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Formation of Ultrathin Polystyrene Films Using a Two-Step Deposition/Polymerization Process

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ABSTRACT: Thin polystyrene films were formed on polycrystalline platinum by styrene deposition followed by UV-initiated polymerization under cryogenic, ultrahigh-vacuum conditions. Temperature-programmed desorption (TPD) experiments showed that styrene chemisorbs weakly on the Pt surface. In the temperature region of 115−145 K, the adsorbed styrene films undergo a crystallization process that can be described by the Avrami equation. The polymerization rate increased with incident UV intensity, as expected, but was found to decrease with increasing temperature, most likely the result of competition between crystallization and polymerization. Ex-situ analysis of the resulting polystyrene films showed that high molecular weight polymer is formed. Finally, it is shown that the thickness can be reproducibly controlled by controlling the initial monomer dosage.

Introduction

Because of the recent push toward smaller electrical and mechanical devices, there is an increasing interest in the formation of thin polymer films. Applications include electroluminescent films for flat panel displays,[1−3] dielectric layers for semiconductor devices,[4] and lubrication coatings for microelectromechanical systems (MEMS).[5,6] Many other advanced applications of ultrathin polymer films can be envisioned, such as all-polymeric semiconducting devices and direct-write lithography.

Currently, the most common method to prepare thin polymer films is by wet techniques, such as electrochemical deposition or spin coating.[7−11] The largest demand for spin coating is in the microelectronics industry, where semiconductor wafers are coated with thin polymeric films and subsequently submitted to a photolithographic process. Film thickness, which is determined mainly by the viscosity of the polymer solution and the spinning speed, can range from tens of microns to well below a micron; however, it is difficult to deposit high quality films of submicron thickness by spin coating. Additionally, spin coating is prone to the so-called “orange peel effect” and “pinhole defects” that occur when solvents evaporate from the film, and the hygroscopic behavior of some solvents can cause precipitation of the polymer, resulting in a cloudy, nonuniform film. Spin coating also poses two specific disadvantages for the application to the production of thin films for electrooptical or electrical insulating applications. First, the process necessitates that the polymer be soluble. This is not a problem in lithographic applications, which typically employ poly(methyl methacrylate), but it can pose a problem for the processing of conducting or dielectric layer polymers, which are typically not soluble in common solvents, if at all. Additionally, if any of the casting solvent remains in the film, the electrooptical properties of the film will be different from that of a pure polymer film.

One possible replacement for spin coating is a process based on vacuum deposition. A variety of deposition processes exist, and it is worthwhile to distinguish between these. First, the process can be broadly categorized into either physical vapor deposition (PVD) or chemical vapor deposition (CVD). Physical deposition processes are those in which no chemical change occurs during the deposition process, while in chemical deposition, a chemical reaction occurs. In the case of the formation of thin polymer films, the chemical change is polymerization. PVD can be further broken down into two categories: simple deposition and deposition−polymerization. Simple deposition involves depositing the polymer from the gas phase directly onto a substrate. In deposition−polymerization, a monomer or prepolymer is first deposited, and then polymerization is carried out on the surface via thermal, photochemical, or other initiation process. In this paper, we will focus only on the deposition−polymerization process, which has distinct advantages over simple PVD of being able to produce uniform, defect-free films and has the advantage over CVD in that a much wider variety of starting monomers can be employed.

Polymerization of monomers adsorbed onto metal or semiconductor surfaces has some obvious advantages in forming ultrathin coatings. Since the thickness of monomer films can be precisely and reproducibly controlled, the final polymer film thickness can also be precisely controlled, making it possible to form submicron films. UV-initiated, in situ polymerization could also be used to form polymer coatings on selected areas of a surface using well-known photoresist techniques. This approach eliminates the use of organic solvents, so the undesired pinhole defects and cloudiness are no longer issues. There is also a growing interest in eliminating solvent waste from processes due to environmental concerns. Vapor deposition polymerization is a solvent-free process, and since all processing is conducted in a well-controlled vacuum environment, any residual monomer can be precisely managed and recovered.

Early work in vapor deposition polymerization involved irradiating a substrate inside of a chamber filled with monomer vapor.[12,13] Although experimentally convenient, the nature of the polymerization process has not been fully explored. Additionally, in this configura-

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tion, it is not possible to distinguish between polymer that has been formed in the gas phase with subsequent deposition onto the surface and that which is the result of polymerization of monomer absorbed on the surface. Since these early works, few vapor deposition polymerization studies can be found in the literature until recently. This is likely due to the resurgence of interest in the production of thin film devices.

The limited literature relevant to physical vapor deposition polymerization includes that of Fleck et al., who studied the adsorption and laser-induced polymerization of submonolayer formaldehyde on Ag (111) using electron energy loss spectroscopy (EELS) and temperature-programmed desorption (TPD).[14,15] They found that molecularly adsorbed formaldehyde polymerizes under 355 nm laser irradiation over a wide range of coverages. The product polymer was most likely in the form of linear chain poly(oxymethylene) and remained stable on the surface up to 210 K. A mechanism involving radicals generated from formaldehyde photodissociation was proposed.

Carlo and Grassian studied the photopolymerization of a styrene thin film on Ag(110) surface with Fourier transform infrared (FTIR) spectroscopy and TPD.[16] They concluded that styrene molecules are oriented nearly perpendicular to the surface; irradiation forms dimers, trimers, and tetramers, and the reaction appears to proceed along the surface normal. A mechanism involving the formation of a biradical species was proposed.

Baumgartner et al. also conducted research on the X-ray-initiated polymerization of thiophene on the Ag(111) surface using X-ray photoelectron spectroscopy (XPS), TPD, and mass spectrometry.[17] They concluded from the XPS data that thiophene physisorbs on the Ag(111) surface, and prolonged exposure to Mg Kα radiation results in the formation of oligomers in the condensed multilayers. The monolayer regime, however, did not show this photochemical reaction, probably because the excitation was rapidly quenched by the metallic substrate. The polymerization yield in the multilayer was found to dramatically increase as the temperature of the substrate increased.

Because of the unique reaction conditions under which these reaction are carried out, i.e., cryogenic, thin layer, bulk (no initiator), photoinitiated, UHV, it is necessary to perform fundamental studies to determine the effect of processing conditions on the polymerization process and ultimately the final properties of the film. The model system chosen here is styrene on polycrystalline Pt. UV irradiation was performed under various substrate temperatures and UV intensities, and the process was monitored by Fourier transform infrared reflection−absorption spectroscopy (FT-IRAS) and TPD. The product film was characterized with gel permeation chromatography (GPC) and ellipsometry.

Experimental Section

All experiments were performed in an ultrahigh-vacuum (UHV) chamber with base pressure below 7×10^{-9} Torr. The chamber was equipped with a quadrupole mass spectrometer (Stanford Research Systems, RGA 300) and a liquid nitrogen cryogenic manipulator (Thermionics) that allowed *x*-, *y*-, and *z*-translational motion and 360° rotation about the *z*-axis. The sample was attached to the head of the cryostat through two tantalum wires. In this configuration, the sample could be cooled to 90 K and also heated resistively through the tantalum wires to over 1200 K. The temperature was recorded with a K-type thermocouple spot-welded directly to the back of the substrate. The chamber was equipped with several viewports to allow visual observation as well as spectroscopic analysis. For UV irradiation, a quartz window was utilized to allow transmission to ~200 nm. For FT-IRAS, two beam ports equipped with KBr windows were employed.

The Pt substrate was prepared from a 0.5 mm thick polycrystalline sheet and was manually polished before being mounted to the head of the cryostat. The surface quality was mirrorlike and allowed a sufficient amount of IR radiation to reach the detector in order to acquire spectra with adequate signal-to-noise ratios. Before initial dosing, the substrate was first cleaned by a cycle of Ar sputtering at 10^{-4} Torr, high-temperature annealing (1000 °C), and O_2 cleaning (650 °C at 10^{-7} Torr). Between polymerization reactions, the Pt substrate was subjected to O_2 cleaning followed by annealing.

TPD experiments were performed to determine the adsorption state of the monomer at various dosages. The sample was held at 100 K, and a specific amount of monomer was dosed by back-filling the chamber through a variable leak valve. All dosages are reported in units of langmuirs (1 langmuir $= 1 \times 10^{-6}$ Torr·s) and were not corrected for gauge sensitivity. Subsequently, the sample was subjected to a heating ramp of 5 K min^{-1}, and desorbing species were detected using the mass spectrometer tuned to the appropriate mass.

Styrene (99%, Aldrich) was prepared by passing it through an inhibitor removal column (Aldrich) and was also subjected to several freeze−pump−thaw cycles. To prevent spontaneous polymerization, the purified styrene was stored in a black tape-wrapped Schlenk tube. Polymerization of monomer films was initiated by exposure to broad-band UV light from a Xe/HgXe lamp (Oriel). All reported UV dosages are the result of a calibration using a UV power meter. To study the temperature effect on the polymerization process, styrene was adsorbed onto the substrate held at 100 K. The substrate was then resistively heated to the desired temperature within 1 min. The temperature was then maintained within 1 K during the entire polymerization process.

FTIR spectra were acquired at an angle of incidence of approximately 80° with respect to the surface normal. A Nicolet Magna 860 FTIR spectrometer was used for collection of all spectral data, and the entire beam path was purged by dry air. Each spectrum is the result of 200 coadditions collected at a resolution of 4 cm^{-1}. For the purpose of polymerization kinetic studies, IR spectra were collected every 2 min during UV irradiation.

After irradiation, the sample could be removed from the vacuum chamber to perform ex-situ measurements of the film properties. The films were dissolved in THF and submitted for GPC analysis. The GPC system was composed of a Waters 2690 separation module with a Waters 2410 differential refractometer detector. The thickness of the films was determined using a Auto EL II A 9819 ellipsometer (Rudolph Research) operating at 633, 546, and 405 nm.

Results and Discussion

Nature of Adsorbed Styrene. TPD experiments were carried out for both thin (mono-) and thick (multi-) layers of styrene adsorbed on Pt at 100 K, and the corresponding TPD spectra, shown in Figure 1, demonstrate distinct desorption temperatures for both the monolayer at 201 K and for the multilayer at 180 K. This is indicative of a weak chemisorption process, with a heat of desorption of 50 kJ mol^{-1} for monolayer and 41 kJ mol^{-1} for multilayer, as obtained from the Redhead equation[18] with a frequency factor $\nu = 10^{13}$ s^{-1} [19] and a heating rate of $\beta = 5$ K s^{-1}. IR spectra were also taken to study the adsorption of both thin (<20 langmuirs, about 4 monolayers) and thick (up to 2000 langmuirs) films of styrene. No additional spectral bands or large band shifts were detected in the FTIR spectra for both thin and thick adsorbed styrene films,

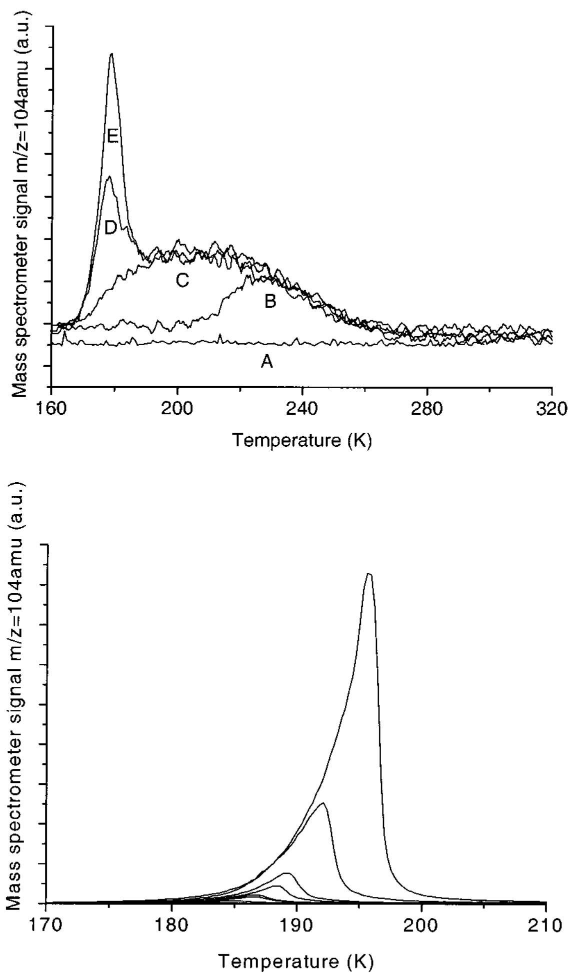

Figure 1. (top) TPD spectra of low dosages of styrene: (A) background, taken without Pt substrate, (B) submonolayer, (C) monolayer, and (D, E) multilayer coverages, generated by plotting the mass spectrometer response at $m/z = 104$ amu. (bottom) TPD spectra of higher dosages of styrene monomer demonstrating increase in peak desorption temperature with increasing coverage, characteristic of zero-order desorption.

as compared to that of bulk styrene. This is further indication that the adsorbed species are, at most, weakly chemisorbed on the surface. The surface selection rule is a well-known method of determining the surface orientation of adsorbed species, and it has been widely used to analyze adsorbed thin layers on metal substrates. In our case, the surface selection rule could only be employed to interpret the thin film IR spectra, since the thicker films are many molecular layers thick and beyond the scope of the surface selection rule. Nevertheless, the similarity between the IR spectra obtained from thin and thick films indicates that the adsorbed styrene molecules are randomly orientated for all films.

RAIRS has been previously employed for studying the amorphous to polycrystalline transition of adsorbed thin films on metal surfaces. For example, vibrational spectroscopy has been adopted to analyze the transition of amorphous ice to polycrystalline ice.[20] The amorphous ice was transformed to polycrystalline ice upon heating to 145 K, which, accordingly, caused the shape of the peak to change from a relatively featureless one centered at 3400 cm^{-1} to a peak with two clear shoulders and a main maximum at 3230 cm^{-1}. In this paper, we report that RAIRS detected the phase transition of styrene from amorphous to polycrystalline state. It is known that amorphous (or glassy) films are often formed during vapor deposition at low temperatures in a vacuum.[21−23] Under our experimental conditions, it is expected that the styrene molecules will possess no preferred orientation upon adsorption, but instead will form an isotropic amorphous film. Additionally, the mobility of the molecules on the surface should be sufficiently low such that little or no reorientation occurs. This becomes apparent upon heating. Figure 2 shows FTIR spectra acquired from a 1000 langmuir styrene film while heating from 100 to 145 K. Obvious spectral changes, including band intensity changes and band splitting, are observed. These spectral changes are indicative of a change in molecular environment brought about by the presence of long-range order. For the spectrum taken at 145 K, almost all the peaks become sharper, which indicates that, upon the phase change, the amorphous styrene film is transformed into a crystalline film, in which all molecules experience essentially the same chemical environment. The above assumption is consistent with recent studies, in which similar behavior was observed of the phase transition of pyridine thin films on Ag (110) and Ag (111) surfaces by second harmonic generation when the surface temperature was raised above 125 K. It was concluded that the transition was from a disordered to an ordered structure and that the annealed film consisted of polycrystallites with an average length scale comparable to or larger than 0.5 μm.[24] Two additional observations are relevant. First, no desorption occurs during this heating process, as long as the temperature is kept below the desorption temperature (150 K). This was evidenced by a lack of change in the IR spectra after the sample was maintained at 150 K for 60 min. Second, the IR spectra also show that the temperature-induced changes remain after the sample was cooled back down to 100 K, similar to what has been reported for pyridine thin films on Ag (111).[24]

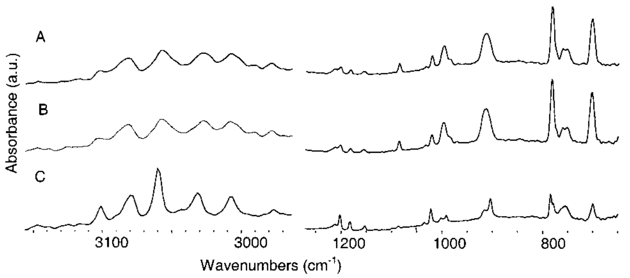

Figure 2. IR spectra of adsorbed styrene on Pt, as dosed at (A) 100 K, annealed to (B) 120 K, and further annealed to (C) 145 K.

An additional set of experiments was performed on the styrene films in order to determine the nature of the crystallization process. In these experiments, films dosed at low temperature (100 K) were heated to several higher temperatures, and infrared spectra were collected as a function of time. The data at each temperature were fitted to the Avrami equation,[25] which describes the kinetics of phase changes by nucleation and growth.[26] This theory has been widely applied due to its mathematical simplicity and good agreement with experiment. The general Avrami equation is given as

$$\chi(t) = 1 - \exp(-kt^n)$$

where $\chi(t)$ is the crystallinity, or fraction of phase transformed, at time t, n is an integral Avrami index characteristic of the nucleation type and dimensionality

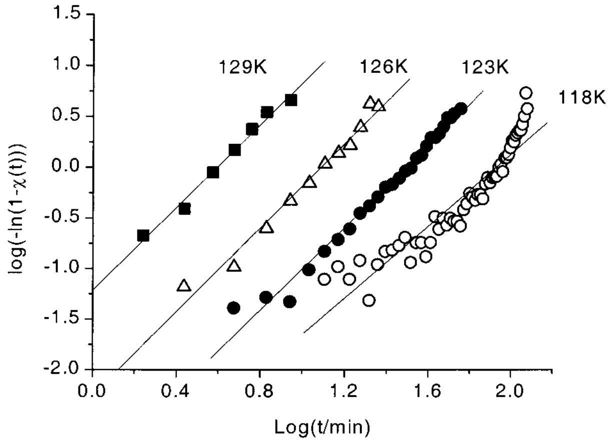

Figure 3. Avrami plot for adsorbed styrene monomer annealed to various temperatures.

Table 1. Avrami Index *n* and *k* of Adsorbed Styrene for Several Annealing Temperatures

temperature (K)	*n*	*k*
129	2.0 ± 0.1	$(6.0 \pm 0.3) \times 10^{-2}$
126	2.1 ± 0.1	$(5.6 \pm 0.5) \times 10^{-3}$
123	2.0 ± 0.1	$(9.1 \pm 0.9) \times 10^{-4}$
118	1.9 ± 0.2	$(3.7 \pm 0.5) \times 10^{-4}$

of growth, and k is a thermally activated constant that can be expressed as an Arrhenius-type equation of the form

$$k = k_0 \exp(-E/RT)$$

In our case, the following definition holds:

$$\chi(t) = \frac{A(t) - A(0)}{A(\infty) - A(0)}$$

where $A(0)$, $A(t)$, and $A(\infty)$ are the baseline corrected peak heights of the 705 cm^{-1} combination band of styrene at the beginning, at time t, and at the completion of the phase transition, respectively. All spectral bands followed the same trend, but this particular band exhibited the greatest change and was therefore selected in order to maximize the data quality. Typically, the Avrami equation is used in the following form:

$$\ln(-\ln(1 - \chi(t))) = \ln(k) + n \ln(t)$$

and a plot of $\ln(-\ln(1 - \chi(t)))$ vs $\ln(t)$ (see Figure 3) gives the values of both k and n. The isothermal phase change of the adsorbed styrene was carried out at 115, 118, 123, 126, and 129 K. For the reaction at 115 K, no phase change could be observed even after 3 h. The resulting values for k and n are listed in Table 1. A plot of $\ln(t)$ against $1/T$ gives an activation energy E of 24.6 kJ/mol. The exponent n in the Avrami equation is typically used to categorize the crystallization process. However, because of the sensitivity of this parameter to the dimensionality and crystallization mechanism, it is difficult to classify this process without further information (i.e., from a microscopy investigation during crystallization) on the nature of the crystallization process in our system.

An additional set of TPD experiments was also performed for the crystallized films. From these experiments, it was seen that, within experimental error, there is no apparent shift in either the monolayer or multilayer desorption peaks. This indicates that the presence of long-range order does not affect the desorption process under this set of conditions.

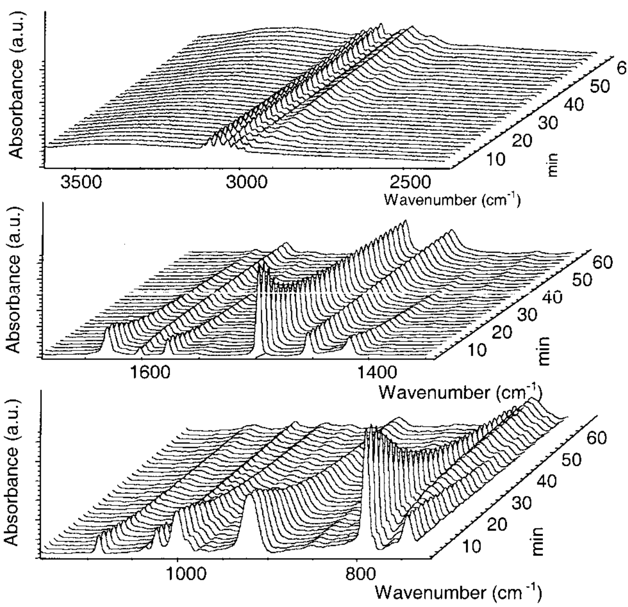

Figure 4. Time-resolved IR spectra from the first 60 min of polymerization.

Effect of UV Irradiation. Exposure of the styrene films to UV radiation produces spectral changes consistent with the polymerization of styrene to polystyrene.[27] Two bands that correspond to moieties directly involved in the polymerization were chosen to follow the progress of the reaction: the 1630 cm^{-1} C═C stretching band of styrene and the 2932 cm^{-1} C−H stretching band of polystyrene. Time-resolved IR spectra of a film during polymerization with final conversion above 90% are shown in Figure 4. After 60 min of UV irradiation, the spectra closely resemble those of polystyrene, except for a few low-intensity peaks belonging to styrene. To determine the proper kinetic treatment to employ, the dependence of the reaction rate on the monomer concentration [M] was first determined using the following relation:

$$\frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} \propto [\mathrm{M}]^n$$

where n is the order of the monomer concentration. The derivative was determined from a plot of [M] vs time. Using a log−log plot of this expression, the order dependence was found by the slope of linear fit of the logarithm of the polymerization rate vs the logarithm of the monomer concentration. This analysis gives the value of $n = 1.0 \pm 0.2$; hence, the dependence was determined to be linear for all reaction conditions. Therefore, a single-exponential relation can be used to fit the polymerization data:

$$A(t) = B \exp(-k_{\mathrm{p}}(t - t_0))$$

where $A(t)$ is the normalized peak height of the 1630 cm^{-1} band used as the measure of the normalized monomer concentration, k_{p} is the rate constant, and B and t_0 are scaling factors. Examples are shown in Figure 5.

Upon heating the polymerized samples up to 250 K (above the desorption temperature of styrene), the observed IR spectra are very similar to that of atactic

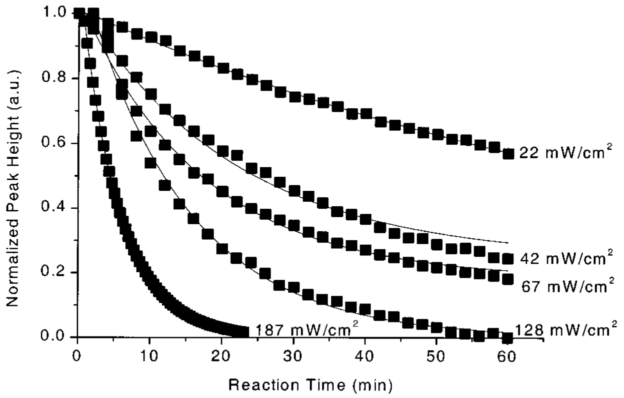

Figure 5. Polymerizations performed at various UV light intensities, monitored by the normalized absorbance intensity of the 1630 cm^{-1} C=C stretching band.

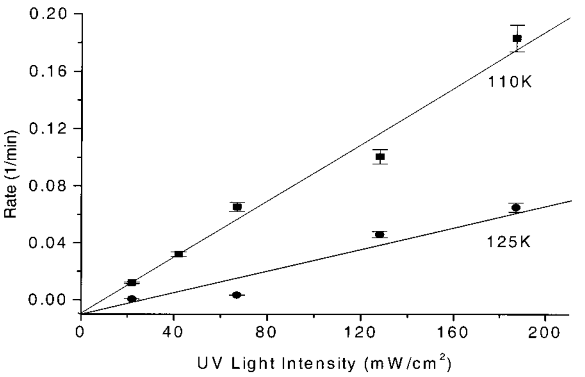

Figure 6. Dependence of rate constant on both reaction temperature and UV intensity.

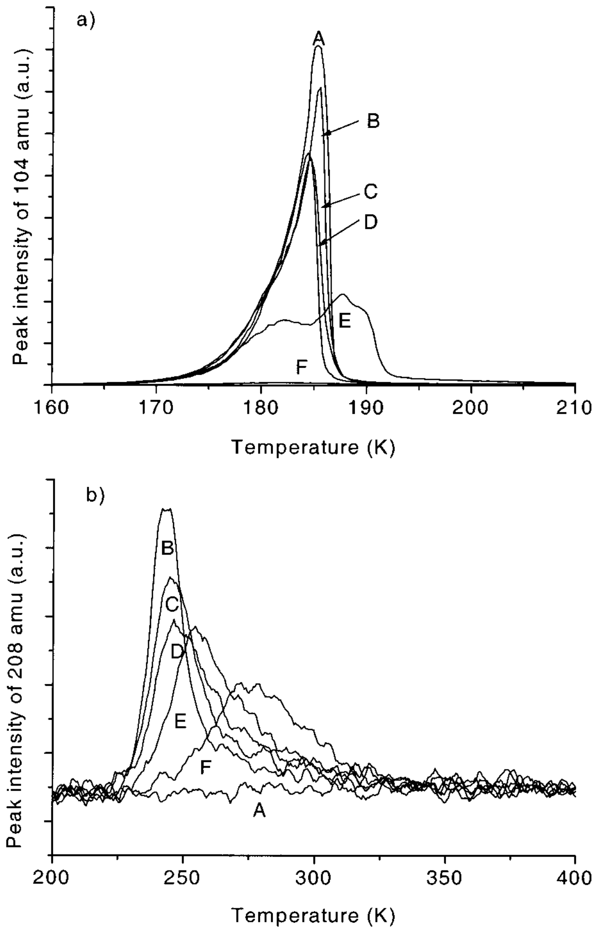

Figure 7. TPD spectra of (a) styrene monomer (m/z = 104) and (b) dimer (m/z = 208) before (A) and after (B) 5, (C) 15, (D) 60, and (E) 120 min of UV irradiation.

polystyrene.[28] No apparent differences can be seen by comparing the IR spectra of the product obtained at reaction temperatures of 110, 125, and 145 K.

The reaction rate constants as a function of both temperature and UV intensity are shown in Figure 6. The temperature data suggest an apparent negative activation energy. This can be explained by taking the physical state of the monomer into account. The styrene films undergo the annealing process at an increasing rate with increasing temperature. The extreme case of a completely crystalline film (as determined by FTIR) was examined by forming a styrene film at a substrate temperature of 100 K, heating to 150 K for 10 min, cooling the film back down to 100 K, and exposing it to UV radiation. FTIR spectra acquired during this time revealed a dramatically slower polymerization reaction, with a conversion below 10% being achieved after 2 h of irradiation. From these data, it is apparent that the preferred crystalline form that styrene adopts upon annealing inhibits the polymerization process. This is most likely due to the styrene molecules being “frozen” in a certain orientation, which does not allow reaction to occur. However, at lower temperatures, the molecules in the as-dosed films adopt random orientations, and polymerization can proceed in much the same way as in solution. During the UV irradiation of styrene, both polymerization and phase transition occurred; however, at 110 K, the rate of phase transition is negligible, and the rate of polymerization is not reduced by the formation of the crystalline state. At 125 and 145 K, the rate of phase transition is much higher, leading to lower polymerization rates.

Additionally, there is no postirradiation effect at temperatures below 150 K. If the UV irradiation was ceased, the reaction stopped immediately and continued once the irradiation was continued. This allows for control of the final conversion of the polystyrene films.

Polystyrene Film Characterization. Postirradiation TPD experiments for a series of polymerization reactions stopped after 5, 15, 30, 60, and 120 min of UV irradiation are shown in Figure 7. Figure 7a shows a decrease in the peak intensity of the signal at 104 amu (corresponding to the styrene parent ion) with irradiation time, which reveals the loss of styrene due to UV irradiation. The 208 amu spectra (parent ion of the dimer) show a well-resolved peak around 250 K after 5 min of UV irradiation (Figure 7b). Higher molecular weight species cannot be investigated with the current experimental setup because the highest mass-to-charge ratio detectable by the mass spectrometer employed here is 300. As the UV irradiation continues, the dimer peak decreases in height and is broadened toward higher temperatures. It is unfortunately not possible to determine whether this is due to dimer species desorbing from the polystyrene film or from fragmentation of higher molecular weight species in the ion source of the mass spectrometer. However, it is clear from these results that higher molecular weight species are being produced in this reaction.

Both IR and TPD results clearly suggest the formation of higher molecular weight species at low temperature; however, it must be known if the product film is

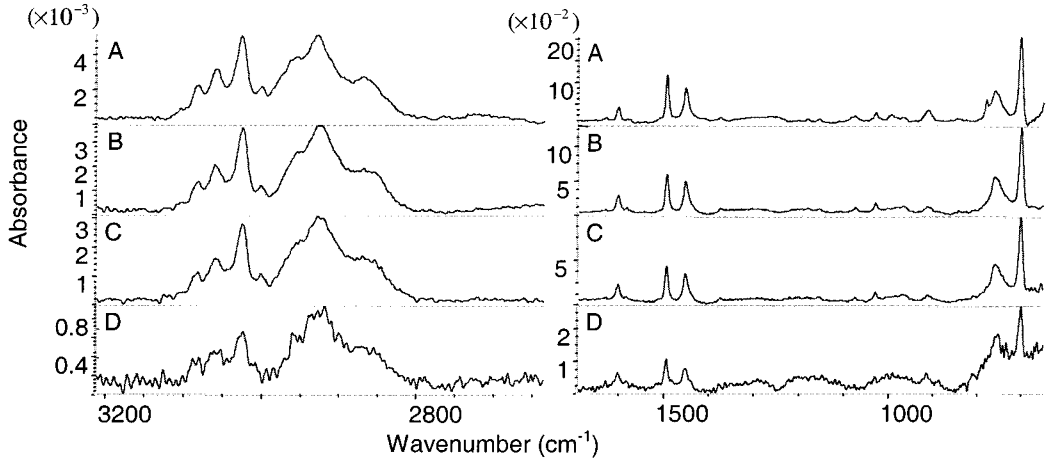

Figure 8. FTIR spectra of a polystyrene film acquired at (A) 110 K, (B) 350 K, (C) 450 K, and (D) 550 K, demonstrating the thermal stability of the final polystyrene films.

stable on the surface at room temperature and above. Therefore, after irradiation at reduced temperature, the sample surface was heated to temperatures between 350 and 550 K, and IR spectra were collected (see Figure 8). All peaks associated with the vinyl bond disappear completely above 350 K when the monomer has desorbed from the surface, and the resulting spectrum resembles that of polystyrene. The spectra taken at 450 and 550 K are very similar to that at 350 K, except for decreased peak intensities, presumably due to desorption of lower molecular weight species combined with partial decomposition of the polymer chains at elevated temperatures.

To test the integrity of the film, the surface was exposed to CO at room temperature and higher, and IR spectra were collected. Peaks characteristic of CO adsorbed on Pt were not observed. This is a preliminary measure of the quality of the films, which demonstrates that the films are continuous and void of pinhole defects.

After 2 h of UV polymerization at 110 K, a polystyrene film formed by irradiating a 2000 langmuir styrene film for 90 min with a UV intensity of 128 mW/cm^2 (conversion ~ 93%) was dissolved in THF and submitted to molecular weight analysis by GPC. The results are M_n = 40 056 and M_w = 249 453, with a resulting polydispersity of 6.23.

The thickness of the final polystyrene films as a function of initial monomer dosage was measured with ellipsometry, and the results are plotted in Figure 9. The reaction temperature was kept constant at 110 K, and monomer conversion was between 90% and 95% for all films examined in order to ensure an accurate comparison. The measured thickness linearly depends on the monomer dosage in the range 500−3000 langmuirs, corresponding to film thicknesses from 25 to 250 nm. This clearly demonstrates that this method of film formation can be used to produce films of reproducibly controllable thickness.

Visual inspection of the films revealed uniform color on the surface due to selective reflection of visible light, which indicates that the surface is smooth and continuous on a macroscopic scale. SEM studies of the films on partially cleaned samples revealed uniform images for the polystyrene film, while features of the polycrystalline Pt substrate, such as grain boundaries, could be clearly resolved. Large scratches on the Pt substrate can also be seen in the final film, which demonstrates the conformity of coatings formed in this way.

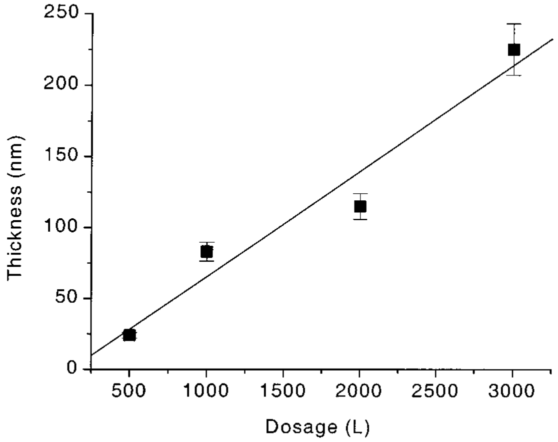

Figure 9. Final polystyrene film thickness as a function of initial monomer dosage, as measured by ellipsometry.

Conclusions

Thin polystyrene films were synthesized via UV photopolymerization on a polycrystalline Pt substrate at temperatures between 110 and 150 K. It was found that the polymerization kinetics was affected by the physical state of the adsorbed monomer and the intensity of the incident UV radiation. Films of a reproducible thickness could be formed by controlling the monomer dosage.

Work is currently under way in our laboratory to more closely examine the effect of the surface on the adsorption and polymerization under these conditions. Future plans include a detailed investigation of the polymerization mechanism as well as the extension to other systems of commercial importance.

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