PHOTOINITIATED POLYMERIZATION ON METAL SURFACES

FREDERICK D. LEWIS,* MARSHALL J. NEPRAS, and HILLARY L. HAMPSCH

Department of Chemistry, Northwestern University,
2145 Sheridan Road, Evanston, IL 60201, U.S.A.

Abstract - Irradiation of acrolein vapors in the presence of films of nickel and other metals results in the formation of thin films of polyacrolein on the metal surface. The polyarcrolein film protects the metal surface from abrasion and corrosion. Polymer growth is more rapid on oxidized vs. unoxidized metal surfaces indicating a role for surface oxide sites in the polymerization process. Several other monomers investigated fail to form adhesive polymer films on metal films, but can be copolymerized with acrolein.

The formation of polymers upon irradiation of the monomers acrolein[1] and methyl methacrylate[2] in the vapor phase was reported nearly 50 years ago. Polymerization of acrolein results in the formation of a white powder on the walls of the irradiation vessel, while polymerization of methyl methacrylate results in the formation of an aerosol which deposits on the walls of the irradiation vessel. Polymerization of a monomer vapor in contact with a metal surface was initially reported in 1961 by White,[3] who observed selective poly-1,3-butadiene deposition on the areas of freshly prepared lead or tin films upon exposure to UV light.[3] Subsequent investigations have established that a number of volatile monomers can be deposited as uniform thin films on metal surfaces using UV, electron beam, or plasma excitation.[4] Recently, UV laser induced polymerization has been used to deposit poly(methyl methacrylate) films with submicrometer linewidths on SiO_2 substrates.[5]

Interest in photoinitiated polymerization on metal surfaces has been spurred by the technological applications for this process. Uniform thin films can be used as insulators in electronic devices or simply to protect the metal surface from corrosion or abrasion.[6] Spatially resolved polymerization can be applied to the fabrication of microelectronic devices.[7] In view of these applications it is not surprising that most previous investigations of photoinitiated polymerization have focused on the effects of various physical parameters (monomer pressure, temperature, light intensity, etc.) on the polymerization process and upon the physical properties of the resulting polymers. Relatively little information is available concerning the photoinitiation process or the effects of monomer structure and surface composition upon the polymerization process. We report here our results for the photoinitiated polymerization of acrolein and several other monomer vapors on oxidized metal films and foils. The selective formation of polyacrolein uniform thin films on oxidized metal surfaces is attributed to the interaction of surface oxide sites with the growing, highly cross-linked polymer.

Irradiation of Monomer Vapors. Monomer vapors were irradiated in quartz or Pyrex tubes on merry-go-round apparatus using a 450 W Hanovia medium pressure mercury arc contained in a quartz water-cooled lamp well. The decrease in acrolein vapor pressure with irradiation time is shown in Figure 1 for irradiation in quartz tubes at 27°C. Following a brief induction period (see Figure 1 insert), the monomer pressure decreases with a rate that decreases with time, reaching a limiting value after 2-3 hr irradiation. The decreasing rate of polymer formation can be attributed to a decrease in light absorption and polymerization rate due to depletion of monomer and to the formation of a light-absorbing film on the walls of the reaction vessel. Irradiation
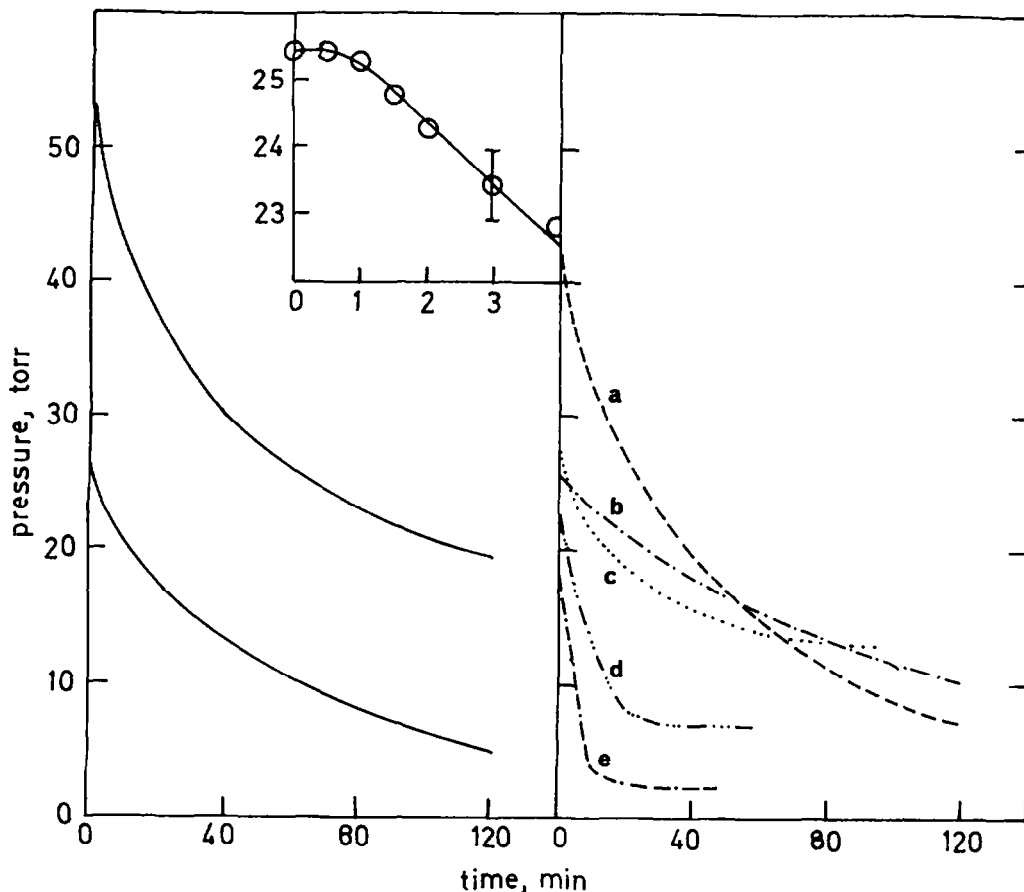
Figure 1. Acrolein monomer vapor
pressure vs. irradiation time.

Figure 2. Monomer vapor pressure vs. irradiation
time for 1,3-butadiene (a), acrylonitrile (b),
crotonaldehyde (c), methyl methacrylate (d), and
methyl acrylate (e).

in Pyrex tubes results in a substantially diminished rate of monomer consumption. These results
are in accord with the wavelength dependence of the quantum yield for disappearance of acrolein
reported by Blacet et al. for 313 nm and 254 nm irradiation ($\phi \sim 0.5$ and 20, respectively).[1]
Evidently, excitation of the lowest, n,π^*, transition results in less efficient homolysis and free
radical initiation of polymerization than does excitation of a higher energy excited state.
Excitation of acrolein vapor at 313 nm is reported to yield CO and C_2H_4 with a quantum yield of 5
x 10^{-3}.[8] Assuming that polymerization is initiated by homolysis products such as vinyl radicals,
the measured quantum yield for disappearance of acrolein at 313 nm requires a chain length > 100
for photoinduced polymerization.

Results obtained for the irradiation of several other monomers under conditions similar to
those used for arolein are shown in Figure 2. The unsaturated esters methyl acrylate and methyl
methacrylate react much more rapidly than do acrolein, acrylonitrile, or 1,3-butadiene. As pre-
viously reported by Melville,[2] no induction period is observed for methyl methacrylate and polymer
growth continues in the dark after irradiation is interrupted.

The differences in the self-initiated photopolymerization processes of acrolein and methyl
methacrylate are no doubt due to the marked difference in the types of polymer formed from the two
monomers. Methyl methacrylate forms a normal vinyl-type polymer which undergoes thermal depoly-
merization only at temperatures above 300°C.[9] Even low-molecular weight telomers are thermo-
dynamically stable at room temperature, accounting for the absence of an induction period for
photoinitiated polymerization and continued polymer growth in the dark. Acrolein does not form a
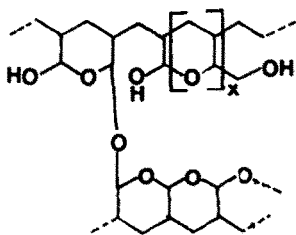stable vinyl-type polymer with pendant aldehyde functional groups, but rather forms highly

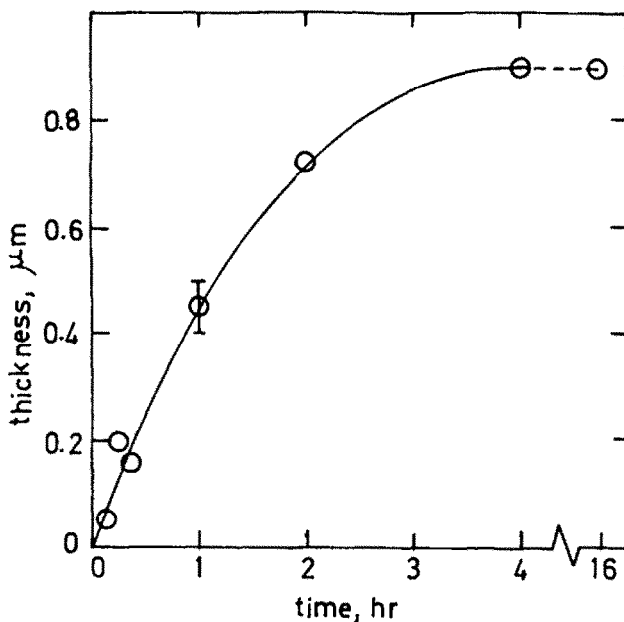Figure 3. Proposed structure for polyacrolein.[10]

Figure 4. Polyacrolein thickness vs. irradiation time.

complexed, crosslinked polymers, often referred to as "disacryl," with cyclic acetal and hemiace-
tal (tetrahydropyran) structural units as well as hydrated and free aldehyde and hydroxyl func-
tional groups (Figure 3).[9,10] Since water is necessary for the formation of the hemiacetal units,
rigorously dried acrolein does not undergo free-radical initiated or photoinitiated polymeriza-
tion.[8,10] The observation of an induction period in the photoinitiated polymerization of acrolein
presumably reflects the thermodynamic instability of small polyvinyl type telomers and the
necessity of water-induced crosslinking to form a stable polymer.

   <u>Polymerization of Acrolein on Nickel Films</u>. Irradiation of acrolein vapor in the presence of
Ni films (ca 5 μm) vapor deposited on poly(ethylene terephthalate) results in the formation of a
thin polymer film on the metal surface. The average thickness of the polymer film can be esti-
mated from the weight gain assuming a bulk density of 1.32 g/cm^3 for polyacrolein.[10] As shown in
Figure 4, the thickness of the acrolein film formed on polymer-supported Ni (100 torr acrolein)
increases rapidly during the first 2 hr of irradiation, but more slowly at longer irradiation
times. The slow rate in polymer growth for long irradiation times parallels the decrease in
monomer consumption (Figure 1). The rate of monomer consumption is essentially the same in the
presence or absence of the metal film; however, 20-50% on the monomer consumed is deposited on the
metal surface, depending upon the reaction conditions. Since the surface area of the metal film
is only ca 5% of that of the quartz reaction vessel, polymer growth on the metal surface must be
more rapid than in the vapor phase or on the quartz surface.

   The acrolein used in this investigation contains 3% azeotropic water. Rigorously dried acro-
lein fails to undergo photoinitated polymerization under the conditions of our investigation;
whereas acrolein vapor to which > 10% water has been added polymerizes nonselectively on all
exposed surfaces of the irradiation tube. The rate of polymer growth is evidently critically
dependent upon the presence of water due to its role in the formation of the thermodynamically
stable, crosslinked disacryl structure (Figure 3).[10]

   The thickness of the polyacrolein film formed on polymer-supported Ni films is dependent upon
the initial acrolein pressure, increasing from ca 0.15 μm at 10 torr to 1.7 μm at 160 torr initial
pressure. This trend is consistent with the observed pressure dependence of monomer consumption
after several hours of irradiation, the acrolein consumption increasing with initial pressure
(Figure 1). Variation of the reaction temperature over the range 10° to 45°C has little effect on
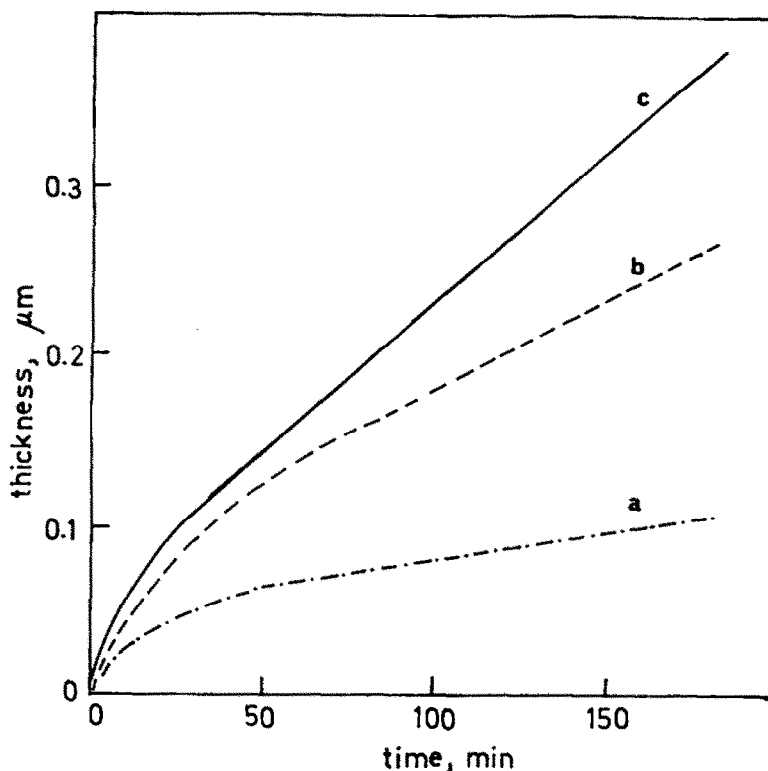
Figure 5. Polymer growth of acrolein (5 torr) on nickel films (0.4 μm), (a) immediately after sputtering, (b) 10 min after sputtering, (c) after 8 hr exposure to the atmosphere.

the rate of polymerization or the ultimate thickness of the polyacrolein. Irradiation parallel or perpendicular to the metal surface for short irradiation periods (<2 hr) gave similar results; however, prolonged irradiation perpendicular to the metal surface results in degradation of the polymer film as reflected by decreased resistance to aqueous HCl (vide infra). The similar rates of polymer formation upon parallel or perpendicular irradiation and the failure of the metal film to increase the rate of monomer consumption indicate that initiation of polymerization occurs in the vapor phase rather than at the metal surface. Diffusion of photogenerated initiating radicals or low molecular weight growing polymeric particles to the metal surface is followed by more rapid polymer growth on the metal surface than in the vapor phase or on the quartz surface. Selective polymer growth on the polymer surface could reflect either a higher concentration of monomer in the metal ad-layer than on quartz or a catalytic effect of the metal surface.

The effect of nickel surface oxidation was probed using 0.4 μm Ni films vapor deposited on a quartz microbalance contained in a stainless steel vacuum chamber. Results obtained for admission of 4 torr acrolein to the vacuum chamber (a) immediately after sputtering of the Ni surface, (b) after a 10 min delay, and (c) after 8 hr exposure of the metal surface to the atmosphere are shown in Figure 5. Irradiation of the Ni-coated microbalance using the unfiltered output of a 200 W Oriel Hg-Xe lamp resulted in a faster rate of polymer growth for the oxidized (c) vs. freshly sputtered (a) surface. The intermediate growth rate for sample (b) indicates that oxidation of the metal surface occurs rapidly even in the vacuum chamber at 5×10^{-6} torr. The data in Figure 5 displays an initial period of rapid surface polymerization followed by a period of slower growth to a thickness of ca 4.0 μm after 3 hr irradiation. The difference in the polymer growth curves for vacuum chamber (Figure 5) vs. quartz tube (Figure 4) reflects the depletion of monomer under the conditions of the latter, but not the former experiment.

<u>Characterization of the Polyacrolein Films</u>. Scanning electron micrographs (SEM) of the poly-acrolein formed on a polymer-supported Ni film are shown in Figure 6. The most prominent surface
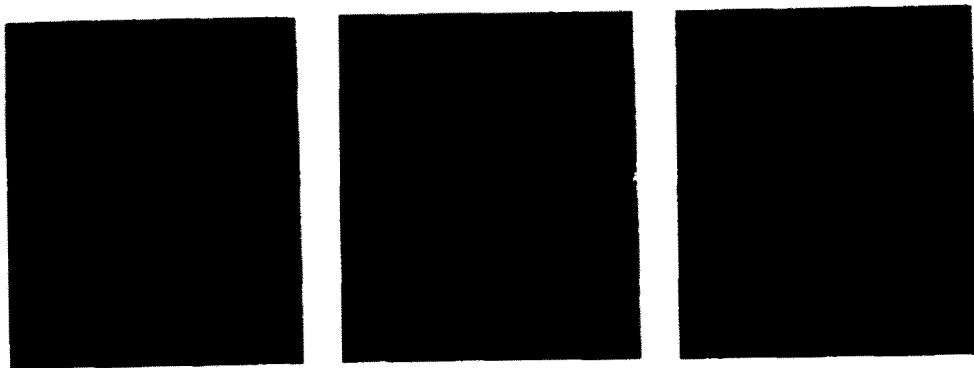
Figure 6. Scanning electron micrographs of polyacrolein on nickel:
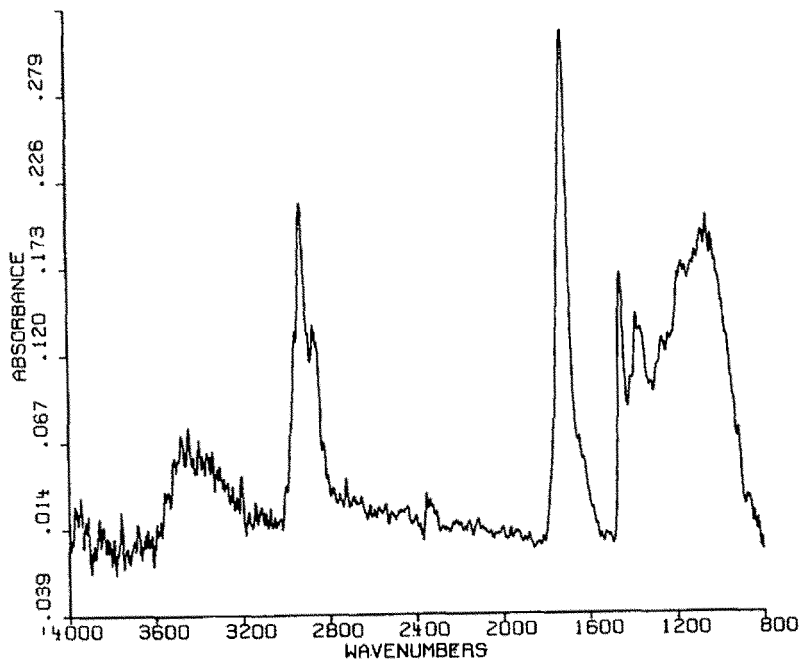(a) 200, (b) 2,000, (c) 20,000 magnification.

Figure 7. FTIR spectrum of polyacrolein on nickel.

feature is an irregular array of ellipsoidal particles with diameters ranging from 2-4 μm. It is interesting to note that particles with a similar size distribution are obtained by radiation polymerization of liquid acrolein at low temperatures.[11] Particle size is limited in solution by the insolubility of the polymer particles in the monomer phase. Particle size in the vapor phase is presumably limited by collision rates with the metal, or quartz surfaces in the irradiation tubes and by collision with other particles. The 2,000 magnification SEM shows evidence of particle aggregation. The use of a focused light source or laser results in the formation of large aerosol droplets which deposit nonselectively on all the surfaces of the irradiation tube. Thus slow initiation of gas phase polymerization is necessary in order to obtain selective polymerization on the metal surface.

The infrared reflectance spectrum of polyacrolein on Ni is shown in Figure 7. The spectrum is similar to that obtained by free radical initiated polymerization of acrolein,[12] except that the ratio of OH/C=O intensities is much smaller for our sample. Immersion of the polymer film in 10% aqueous HCl followed by drying results in an increase in the OH/C=O intensity ratio. Evidently the ratio of free aldehyde/acetal or hemacetal groups in the cross-linked polymer (Figure 3) is larger for the vapor-deposited polymer film than for polyacrolein formed by more conventional free-radical initiated polymerization.

Polyacrolein films of 0.1-2.0 μm thickness on Ni are resistant to abrasion and corrosion. The

Ni film can readily be removed from its poly(ethylene terephthalate) support using a pencil eraser
with moderate pressure. Polyacrolein coated films are resistant to this crude abrasion test. The
Ni film can also be removed by dissolution from its polymer support by 10% aqueous HCl within
several min at 25°C. Polyacrolein films protect the Ni surface from corrosion by HCl. After >30
min exposure the poly(ethylene terephthalate) support and metal film are dissolved leaving a clear
continuous film of polyacrolein. The metal-free polyacrolein film thereby obtained has an IR
spectrum similar to that of the metal-supported film (Figure 7), except for a larger OH/C=O inten-
sity ratio.

The fact that continuous polyacrolein films can be obtained by dissolution of the Ni film and
its polymer support indicates that the ellipsoidal particles observed by SEM (Figure 6) must be
located on top of a continuous polymer film. The continuous film is presumed to be formed by
polymer growth in the adlayer formed by the monomer on the metal surface rather than by agglomera-
tion of polymer particles formed in the vapor phase.

The strong adhesion of the polyacrolein films to the Ni surface suggests the existance of a
strong physical or chemical bonding interaction between the metal surface and polymer. In view of
the more rapid growth of polymer on oxidized vs. unoxidized metal surfaces (Figure 5) it seems
likley that surface oxide sites are responsible for adhesion. In order to test this hypothesis,
oxidized Ni films were exposed to the Lewis acid BF_3, which should coordinate strongly with basic
surface oxide.[13] Removal of nonabsorbed BF_3 followed by introduction of acrolein vapor and irra-
diation produced a polymer film which could easily be removed from the Ni surface by abrasion or
simply by flexing the poly(ethylene terephthalate) support.

Polymerization of Acrolein on Other Metals. The photoinitiated polymerization of acrolein
vapor on vapor deposited films of Ag, Al, Co, and Cu on poly(ethylene terephthalate) was also
investigated. Polymerization was observed in all cases as evidenced by weight gain and by
resistance of the acrolein-coated films to abrasion and to 10% aqueous HCl. Polymer growth on
oxidized Ag, Al, Cu, and Ni films occurred at comparable rates while Co films appeared to be more
reactive. Polymerization of acrolein was also observed to occur on pure metal foils of Ag, Al,
Co, Cu, Ni, and Zn.

Results obtained for polymer growth on Cu films deposited on a quartz microbalance in a vacuum
chamber are shown in Figure 8. As is the case for Ni films, polymer growth is more rapid on Cu
films which have been exposed to air prior to introduction of acrolein vapor (curve a vs b). The
rate of polymerization is similar for 5 vs 60 torr acrolein and for 2 vs 10 μm thick Cu films.
The initial rates of polymerization of acrolein of Cu and Ni films is similar; however, the change
in rate obvserved for Ni (Figure 5) is not evident for Cu.

Polymerization of Other Monomers on Nickel. The irradiation of several volatile monomers in
the presence of Ni films was investigated. Acrylonitrile yielded very thin films (<0.1 μm) which
provided the Ni surface with some protection from corrosion and abrasion; however, the degree of
protection is less than that obtained from thicker acrolein films. Several other monomers
(crotonaldehyde, methyl acrylate, methyl methacrylate, methyl vinyl ketone, and 1,3-butadiene)
which undergo polymerization upon irradiation in the vapor phase (Figure 2), fail to form protec-
tive polymer films on the metal surface. The polymer oils or powders deposited on the metal sur-
face can be easily wiped off of the metal and offer little or no protection from corrosion or
abrasion.

The irradiation of mixtures of acrolein and other momomer vapors in the presence of metal
films was also investigated. Protective metal films were obtained using 2:1 or 1:1 mixtures of
acrolein vapor with acrylonitrile, methyl acrylate, and methyl methacrylate. An infrared spectrum
of the polymer film obtained from a 2:1 mixture of acrolein and methyl acrylate more nearly
resembles that of poly(methyl methacrylate) than that of polyacrolein. Copolymerization of
acrolein with a number of common momoners has been investigated by Schulz et al.[14] and found to
obey the expression

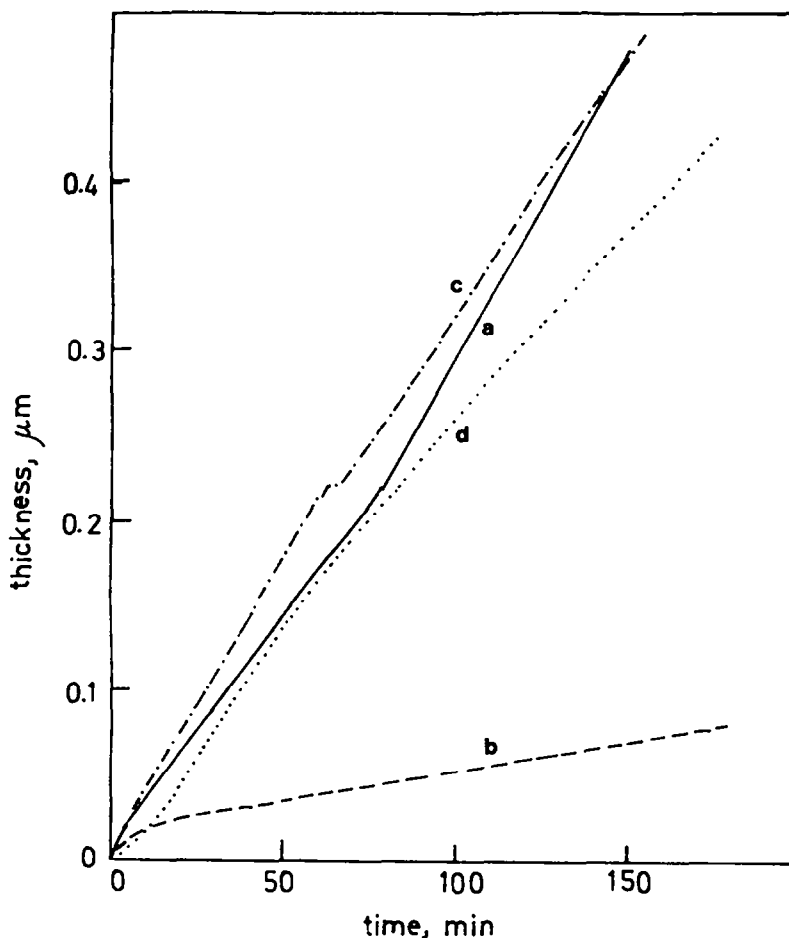$$\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1]+M_2}{[M_1]+r_2[M_2]}$$

Figure 8. Polymer growth of acrolein on copper. (a) 5.0 torr acrolein
(a) 5.0 torr acrolein on 10 μm oxidized copper, (b) 5.0 torr acrolein on 10 μm par-
tially oxidized copper, (c) 60 torr acrolein on 10 μm oxidized copper, (d) 5.0 torr
acrolein on 2 μm oxidized copper.

in which m_1 and m_2 are the mole fractions of acrolein and the second monomer in the copolymer,
M_1 and M_2 are the original monomer mole fractions, and r_1 and r_2 are the reaction rate ratios,
k_{11}/k_{12} and k_{22}/k_{21}, as normally defined. Based on Schulz's values of $r_1 = 0.2$ and $r_2 = 10.0$ for
acrolein/methyl methacrylate and the pressures of acrolein (70 torr) and methyl methacrylate (30
torr), values of $m_1 = .22$ and $m_2 = .78$ would be predicted, in accord with the observed changes in
the IR spectra. Thus a copolymer with a high acrylate content can be obtained on the metal
surface. Layered polymers can also be prepared by first irradiating the metal film with acrolein
vapor at 254 nm and then introducing methyl methacrylate and irradiating at 313 nm. A polymer
film with superior resistance to 10% HCl was obtained in this manner.

Concluding remarks. The selective formation of polyacrolein films on oxidized metal surfaces
appears to be dependent upon both the kinetics of photoinitiated polymerization and the interac-
tion of the metal surface with acrolein monomer and polymer. The slow growth on polyacrolein in
the vapor phase allows selective polymerization at the metal surface to compete with nonselective
polymer deposition on all surfaces of the irradiation tube. The faster rate of polymer growth on
oxidized vs unoxidized metal films and the absence of adhesion to BF$_3$-treated films indicates a
special role for surface oxide sites in both the polymerization and adhesion process. Carbonyl-
containing molecules are proposed to interact with metal-oxide surfaces by interactions of surface
oxide (Lewis base) with carbonyl carbon (Lewis acid)[15] or surface metal with carbonyl oxygen.[16,17]

Acrolein is known to be strongly adsorbed on cuprous oxide[18] and zinc oxide[19] surfaces, thermal desorption from the latter surface reqiring a temperature of 180°C.

Surface metal oxide may serve to promote free radical initiated polymerization by chemically bonding to the aldehyde carbonyl carbons and thus help convert the unstable "polyacrolein" to the stable crosslinked "disacryl." The variation in the rate of acrolein polymerization may reflect differences in the Lewis base strength of the various metal oxides. For example, the metal oxides of Co and Ni are known initiators of anionic polymerization reactions, whereas the oxides of Al are relatively unreactive with organic molecules.[17]

Experimental Section. Monomers were all commercially available materials and were distilled under vacuum and degassed via freeze-pump-thaw cycles prior to use. Acrolein (Aldrich, 3% H_2O) was used as received or rigorously dried by repeated distillation from $CoCl_2$. Vapor deposited metal films supported on poly(ethylene terephthalate) were provided by 3M. Metal foils (Aldrich, gold label) were used as received. Metal films and foils were cut into 0.6 x 9.0 cm strips and placed into quartz or Pyrex tubes (1.3 x 15 cm) equipped with #7 Ace tread joints. Non-rigid films or foils were supported on ground-glass flats with 3M double-stick tape. The tubes were connected to the vacuum line via the Ace thread and a high vacuum Teflon stopcock attached to an O-ring joint. The tubes were evacuated, filled with a known pressure of monomer, removed from the vacuum line, and irradiated on a merry-go-round apparatus in a water bath with a 450 w Hanovia medium pressure mercury arc contained in a quartz water-cooled lamp well. Monomer pressure was measured at various irradiation intervals by replacing the monomer on the vacuum line and determining the pressure in a small confined volume with a MKS baratron gauge. The volatile contents of the tube were recondensed at 77°K, the tube reclosed, warmed, and irradiation continued. Following irradiation, the films were removed from the tube and weighed.

The stainless steel vacuum chamber was constructed at 3M and is equipped with four 1.5 x 10 cm quartz windows. The chamber is evacuated using a standard roughing pump and a CTI-Cryo-Torr 8 pump which can be isolated from the main chamber. Metals were deposited on a quartz microbalance using a 5 x 12 in Vacuum Technology magneton cathode with a Plasma-Therm Type HFS 3000E RF generator with automatic matching. The microbalance was cooled with 2°C circulating water during metal deposition and polymerization studies. Copper and nickel were sputtered onto the microbalance using argon gas at a pressure of 10 microns and a flow of 10 cm^3 s^{-1}. Copper deposition at a power of 300 W occurred at a rate of 1.5 Å s^{-1} producing metal films < 100 Å thick. Nickel was deposited from 0.125 mm thick nickel foil mounted on the cathode with its magnets left in place. Nickel deposition at a power of 250 W occurred at a rate of 0.5 Å s^{-1} producing metal films < 400 Å thick.

At given delay times after metal deposition, acrolein vapor was admitted to the vacuum chamber. After stabilization of the microbalance, irradiation was initiated using the unfiltered output of a 200 W Oriel Hg-Xe lamp. The collimated light beam was larger than the microbalance surface and was directed at the microbalance surface with an incident angle of ca. 15°. The weight gain recorded upon illumination was recorded as a function of time and the results converted to polymer thickness, assuming uniform surface coverage and a polymer density of 1.32 g/cm^3.

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