemically initiate polymerization of the acrolein. Hence, the application of SSHG measurement to study the adsorption and UV-initiated polymerization of acrolein on a metal surface will not complicate the reaction kinetics.

Real-Time SSHG Reaction Cell. The anodized aluminum reactor consisted of two parts (top and base) connected by O-ring seals to facilitate cleaning of the cell and loading/unloading of the sample. As shown in Figure 2, the incident and reflected laser beams passed through ports (0.39 in. diameter) covered with windows (0.75 in. diameter) normal to the 70° incident laser beam. There was a 0.062 in. slot of dimension 50 × 10 mm on the center of the stage to locate the metallic substrate and to ensure accurate positioning for each experiment. The top window (fused silica, 2.25 in. diameter, 3 mm thickness) on the reaction cell was designed to allow UV light irradiation of the sample. The reactor was equipped with three tubes for the monomer and gas feedthrough and the pressure sensor. Pressure in the reactor was measured with a transducer (Omega PX213-015A5V) and displayed on a panel meter. A Xe/Hg lamp with a 200−500 W arc lamp power supply was the source of incident UV light. Uniformly collimated incident light was achieved by the appropriate arrangement of lenses and a mirror. An UV bandpass filter (250−410 nm) was inserted between the two lenses to keep the light intensity that was incident on the metal surface less than 60 mW/cm^2, minimizing the possibility of a thermally induced reaction.[28]

Monomer and Metal Preparations. Acrolein (Aldrich, CH_2=CHCHO) was passed through an inhibitor removal column, then vacuum distilled, and degassed via five freeze−pump−thaw cycles. Purified monomer was introduced into the reaction cell by thermoequilibrium between a Schlenk tube and the reaction cell. The reaction cell was preevacuated to a pressure less than 5 × 10^{-3} Torr. To avoid the exposure of monomer to room light, the introduction of monomer was performed in the dark and the windows were properly blocked. This technique, similar to that used by Nepras *et al.*, has been shown to remove as much oxygen and other impurities as possible and to lead to homogeneous reaction conditions.[33]

The polycrystalline Au films were prepared by evaporating Au (99.99%) onto a Si wafer (100) using an electron-beam source. The Au film was degreased with acetone, dried, and weighed prior to introduction into the reaction cell. Other metal foils such as aluminum (Al) and nickel (Ni) foils (99.9%, Johnson-Matthey) were polished with micropolish alumina

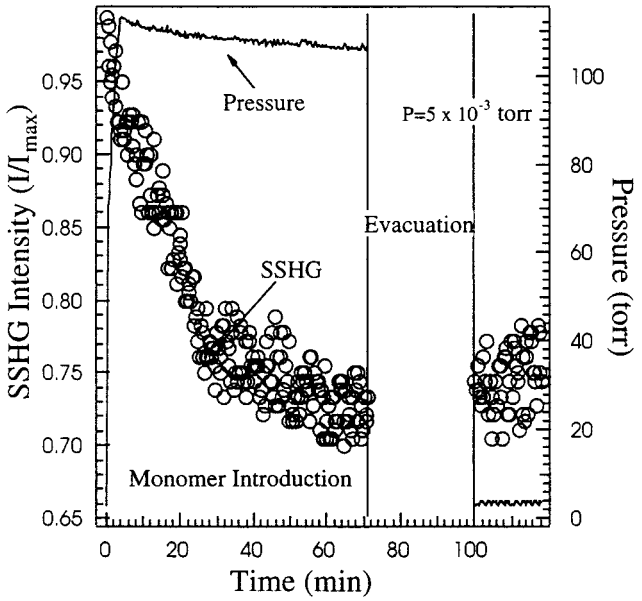

Figure 3. Second harmonic signal from the Au surface as a function of time during the introduction of acrolein vapor into the preevacuated reactor and the evacuation of acrolein vapor from the reactor.

(0.05 micron) to a mirrorlike surface, degreased, and dried. The foils were then kept in a desiccator with anhydrous blue silica for drying at 22 ± 1 °C for 2 h before they were placed in the reactor. The metal surfaces were characterized with XPS before being placed in the sample holder.

Results

Adsorption of Acrolein Monomer onto Au Substrate. The adsorption of acrolein on Au surfaces was identified and characterized through its effect on the interfacial polarizability. A metal often possesses large surface nonlinearity because of the nearly free electrons that can move freely in the volume of the metal. The change in surface nonlinearity as a result of adsorption is expected when the acrolein monomer is brought into contact with the Au surface. Figure 3 shows a plot of the SHG signal from the Au surface as a function of time and how it varied as the surface was continuously exposed to the acrolein vapor. The intensity of the SH signal from the "bare" Au substrate was monitored before acrolein vapor introduction, the SHG intensity at $t = 0$, as shown in Figure 3. The monomer was introduced at a temperature of 22 ± 1 °C, with an initial gas pressure of 120 Torr. The SHG intensity began to decay immediately following the introduction of monomer into the reactor. It dropped monotonically to a saturated value that was 70% of the bare Au SHG intensity in approximately 20 min, indicating a near saturation coverage of acrolein. The noise of signal is about 10% of the total signal, and is believed to be caused by the electron charge effect of the metal surface.[14]

The bare Au surface has a larger SHG signal than that of the acrolein-covered surface. The relatively large SHG signals from a metal surface may be because the nearly free electrons of a metal often dominate the surface nonlinear polarizability. The adsorption of acrolein molecules onto the Au surface resulted in the decrease of the interfacial nonlinear polarizability of the Au/acrolein interface and led to the observed decay of the SHG intensity during the introduction of acrolein into the reactor. The result clearly indicates that SSHG can differentiate between bare metal and monomer-covered metal. After the SH signal from the monomer-covered surface reaches a saturated value, the SH intensity was monitored for another 30 min and no change in the SH intensity was observed. This ensures that there is negligible thermal desorption as a result of the incidence of laser light. The monomer in the reactor was then pumped out at room temperature to a pressure less than 5×10^{-3} Torr, and the reactor was pumped for another 50 min. The SH signal from Au was found not to change, which indicated that an irreversible adsorption occurred at the surface.

There are three nonlinear current sources that contribute to the generation of a second harmonic signal at a metal surface: a bulk source of magnetic dipole character and two surface sources (parallel and normal components) caused by the variation of the electric field near the vacuum−metal interface.[23a] It has been shown that the normal component of the surface current is very sensitive to the nonlinear electronic properties in the interfacial region and determines the interfacial nonlinear polarizability. It is because of this that the second harmonic signal is predicted to be sensitive to surface conditions such as the surface structure, roughness, and adsorbate presence/concentration.[29,30] The asymmetry of the charge densities of surface atoms give rise to a redistribution of charge density, which induces a surface dipole to modify the barrier potential. The excitation of the delocalized free electrons by the external field thus generates a large polarization at the surface. It is therefore not surprising that a larger second harmonic signal was observed from the Au surface before the introduction of the monomer. When the acrolein monomer was brought into contact with the Au substrate, the force of attraction existing at the surface resulted in the adsorption of acrolein molecules. The adsorbates on the Au surface may modify the normal component of the surface current and result in a change in nonlinear electronic properties at the interface and a measurable change in the SH signal upon adsorption. Notice that the SH signal from the monomer-covered Au surface still exhibits a relatively large second harmonic signal. This may be understood as follows: the unsaturated acrolein has C=C and C=O bonds which form a π-conjugated structure. The delocalized behavior of the π-electrons enables their distribution to be highly deformable and may give rise to a large optical nonlinearity. The interaction between the π-electrons of the acrolein molecules and the nearly free electrons of the metal surface has two effects: to decrease the interfacial nonlinear polarizability because of the localization of the free electron cloud of the metal (which contributes to the large interfacial nonlinear polarizability of the bare metal) and to increase the interfacial nonlinear polarizability because of the large induced point dipoles in the interfacial layer. Overall, the acrolein molecules that covered the Au substrate still possessed relatively large nonlinear polarizability and showed a relatively large second harmonic intensity. The relatively large SHG signal from the Au/acrolein interface enabled us to utilize SHG to study the polymerization dynamics *in-situ*. This result also indicated that the interfacial nonlinear polarizability was sensitive to the nature of the adsorbate, which is essential for its application as an optical probe in surface studies.

The adsorption of acrolein on Au was found to be an irreversible process once it was introduced into the

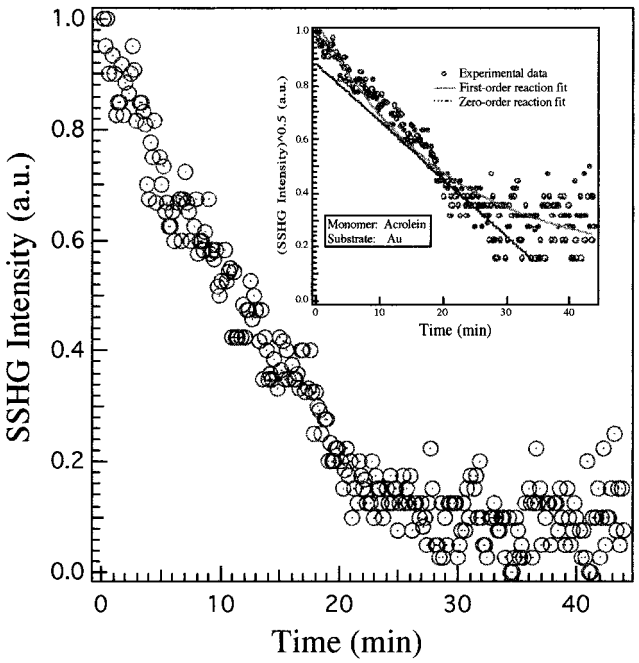

Figure 4. Second harmonic signal as a function of time during the photopolymerization of gas phase acrolein in contact with the Au substrate. Light intensity = 22.6 mW/cm^2, initial acrolein pressure 162 Torr, 22 ± 1 °C.

sample cell by three reproducible trials. As illustrated in Figure 3, the second harmonic signal remained unchanged after the monomer in the reaction cell was pumped out at 22 ± 1 °C to a pressure of 5×10^{-3} Torr for 50 min. This result implied that a residual layer of acrolein monomer adhered to the metal surface and was not removed when the reactor was pumped out under these conditions, also an indication of the irreversible adsorption. The observed decrease in SH intensity caused by a reversible adsorption would be recovered completely when the molecules were removed by evacuation. In contrast, the SH signal would not recover completely to the value of the bare metal surface if bonds were formed between the molecule and the substrate and were not broken upon the evacuation. The bound layer of acrolein on Au may be attributed to the formation of a metal−adsorbate complex that may affect the photoinitiation of the adsorbate on the surface and to the improvement of the adhesion between the polymer and the metal surface.

Photopolymerization of Acrolein on Au. After the formation of a layer of acrolein monomer on the Au surface, the monomer vapor in the reaction cell was irradiated using an Hg/Xe arc lamp. The kinetics of the photopolymerization were monitored using simultaneous SSHG and vapor pressure measurements. Figure 4 illustrates a plot of the second harmonic intensity from the acrolein-covered Au surface as a function of irradiation time and how it varies as the monomer-covered surface was continuously exposed to the UV light. The reaction was carried out at 22 ± 1 °C with an initial acrolein pressure of 160 Torr and light intensity of 22.6 mW/cm^2. The second harmonic intensity decayed monotonically immediately upon exposure to the UV irradiation and dropped to almost a nondetectable level after approximately 30 min of irradiation without an induction period.

Apparently, the formation of polyacrolein on the Au surface decreased the interfacial nonlinear polarizability, decreasing the observed second harmonic signal. The fact that the polymerization resulted in the decrease of the SH intensity can be understood as follows: the polymerization converted the carbon−carbon double bonds to carbon-carbon single bonds and resulted in the formation of polymer with a structure that had less π-conjugation and was less polar than the monomer. The loss of π-conjugated electrons through the polymerization resulted in a smaller induced dipole at the polymer/metal interface. Hence, less interfacial nonlinear polarizability from the polyacrolein/Au interface than the acrolein/Au interface would be expected. This difference enables one to indirectly determine the kinetics of polymerization on the surface by monitoring the SH intensity as the reaction proceeds. As the monomer concentration on the surface decreased, the SH signal showed the change from the monomer-covered Au surface to the polyacrolein covered Au surface.

To analyze the kinetics of the reaction, the method of Berkovic and Shen was used.[26] The time dependent SH intensity may straightforwardly be related to the change of the fraction of unreacted monomer concentration, θ, at the surface using eq 4 as follows:

$$\theta_s(t) \propto \chi^{(2)}_{s,eff}(t) - \chi^{(2)}_{s,eff}(\infty) = I_s^{1/2}(t) - I_s^{1/2}(\infty) \quad (5)$$

where $\chi^{(2)}_{s,eff}$ and $I(\infty)$ are the second-order nonlinear susceptibility and the SH intensity when the monolayer surface reaction is complete, respectively. The rate of polymerization follows certain reaction rate laws. Since the measured $I_s(\infty)$ is zero when a layer of polymer was formed, the rate of monomer coverage change can be expressed as a function of surface monomer concentration and light intensity by

$$\frac{d\sqrt{I_s(t)}}{dt} = -k_s\sqrt{I_s(t)}^m[I]^n \quad (6)$$

where m and n are the reaction orders in surface monomer concentration and light intensity and k_s is the surface rate constant. For a polymerization occurring at a surface, both zeroth ($\theta \propto t$) and first-order reaction ($\ln \theta \propto t$) kinetics are possible.[34] In all cases, the best fit to the kinetics should be found in the initial stage of the reaction, since some deviation may occur as the reaction proceeds toward completion. It is clearly shown in the inset of Figure 4 that the zeroth order fit was not acceptable. The better fit was found to be an exponential function, which suggested that the surface reaction was first-order in the monomer concentration on the metal surface.

The apparent rate of polymerization in the gas phase may be determined by monitoring the time dependent monomer pressure during the UV irradiation. Figure 5 shows a plot of acrolein vapor pressure as a function of the irradiation time, measured simultaneously along with the SSHG measurement. First, it should be noted that there existed a 30 min induction period, indicated by the delay of the onset of pressure decay after the UV source was turned on. Following the induction period, the monomer pressure started to decrease with time, which may be attributed to the formation of polymer in the gas phase or the diffusion of monomer molecules to the surface and the consumption of monomer there. When the UV light was switched off, the rate of polymerization immediately dropped to zero, as indicated by the plateau region on the pressure−time plot. This may suggest that the steady state polymerization was a gas phase process. There was no measurable

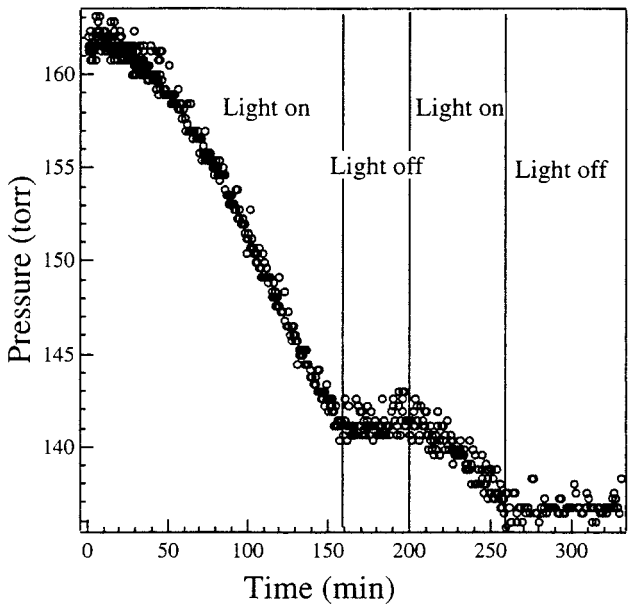

Figure 5. Acrolein vapor pressure as a function of time during the photopolymerization of acrolein in contact with the Au substrate. This set of data was obtained simultaneously with the second harmonic data illustrated in Figure 4.

amount of polymerization occurring in the gas phase in the dark. This result also implied that there was a minimal possibility of the occurrence of thermally-induced polymerization. The decay of gas pressure can be divided into three regions: an induction period, a transition period, and a rapid decay period. Curve fitting was applied to the data obtained during the rapid decay period. The plot of the logarithm of the gas pressure versus irradiation time resulted in a straight line and indicated a first-order reaction in the gas phase. The existence of an "induction period" was also reported during the photopolymerization of acrolein, methyl methacrylate, and acrylonitrile in the presence of a nickel surface.[33] The reason for this induction period has not yet been firmly established.[31,32] It is usually regarded as the time required for the photochemical destruction of certain inhibitors present in small quantities or may be caused by the nucleation of some active species for reaction to proceed. Blacet[32] attributed the existence of an induction period to the recombination of free radicals with the impurities in the reactor such as water contamination. In acrolein photopolymerization, the existence of the induction period may be caused by the low quantum yield of the monomer due to the high internal conversion of the excited species.

The comparison of decays of the SH signal and the gas pressure upon UV irradiation indicated that the SH intensity decreased immediately after the UV irradiation, while the gas pressure showed almost no change. Polymerization initially occurred selectively on the adsorbed layer at the surface. The formation of polyacrolein on a solid surface depends on both the kinetics of the photoinitiated polymerization and the interaction of the surface with the acrolein monomer and polymer. The slow growth rate of polyacrolein in the gas phase allows selective polymerization at the surface to compete with the nonselective polymer deposition on all surfaces of the reactor. This may be caused by the possible interaction between the metal and the monomer adsorbate that may enhance the formation of free radicals on the surface. Hence, it can be inferred that the photopolymerization took place on the adsorbed layer of the surface instead of in the gas phase. The result also demonstrated that, as compared to the monomer pressure decay measurement, the time scale of SSHG measurement was much shorter. The SSHG technique was effective in studying the fast surface reaction in real time. However, it is sensitive only for thin film thickness, whereas vapor pressure measurements are feasible even when the film is several monolayer thicknesses.

It is expected that the SSHG measurement would be more sensitive to the concentration of the unreacted monomer on a metal surface, whereas the decay of the monomer vapor pressure is more sensitive to the initial monomer vapor pressure. In the following, the effects of the UV light intensity and initial vapor pressure on the surface and gas phase reaction were monitored *in-situ*.

Effects of UV Light Intensity on Reaction Rate. The rate of polymerization was investigated as a function of the UV light intensity and the initial monomer pressure. Figure 6a illustrates a plot of the second harmonic intensity as a function of irradiation time when the UV light intensity at the metal surface varied between 11.3 and 45 mW/cm^2. The light intensity was kept low in order to minimize the possibility of thermal polymerization and/or damage to the reactants. It was reported that the control of light intensity below 100 mW/cm^2 can minimize the occurrence of thermal polymerization.[28] It was found that for each UV light intensity tested, the SH signal decreased immediately after the UV light source was turned on. An increase in light intensity increased the rate of the second harmonic signal decay. It was also observed that the increase in the light intensity decreased the time needed to form a monolayer of polymer on the metal surface, where the time of monolayer polymer formation was defined as the time it took for the SH signal to decay to zero.

Figure 6b illustrates a plot of the acrolein gas pressure as a function of irradiation time when the UV light intensity was varied between 11.3 and 45 mW/cm^2. It was also found that, similar to the previous situation, the increase in the light intensity increased the rate of the vapor pressure decay. An induction period (approximately 30−60 min) was observed in each reaction, and an increase in the light intensity was found to decrease the duration of the induction period. No dark reaction after the irradiation occurred during the polymerization. However, the rate of the pressure decay decreased after about 180 min of irradiation for the higher intensity irradiations. This may be caused by the deposition of polymer on the top window of the reactor that may block the passage of the UV beam into the sample cell, decreasing the reaction efficiency. (Note that this is why the kinetic studies were performed at low monomer vapor concentrations.)

The reaction rates at different light intensities were determined using the same approach described above. At each light intensity, the best fit to the second harmonic data was found when an exponential function was used. Hence, the surface reaction was observed to be first-order in surface monomer concentration. The plot of the logarithm of acrolein pressure versus irradiation time showed a straight line, which also indicated a first-order reaction in the gas phase. As shown in Figure 6c, a linear relation between the reaction time constants and the square root of light intensity was observed. This implied that the reaction rate laws of

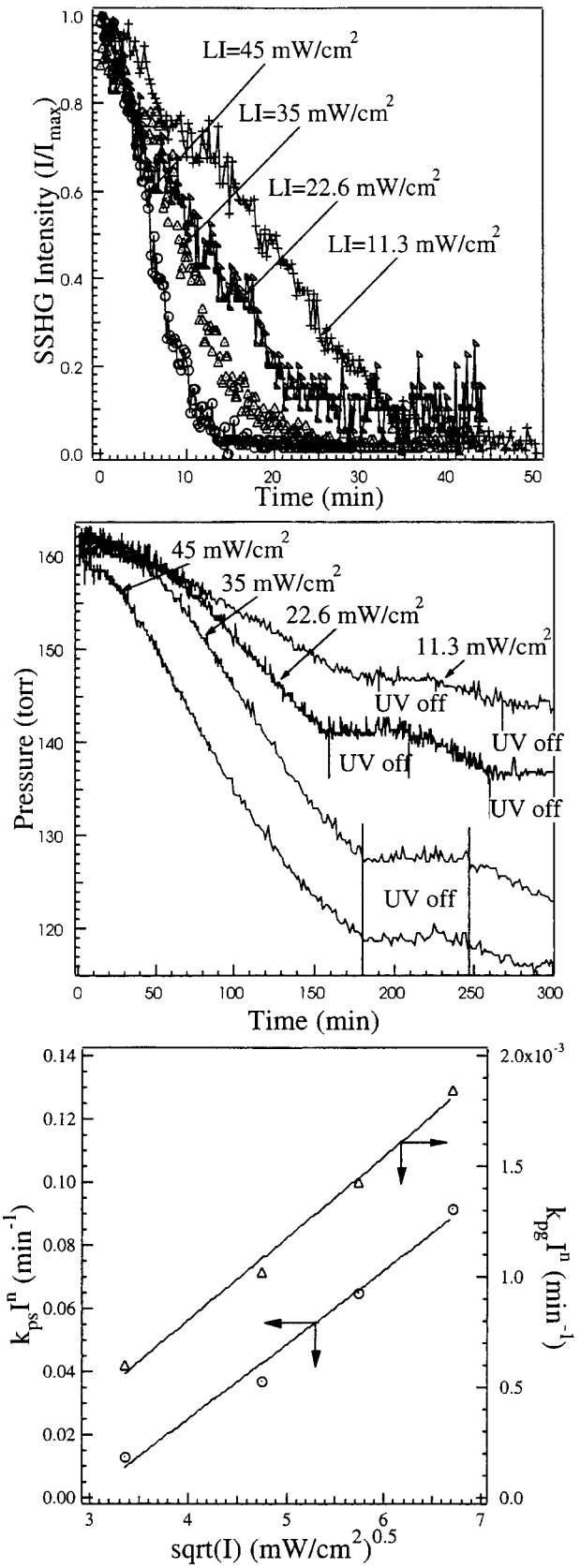

Figure 6. (a) Effect of UV light intensity magnitude on the second harmonic signal during the photopolymerization of acrolein on Au. The reactions were carried out at the initial monomer pressure of 160 Torr at 22 ± 1 °C. (b) Effect of UV light intensity on the decay of acrolein monomer vapor pressure during the photopolymerization of acrolein on Au. (c) Effect of the magnitude of the UV light intensity on the reaction time constants (product of reaction rate constant and light intensity) of the surface reaction and the gas phase reaction during the photopolymerization of acrolein on Au.

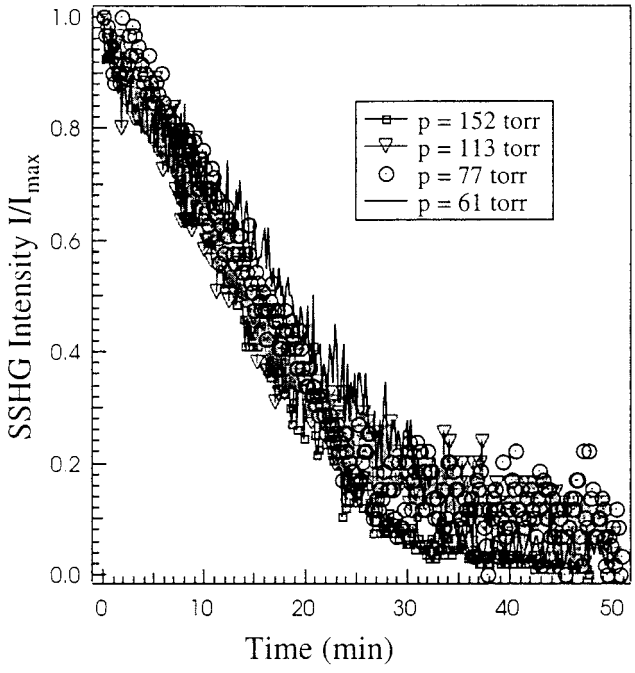

Figure 7. Effects of the initial acrolein gas pressure on the SH signal during the photopolymerization of acrolein on Au. The reactions were carried out at light intensity of 22.6 mW/cm^2 and temperature of 22 ± 1 °C.

both the gas phase and the surface reaction were one-half-order in light intensity. The slopes of the plot were the rate constants for the gas phase and the surface reactions. The rate equation of the surface reaction was found to be $d[M]/dt = 2.35 \times 10^{-2}[M_a]I^{0.5}$ min^{-1}, while the rate equation of the gas phase reaction was found to be $dP/dt = 3.71 \times 10^{-3}[P]I^{0.5}$ Torr/min. The intensity law enables one to draw an important conclusion concerning the mechanism of termination of the gas phase reaction and the surface reaction. As was suggested by Flory, the fact that the polymerization rate is proportional to the square root of the intensity indicated that the termination occurred by the interaction of two active centers.[34] This type of analysis can thus be used to make inferences concerning the mechanism of the polymerization. Equations describing the microscopic reaction kinetics may be derived on the basis of the possible individual surface and gas phase reactions and their interactions. By comparing the microscopic reaction kinetics with the macroscopic rate law obtained via the SSHG and gas phase pressure measurements, a reasonable reaction mechanism may be obtained; see details in the Discussion.

Effects of Initial Monomer Pressure on Reaction Dynamics. The effects of the initial monomer pressure on the surface and the gas phase polymerization were studied. The initial monomer pressure was varied between 61 and 152 Torr, at a constant temperature of 22 ± 1 °C and a constant light intensity of 22.6 mW/cm^2. The upper limit of the initial monomer pressure was determined by the monomer vapor pressure. Figure 7 shows a plot of the SH intensity as a function of UV irradiation time for several initial monomer pressures. It was found that at each initial monomer pressure, the SH signal decreased immediately upon the irradiation and the monolayer of polymer was formed within 30 min. It was interesting to note that the rate of decay of the SH signal showed no dependence on the initial monomer pressure, within experimental error (noise of the signal, i.e., ~10%). As will be discussed

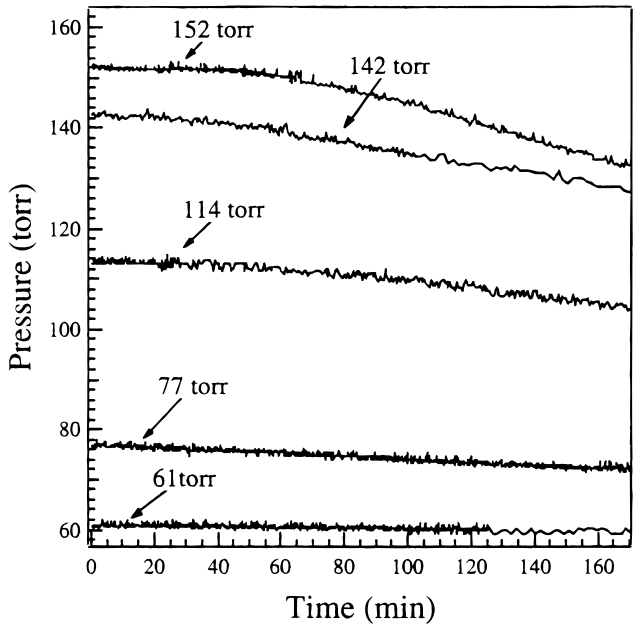

Figure 8. Effects of the initial acrolein gas pressure on the gas pressure decay during the photopolymerization of acrolein on Au.

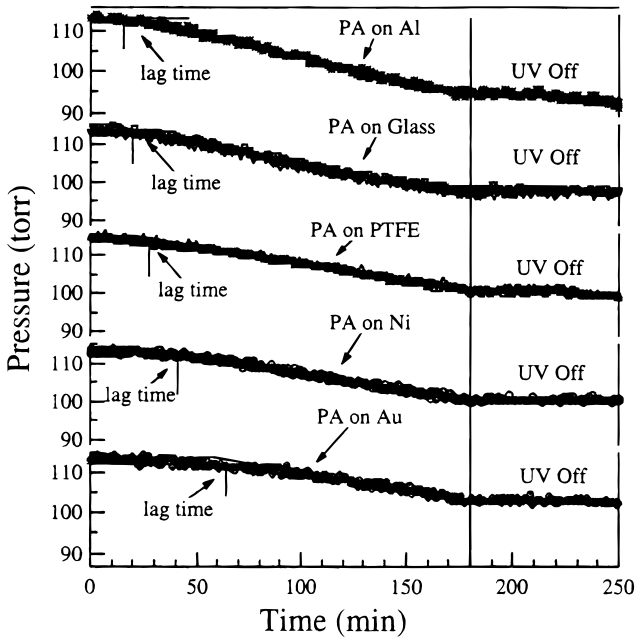

Figure 9. Decay of gas pressure during the photopolymerization of acrolein in the presence of Al, Ni, Au, PTFE, and glass substrates. The reactions were carried out at light intensity of 22.6 mW/cm^2 and temperature of 22 ± 1 °C.

later, there are good reasons to believe that the polymerization may take place on the adsorbed layer on the metal surface and proceeds by a chain reaction.

The decay of the acrolein vapor pressure as a function of the initial monomer pressure is shown in Figure 8. In contrast to the observed lack of dependence of the SH signal decay on initial acrolein pressure, it was found that an increase in the initial monomer pressure increased the rate of the gas pressure decay. The total pressure difference after a certain irradiation time decreased when the initial monomer pressure decreased. The rate of radical formation in a photochemical process is proportional to the light intensity and the monomer concentration. The increase in the monomer pressure may thus be attributed to the increase in rate of radical formation as well as the rate of propagation in the gas phase.

The decay of the gas pressure at each initial pressure was fit using an exponential function and a linear function. Both plots showed reasonably good fits over the available range of data. However, if a zeroth-order reaction occurred, the reaction rate would be expected to be independent of the initial monomer pressure. The observed dependence of the reaction rate on the initial monomer pressure is consistent with the first-order reaction mechanism, as compared to the zeroth order reaction in the gas phase. The observed nearly linear pressure decay could be understood as the result of the fact that the rate constant was too small to observe the apparent exponential decay. The apparent rate of the polymerization in the gas phase is thus assumed to be first-order in monomer concentration.

Effects of the Nature of Substrate on the Polymerization. The irradiation of acrolein vapor in the presence of a metallic or a nonmetallic substrate was also studied to see if whether more than the first monolayer of polymer formed is affected by the type of substrate. The polymerization resulted in the formation of thin polymer films on all the substrates. The aluminum (Al) and nickel (Ni) polycrystalline metallic substrates were chosen so as to compare the oxidized metal with the gold substrates and, additionally, to serve as a comparison to the work performed by Lewis *et al.*[33] A soda-lime glass substrate was selected to represent an inert nonmetallic substrate. A Teflon (PTFE) substrate was also examined. The polymer, while relatively rigid and with high melting temperature, was essentially a molecular solid on a local scale since the adjacent polymer strands interact mutually through ordinary Van der Waals forces. The difference in the structure of these substrates was predicted to result in a difference in the interaction between the adsorbant and the substrate, and hence the radical formation of the adsorbed molecules on the substrate surface upon irradiation. The photopolymerizations were carried out at a light intensity of 22.6 mW/cm^2 at 22 ± 1°C, with an initial monomer pressure of 113 Torr. Figure 9 illustrates a plot of the acrolein monomer vapor pressure decay as a function of irradiation time during photopolymerization in the presence of Al, Ni, Au, PTFE, and glass substrates. To more readily compare data, the pressure decays were plotted on the same scale. It was found that the change of the acrolein vapor pressure during the UV irradiation could be divided into a lag phase and steady decay regions. The lag phase was defined as the region when the pressure started to change until it reached a steady rate, as indicated in Figure 9. The steady decay region was defined as the region in which the pressure change was rapid. It was apparent that the presence of different substrates resulted in different lag phase times; however, it had a negligible effect on the steady state rate of gas pressure decay. The difference in the lag phase time was suggestive of a surface effect in the formation of free radicals, and further indicated that surface reaction predominated over the gas phase reaction initially. As also illustrated in Figure 9, the lag phase time observed in the decay in the presence of Al or Ni substrates was shorter than that for the Au substrate. The surface oxidation appeared to promote the gas phase reaction, which was also observed by Lewis *et al.* in their studies of the effects of oxidized Ni and unoxidized Ni on the rate of polyacrolein formation.[33] This result suggested

the effect of the substrate on the photoinitiation and is consistent with a mechanism requiring that the surface reaction dominate the initial polymerization. No dark reaction after the irradiation was observed in the presence of any substrate, indicated by the flat region when the UV light was switched off, as shown in Figure 9.

Polyacrolein has been reported as a complex, cross-linked polymer, often referred to as "disacryl", with cyclic acetal and hemiacetal (tetrahydropyran) structure units as well as free aldehyde and hydroxyl functional groups.[35] The glass transition temperature of the polyacrolein formed on the Al substrate was determined using differential scanning calorimetry (5 °C/min) to be 118.7 °C. It was also found that at temperatures above 250 °C the polymer charred, indicating a cross-linked polymer structure. The polymer formed on the metal surface was insoluble in all common solvents and became swollen after extensive soaking in a base bath (KOH + ethanol) and in acidic solution (such as 10% HCl) for 48 h. These results demonstrated that formation of polyacrolein on metal surfaces can protect the metal surface from corrosion.

Discussion

It has been demonstrated in this work that the surface second harmonic generation can present a valuable source of information for the study of polymerization kinetics on metal surfaces. In an attempt to interpret the governing of the formation of a polymer film on a metal surface, many authors have suggested mechanisms based on experimental results obtained using either gas phase photolysis or the mass change of the surface upon UV irradiation.[1,2,12] The surface second harmonic generation was found to be useful in determining the monomer coverage on a metal surface *in-situ*, which provided another means to interpret the mechanism of the polymer formation. Polymerization reactions leading to the formation of a polymer film on a metallic substrate can take place in the gas phase or on the surface. Precipitation of polymer molecules formed in the gas phase is important in some photochemical polymerization. The polymerization of a surface adsorbed layer allows for the configurational deposition of high-integrity polymeric films.

The reaction system initially consisted of an acrolein-covered metal surface in contact with acrolein vapor. The interaction between the adsorbed gas and the underlying substrate might be expected to have a significant effect on the rate of polymer formation, as was indicated in a preliminary way in earlier literature.[1−9] However, after the formation of a layer of polymer on the substrate, the reaction system changed to a polyacrolein surface in contact with acrolein vapor molecules. The reaction kinetics in these two stages might not be the same, depending on where the photoinitiation occurred. Four hypotheses may be considered in order to explain the polymerization that led to the formation of the first layer of polymer film on the metal surface. These would be that (i) polymerization was initiated and propagated on the adsorbed layer on the surface; (ii) polymerization occurred in the gas phase, and the polymer formation was the result of deposition of particles formed in the gas phase; (iii) polymerization was initiated on the surface-adsorbed layer and propagated through the flux of the gas phase molecules; and (iv) polymerization was initiated in the gas phase and propagated through the surface-adsorbed layer.

The fourth hypothesis was considered to be the least probable. In the operating pressure range, the mean free path for each molecule was calculated to be approximately 200 nm (at pressure of 100 Torr) based on the kinetic theory of gas molecules. With such a short mean free path, once the radical was formed in the gas phase, it was less probable that it could arrive at the surface and initiate polymerization on the surface without colliding with other gas molecules. Hence, it is less probable that the polymerization would proceed through gas phase initiation and surface-adsorbed layer propagation. The second hypothesis would fail to explain the observed induction period in the gas phase (Figure 4) (observed in this study and by others[1,4,12]) when the polymer was found to form on the surface, as indicated by the decay of the SH signal from the Au surface upon the UV irradiation (Figure 3). The observation of the induction period also suggested that the gas molecules did not participate in the polymer propagation, required either in case i or iii, because the consumption of monomer would result in the decay of the gas pressure.

The observed induction period in the gas phase and decay of the second harmonic signal from the Au surface suggested that polymerization proceeds through the initiation and propagation of the adsorbed layer on the metal surface. The observed lack of dependence of the surface reaction rate on the initial monomer pressure also suggested that the polymerization initially occurred on the surface-adsorbed layer. The rate of a gas phase reaction is generally proportional to the number of molecules available for reaction, i.e., the pressure in the gas phase. A surface reaction may be dependent on the pressure only to the extent that the pressure controls the concentration of the adsorbed gas taking part in this reaction. At very low pressures, the number of adsorbed gas molecules must be small, and the rate of reaction will be proportional to the number of adsorbed molecules and the gas pressure, provided there is sufficient UV energy. As the monomer pressure increases, the concentration of the adsorbed molecules on the surface increases, and a condition must arise in which the number of active species created depends only on the UV energy. The increase in the reaction rate is independent of the number of adsorbed molecules. Hence, if the reaction proceeds through a mechanism involving the adsorbed layers on the surface, the reaction rate at any particular value of light intensity is expected to be independent of the gas pressure as long as there is a full layer of monomer coverage at the surface. It is reasonable to assume a full layer coverage of acrolein on Au since the experiments were operated in the pressure range 61−152 Torr. The study of the adsorption of acrolein on the Au substrate using SSHG, as shown in Figure 3, showed that the second harmonic intensity reached a saturated value after approximately 20 min of adsorption, which also indicated that a full layer coverage of acrolein on Au had been achieved.[17d,22] The selective polymer growth on the metal surface could reflect either a higher monomer concentration in the adsorbed layer at the metal surface or the catalytic effect of metal surface on the polymerization.

The formation of polyacrolein on a solid surface depends on both the kinetics of photoinitiated polymerization and the interaction of the surface with acrolein monomer and polymer. The slow growth rate of polyacrolein in the gas phase allows selective polymerization at the surface to compete with the nonselective polymer

deposition on all surfaces of the reactor. It has been previously reported that the quantum yield of acrolein was low owing to the fast rate of the internal conversion.[32] The gas phase reaction is thus expected to be low initially. However, a metal surface may enhance the radical formation at the surface-adsorbed layer. Hence, a surface reaction may be able to proceed predominantly over the gas phase reaction. This is consistent with the observed fast decay of the second harmonic signal and the initial lack of change in the acrolein vapor pressure. The lag phase time observed in the presence of Al or Ni substrates is shorter than that observed for the Au substrate (Figure 9). The surface oxidation appeared to promote the gas phase reaction, as was also observed by Lewis *et al.* in their studies of the effects of oxidized Ni and unoxidized Ni on the rate of polyacrolein formation.[33] This suggested the effect of the substrate on the photoinitiation and that the surface reaction dominates the initial polymerization.

No matter what substrate was used initially, after the first few monolayers of adsorbed gas monomer have been converted to polymer, subsequent layers will be adsorbed on a freshly formed polymer surface. The polymerization may take place on the adsorbed layer or in the gas phase. In either case, the rate of polymerization should be independent of the original substrate material. This argument explains the lack of dependence of the time constant of the gas phase reaction on the nature of substrate shown in Figure 9. The observed lack of dark reaction after irradiation suggested that the gas phase polymerization may predominantly contribute to the formation of the subsequent layers of polymer on the substrate. After the formation of the polymer layer on Au, the enhancement of the surface to radical formation of the adsorbed layer diminished. Hence, the rate of the radical formation in the gas phase may exceed the rate of radical formation on the surface-adsorbed layers, and thus the gas phase reaction becomes important.

The observation that photopolymerization occurred on a metal surface initially has practical applications in the processing of metal coatings. A polymer film can be deposited onto the metal surface by the appropriate choice of the gas pressure, the nature of substrate, and the irradiation time. Thin and uniform polymer coatings can be achieved if the gas pressure can be maintained low yet large enough for a full layer coverage of monomer-adsorbed layer.

Conclusions

The determination of the kinetics of the gas phase photopolymerization of vinyl monomer onto metallic substrates is important when attempting to control thin film growth and film properties. A unique method was established to study the photoinitiation and dynamics of photopolymerization on gold substrates by monitoring the gas phase kinetics and the surface dynamics *in-situ* and in real time. The surface second harmonic generation was employed to monitor the adsorption and reaction of acrolein on Au substrates. The change of interfacial nonlinear polarizability caused by the adsorption and reaction of acrolein molecules on Au surfaces can be related to the surface monomer coverage. It has been demonstrated that the SSHG technique is an effective optical method that can be used to determine the kinetics of polymerization on the metal surface in real time.

The SH signal was found to be sensitive to the nature of the adsorbate on the metal surface. The adsorption of acrolein on Au resulted in a decrease in the second harmonic intensity as compared with that of the bare metal surface. The adsorption of acrolein was found to be an irreversible process. A thin layer of polymer was formed on the Au surface upon ultraviolet irradiation. The second harmonic signal was found to decrease immediately after the UV source was turned on as a result of the decrease in monomer surface coverage, while an induction period was observed in the gas phase. The SSHG measurement was able to monitor the reaction rates at different UV light intensities and the initial monomer pressures. The surface reaction rate was found to be first-order in surface monomer concentration, one-half-order in light intensity, and independent of the gas pressure in the range of pressure studied, 61−152 Torr. The lack of dependence of surface reaction rate on the initial monomer pressure suggested that the photopolymerization took place initially at the surface-adsorbed layer instead of in the gas phase. The observed dependence of the lag phase time on the nature of the underlying substrate agreed with this mechanism. Deposition of the uniform thin film for metal coatings can be achieved by the appropriate choice of reaction parameter.

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