

Fabrication of Highly Reflective Composite Polyimide Films via in Situ Reduction of Matrix Constrained Silver(I)

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Optically reflective composite polyimide films have been prepared by casting a dimethylacetamide solution of silver(I) acetate, hexafluoroacetylacetone, and the poly(amic acid) derived from 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) and 4,4'-oxydianiline (4,4'-ODA) onto an fully imidized parent BTDA/4,4'-ODA base. Thermal curing of the silver(I)-containing poly(amic acid) topcoat leads to imidization with concomitant silver(I) reduction followed by silver(0) migration/aggregation yielding a reflective, but not conductive, silver surface. This "film-on-film" composite approach minimizes the silver required for the formation of a reflective surface and preserves the essential mechanical and thermal properties of the parent polymer. The metallized films exhibit outstanding metal-polymer and polymer-polymer adhesion, with the strong metal-polymer adhesion attributable to mechanical interlocking and/or encapsulation. Films were characterized by X-ray, DSC, TGA, XPS, TEM, and AFM.

Introduction

The formation of metallic films on inorganic and organic polymeric substrates is of substantial interest. Surface metallization is usually accomplished by some form of vapor deposition, i.e., chemical, physical, or sputtering deposition techniques.¹ Our interests have centered on the metallization of polymeric films.^{2,3} Organic polymeric films supporting metal layers offer advantages in weight, flexibility, and elasticity. Applications for metallized polymeric films are numerous, including: (a) highly reflective thin-film concentrators/reflectors in space environments for solar thermal propulsion,⁴ solar dynamic power generation,⁵ and γ -ray imaging telescope systems;⁶ (b) the terrestrial concentration of solar energy to generate electric power and

process heat;⁷ (c) large-scale radio frequency antennas in space;⁸ (d) bactericidal coatings;⁹ (e) surface conductive flexible polymeric tapes,¹⁰ (f) contacts in microelectronics,¹¹ and (g) the construction of "adaptive optical"¹² and "elastomeric optical"¹³ devices. For large-scale space applications metallized polymeric films are particularly attractive. Such film-based metallic reflectors, concentrators, or antennas have the ability to be packaged into relatively small volumes of low weight and subsequently unfurled upon deployment to form large structures. It is the synthesis of smooth, continuous, flexible, and large surface-silvered polymeric films, which is the subject of this report.

We have chosen to focus on the silver metallization of polymeric films since silver yields a superb mirror. The specular reflectance of silvered mirrors over the range of the solar spectrum is unmatched.¹⁴ Silver also has the highest electrical conductivity at $6.3 \times 10^{-7} \Omega$

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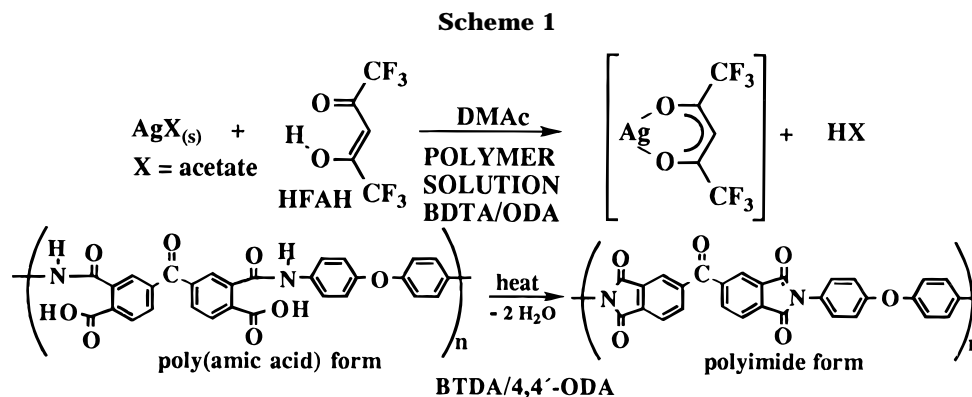
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m)⁻¹. The silver(I)–silver couple has a favorable standard electrode potential which allows it to be readily reduced during thermal imidization of a poly(amic acid) film. We chose to study the construction of silvered surfaces on polyimide films derived from 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) and 4,4'-oxydianiline 4,4'-ODA, (Scheme 1) since polyimides have unusual thermal-oxidative and chemical stability.^{15–17} Such stability is essential for the composite film to survive thermal curing in an oxygen atmosphere where silver(0) is known to function as an oxidation catalyst toward carbon framework molecules.¹⁸ BTDA/4,4'-ODA has also given excellent silver and palladium films in previous work involving similar in situ formation of metallized surfaces.^{2,3,19}

Recently we reported^{2b,c} the successful surface silver metallization of thermally stable polymers which involves the in situ synthesis (Scheme 1) of the soluble (hexafluoroacetylacetonato)silver(I) complex, [AgHFA], in dimethylacetamide containing the poly(amic acid) form of the BTDA/4,4'-ODA. During all stages of film processing the [AgHFA] complex remains homogeneously and presumably mononuclear^{20,21} or at most dinuclear²² dispersed in the polymer matrix. The procedure produces films on the order of 15 cm² or smaller, which have smooth and continuous highly reflective, but not electrically conductive, silver layers. This silver mirror (60–80 nm thick) exhibits outstanding adhesion to the polyimide surface, and the composite metal–polymer films retain the essential mechanical properties of the unmetallized parent polymer.

During thermal curing of the [AgHFA]–BTDA/4,4'-ODA films the formation of silver metal on the glass side causes the film to become completely detached from

the glass plate except at the very edges where the film remains firmly adhered. Thus, during the cure, beginning at ca. 180 °C, the entire metallizing film, except for the edges, lifts from the glass plate due to the formation of gaseous effluents such as residual solvent. Eventually, the released gases permeate through the polymer, and the film relaxes smoothly back down onto the plate by ca. 220 °C. While this film-detachment process does not adversely affect the reflective properties of films which are of smaller size (ca. 225 cm²), with films of larger area the weight of the film itself becomes such that the gas pressure generated during the cure is insufficient to sustain a single inflated dome. Thus, with large-area films, the curing metallizing films are inflated during the thermal cycle from the glass plate in several sections, like a relief map, which ultimately results in irregularly placed crease lines. These crease lines provide distortions of the reflectivity and compromise mechanical properties, and it is essential to exclude them. In this paper we report on a procedure that eliminates the crease lines in the synthesis of films of large area and produces an overall composite mirror which has mechanical properties more like those of the parent polymer. Also, the procedure reported herein enables polymeric silver mirrors to be produced with an enhanced silver economy for the following reason. During the reduction of the silver(I)–HFA complex to native silver, only a small portion of the silver atoms or clusters migrates to the surface to form the mirror. The majority of silver clusters remain uniformly dispersed as nanometer-sized particles throughout the polymer matrix. Thus, most of the silver in the polymer does not contribute to the reflectivity of the surface.

In this paper we report the synthesis and characterization of highly reflective silver-metallized BTDA/4,4'-ODA films which are cast onto undoped BTDA/4,4'-ODA bases leading to entirely smooth and continuous metallized surfaces. We report the characterization of these silvered films with respect to reflectivity, composition, poly(amic acid) viscosity, thermal properties, electrical conductivity, adhesion at the polymer–polymer and polymer–metal interfaces, and transmission electron, scanning electron, and atomic force microscopy.

Experimental Section

Materials. 4,4'-ODA and "Ultrapure" BTDA were obtained from Wakayama Seika Kogyo Co., Ltd. (via Kennedy and Klim, Inc.) and Allico Chemical Corp., respectively. The 4,4'-ODA was used as received. Depending on the viscosity desired, the BTDA was used as received, dried at 100 °C for 4 h, or dried under vacuum at 150 °C for 5 h prior to use. The

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latter drying condition gave the highest molecular weight poly(amic acid). Presumably the lower viscosity resins result from carboxylic acid rather than dianhydride termini on the BTDA monomer. The melting points of the dry monomers as determined by differential thermal analysis were 218 and 188 °C, respectively. DMAc (HPLC grade <0.03% water) and silver(I) acetate (99.99%) were purchased from Aldrich Chemical Co. and were used without further purification. Hexafluoroacetylacetone (HFAH) (Aldrich and Eastman Organic Chemicals) was redistilled under nitrogen before use.

The BTDA/4,4'-ODA poly(amic acid) solutions employed in this study were prepared with the dianhydride offset at 1 mol % relative to the diamine at 12% solids (w/w) in DMAc. The resin preparations were performed by first dissolving the diamine¹⁸ in DMAc in a resin kettle flushed with dry nitrogen and then adding the dianhydride. The resin was stirred for a minimum of 5 h. The inherent viscosities are cited in the Table headings for each group of films.

Preparation of BTDA/4,4'-ODA Metallized Films. Silver(I) acetate is not soluble in DMAc or a DMAc solution of the BTDA/4,4'-ODA poly(amic acid). If silver(I) acetate without hexafluoroacetylacetone is added to the amic acid form of BTDA/4,4'-ODA immediate gelation of the resin occurs. However, if one or more equivalents of HFAH is dissolved in DMAc followed by the addition of silver(I) acetate, dissolution occurs readily and completely with formation of the (hexafluoroacetylacetonato)silver(I) complex. Thus, silver-containing resins were prepared by first dissolving silver(I) acetate in a small volume of DMAc-containing HFAH. (DMAc (1 g) containing the required amount of HFAH was used to dissolve silver(I) acetate for every 5 g of 12% BTDA/4,4'-ODA solution.) The 12% poly(amic acid) solution was then added by weight to give the desired concentration. The light yellow silver(I)-doped resins were stirred thoroughly for 30 min before casting films. Although there is always concern for photochemical decomposition with silver systems, these doped films did not appear to be light sensitive for at least a 24 h period, i.e., no silver particles were observed and no discoloration of the poly(amic acid) films was observed. Thus, special precautions were not necessary nor taken to protect the films in this study from light.

A series of films with BTDA/4,4'-ODA solutions of viscosities 1.1, 1.7, and 2.2 dL/g with varying concentrations of silver(I) acetate and HFAH were prepared on undoped BTDA/4,4'-ODA bases which were cast on soda lime glass plates and thermally imidized in a forced air oven with the following thermal cycle: 10 min to 100 °C for 1 h, 15 min to 200 °C for 1 h, and 30 min to 300 °C for 1 h. This thermal cycle is referred to as the standard cure cycle. The thicknesses of the BTDA/4,4'-ODA bases are reported in the Tables and were generally in the range 0.60–1.0 mil. Doped poly(amic acid) solutions were cast as films onto the BTDA/4,4'-ODA bases using a doctor blade with cured thicknesses for the composite films in the range 1.5–2.0 mil. After remaining in an atmosphere of dry slowly flowing air (10% relative humidity) for 18 h, the tack-free films were thermally cured in a forced-air oven using the standard cure cycle. The tack free films still retained ca. 20% solvent. The films were removed easily from the glass plates by soaking in distilled water for ca. 15 min after scoring the edges with a razor blade. Samples for reflectivity measurements were made by casting or affixing films onto 35 cm² glass plates; no difference in reflectivities between these two techniques was observed.

Characterization Techniques. Monomer melting points were determined by DTA at a heating rate of 20 °C/min on a DuPont Thermal Analyst 2000. Inherent viscosities of the poly(amic acid) resin were obtained at a concentration of 0.50% (w/w) in DMAc at 35 °C. Thermogravimetric analyses (TGA) were obtained on the cured films in both flowing air and nitrogen (50 mL/min) at a heating rate of 2.5 °C/min using a Seiko TG/DTA 200 or TG/DTA 220 instrument. Glass transition temperatures were determined on films in sealed pans with a Seiko DSC 210 system with a heating rate of 20 °C/min. Linear coefficients of thermal expansion (CTE) were obtained with a Seiko TMA 100 station and are reported as the average value over the temperature range 70–125 °C. The

CTE samples were desiccated for 24 h before analysis. Surface resistivities of all films were measured with an Alessi four-point probe. Mechanical properties were determined with a Sintech 2000/2 table-top load frame. Transmission electron microscopy (TEM) was done at the Virginia Institute of Marine Science, Gloucester Point, VA, on a Zeiss CEM-920 transmission electron microscope. Scanning electron microscopy (SEM) was performed on a Hitachi S-510 instrument. Reflectivity measurements were made (relative to a Perkin-Elmer polished aluminum mirror with a reflectivity coefficient of 0.92 at 531 nm) with a Perkin-Elmer Lambda 5 or 9 UV/vis spectrophotometer equipped with a variable-angle specular reflectance accessory using a wavelength of 531 nm. X-ray data were obtained with a Philips 3600 diffractometer. X-ray photoelectron spectra were obtained with a Perkin-Elmer Phi Model 5300 ESCA system by Dr. F. Cromer at Virginia Polytechnic Institute and State University. Atomic force micrographs were done in the contact mode with a Digital Instrument NanoScope III Multimode Scanning Probe Microscope.

Results and Discussion

Film Fabrication Considerations. An increasingly important route to metallized films is chemical vapor deposition,^{1,23} which externally deposits metal on a substrate surface by thermal decomposition of an appropriate molecular precursor. For silver there is a distinct lack of stable, volatile complexes which serve as CVD precursors. Although recent progress has been reported by Girolami et al.,^{21,24} Puddephatt et al.,²⁵ and Kudas et al.²⁶ in the synthesis of appropriate silver complexes for CVD and in understanding why earlier silver complexes have not been as volatile as anticipated from copper(I) analogues,²⁷ yet the preparation of very large films via silver CVD will most likely remain a difficult and costly technical problem. The approach to silver metallized films that we have developed with silver(I) acetate and hexafluoroacetylacetone⁹ is an internal rather than external deposition of metal from a molecular precursor which is a silver(I) β -diketonate complex. Surface-metallized polymeric films are generated with outstanding adhesion of metal to polymer. The approach of our work might be considered to be the inverse of chemical vapor deposition since the native metal arises via reduction from within the polymer matrix to ultimately generate the metallized surface. Whereas in CVD a silver(I) complex such as [(HFA)-(PEt₃)Ag]²⁰ or [(HFA)(PMe₃)Ag]^{21b} is volatilized and externally passed over a heated substrate surface (often with a carrier gas such as hydrogen), in this study the silver(I)–HFA complex, which is virtually identical with the CVD complexes above, has been prepared in situ in a BTDA/4,4'-ODA poly(amic acid)–DMAc solution. A thermal cycle reaching a maximum temperature of 300 °C leads to reduction of silver(I) to native silver with partial phase separation to give a highly mirrored polymer surface on the air-side of the cured composite film as is apparent from the reflectivity data in our previous work⁹ and in the tables of this paper. Signifi-

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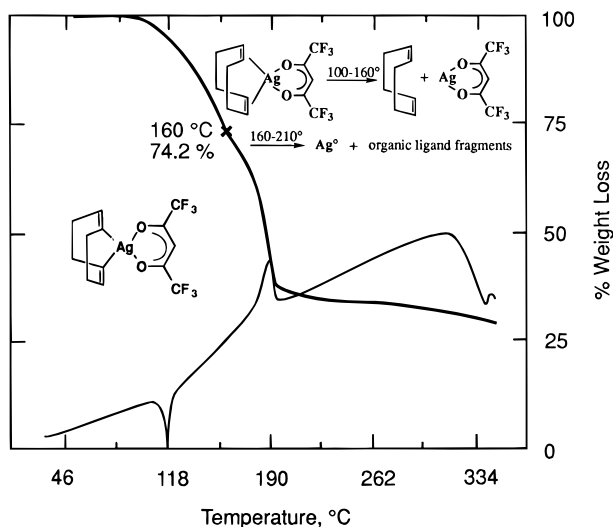


Figure 1. Thermal gravimetric curve for (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)(η^4 -1,5-cyclooctadiene)silver(I) run under nitrogen. (The initially lower trace is the DTA curve.)

cant reflectivity is obtained for polymeric films containing 4–12% silver(0) by weight in the cured metal-doped polyimide. Such an in situ reduction of silver(I) in poly(amic acid) films has been demonstrated previously using simple silver(I) salts such as nitrates and carboxylates by Auerbach,²⁸ St. Clair and Taylor et al.,^{29–31} and Endrey³² but has had only limited success; reflectivities, where reported, were 18–46% for the best films. Furthermore, the films formed with silver nitrate and several other silver salts were embrittled and partially degraded. The striking absence of followup publications with other polymeric systems is consistent with a conclusion that these earlier basal silver(I) systems such as nitrate and carboxylates for in situ metallization are of uncertain usefulness.

As described earlier, a BTDA/4,4'-ODA-[AgHFA]-doped resin is cast and thermally cured on a glass plate,⁹ the metallizing film lifts from glass plate in the temperature regime from ca. 180–200 °C. The TGA curve (Figure 1) for the 1,5-cyclooctadiene adduct of [AgHFA]³³ clearly shows that [AgHFA] decomposes over the temperature range of ca. 160–200 °C. This is the same general range where film inflation occurs. No bubbling is observed for silver-free films. It is this film detachment phenomenon that has been solved by the work reported herein as summarized in Tables 1–6, where doped silver(I) BTDA/4,4'-ODA films have been cast on undoped, fully cured, and imidized parent BTDA/4,4'-ODA film bases. All of the composite films reported in the tables remain firmly adhered to the glass base and give smooth and uniformly flat metallized panels. Furthermore, there is both outstanding adhesion at the polymer–polymer interface and at the metal–polymer interface. The films have strongly adhered surface

metal layers and are completely stable to removal of silver by a variety of adhesive tapes. We attribute this adhesion primarily to mechanical interlocking or encapsulation as discussed below. The polymer–polymer interface has never shown any signs of separating even with soaking in water for months. While fully imidized BTDA/4,4'-ODA is generally insoluble in DMAc and other organic solvents, it may be that the strong polymer–polymer interface is due to the fact that on standing for 18 h at room temperature before being subjected to thermal curing a very small portion of the doped BTDA/4,4'-ODA film dissolves into the base film to give excellent adhesion, perhaps involving transimidization between the two layers. Since T_g for BTDA/4,4'-ODA is ca. 275 °C, and the composite metallized films are cured some 25 °C above T_g , the two polymer films may simply thermally weld. However, studies by Kramer et al. of PMDA/4,4'-ODA, which had a T_g of 395 °C, showed that a second PMDA/4,4'-ODA film cast on a fully imidized PMDA/4,4'-ODA base film gave a very sharp interfacial boundary, and the layers were easily peeled apart. They concluded that strong interfacial bonding occurred only when an interpenetration layer of more than 50 nm occurred; with a diffusional distance of 200 nm the composite film exhibited the same strength as the bulk material.³⁴ TEM data, presented later, show a distinct boundary between the silver-containing BTDA/4,4'-ODA layer and the BTDA/4,4'-ODA base layer. Thus, it appears that there is minimal diffusion of silver atoms and clusters into the base BTDA/4,4'-ODA film.

Film Reflectivity. Films for reflectivity and other measurements were prepared using BTDA/4,4'-ODA resins in DMAc with inherent viscosities of 1.1–2.2 dL/g at 35 °C. Since it is essential that there be at least partial migration or phase separation of native silver to give a reflective surface, we thought that there might be an effect of chain length on the diffusion characteristics of the metal atoms and clusters forming within the polymer matrix, with the higher molecular weight resin inhibiting diffusion and the formation of a critical layer of metallic silver at the air-side surface. The data in Tables 1 and 3–5 indicate that for films of similar concentration, such as those with 7.4–8.6% silver, the reflectivity values range from 70 to 81% (at an angle of incidence of 20°). The lowest viscosity resin (1.1 dL/g, Table 1) yielded films with the highest reflectivity. Indeed, for the range of concentrations from ca. 4 to 8.5%, the 1.1 dL/g films gave the highest reflectivities by 5–15 reflectance units (percent). On the other hand, the reflectivity of the 2.2 dL/g films are noticeably higher than the 1.7 dL/g films. Thus, there is no clear trend as to the effect of polymer molecular weight on reflectivity, although the higher reflectivities for the lowest molecular weight resin is consistent with greater ease of metal migration or phase separation in the film of lowest chain length. The 2.2 dL/g resin (at 12 wt %) is much more difficult to process than the other two lower viscosity resins, and as a practical matter, the viscosity of the BTDA/4,4'-ODA resins should not exceed 1.7 dL/g with 12 wt % solutions. All of the silvered films show a decrease in reflectance as the angle of incidence increases. We are uncertain as to the origin of this decrease: it is most likely related to irregularity in particle size and morphology. However, we tentatively

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Table 1. Reflectivity, Resistivity, and X-ray Data for Silver(I) Acetate–Hexafluoroacetylacetone Metallized BTDA/4,4'-ODA ($\eta = 1.1$ dL/g at 35 °C) Films (Base Layer ca. 0.4 mil after Thermal Imidization)

% silver (calc) ^a	polymer repeat unit to silver(0) ratio	HFAH to Ag(I) ratio	% reflectivity of silvered films ^b (as a function of angle)					X-ray <i>d</i> values (10 ⁻⁸ cm)
			20°	30°	45°	55°	70°	
4.3	4.9:1	1.7:1	75	73	63	55	38	2.36 (100), 2.04 (29), 1.44 (13), 1.23 (11)
6.6	3.1:1	1.6:1	77	74	66	58	47	2.36 (100), 2.04 (28), 1.44 (14), 1.23 (12)
8.6	2.4:1	1.8:1	81	77	68	59	51	2.36 (100), 2.04 (30), 1.45 (11), 1.23 (9.1)

^a Calculated for the silver(I) acetate–HFAH dopant system decomposing completely to silver metal and volatile components which are lost from the film. ^b Reflectivity values are relative to a Perkin-Elmer polished aluminum optical mirror set at 100%. See Experimental Section.

Table 2. Thermal and Mechanical Data for the Silver(I) Acetate–Hexafluoroacetylacetone Metallized BTDA/4,4'-ODA ($\eta = 1.1$ dL/g at 35 °C) Films of Table 1

% silver (calc)	polymer repeat unit to silver(0) ratio	CTE (ppm/K)	<i>T</i> _g (°C, DSC)	10 % wt loss °C (air)	10 % wt loss °C (N ₂)	tensile strength (Ksi)	% elongation at break	modulus (Ksi)
control	∞	42.8	275	524	540	21.0	8.3	449
4.3	4.9:1	33.2	276	416	538	22.0	9.8	494
6.6	3.1:1	32.6	275	396	533	20.4	9.1	455
8.6	2.4:1	32.8	275	393	533	20.2	8.7	474

Table 3. Reflectivity, Thermal, Resistivity, X-ray, and Mechanical Data for Silver(I) Acetate–Hexafluoroacetylacetone Metallized BTDA/4,4'-ODA ($\eta = 1.7$ dL/g at 35 °C) Films (Base Layer ca. 0.7 mil after Thermal Imidization)

% silver (calc) ^a	% reflectivity of silvered films ^b (as a function of angle)			<i>T</i> _g (°C, DSC)	10 % wt loss °C (air)	10 % wt loss °C (N ₂)	X-ray <i>d</i> values (10 ⁻⁸ cm)	tensile strength (Ksi) ^c	% elongation at break ^c	modulus (Ksi) ^c
	20°	30°	45°							
control	na	na	na	273	520	535	na	19.7	15.7	450
4.6	60	48	16	276	415	541	2.36 (100), 2.05 (26), 1.44 (12), 1.23 (10)	19.7	11.5	462
6.3	64	52	21	275	413	534	2.35 (100), 2.04 (25), 1.44 (13), 1.23 (12)	20.7	10.6	496
8.6	70	58	29	276	403	540	2.36 (100), 1.45 (30), 1.36 (13), 1.23 (11)	19.6 (20.4) ^c	12.1 (7.5) ^c	462 (480) ^c
10.8	72	60	39	273	405	541	2.37 (100), 1.45 (32), 1.45 (13), 1.23 (12)	17.5	12.5	420

^a Calculated for the silver acetate–HFAH dopant system decomposing completely to silver metal and volatile components which are lost from the film. ^b Reflectivity values are relative to a Perkin-Elmer polished aluminum mirror set at 100%. See Experimental Section. ^c The mechanical measurement values in parentheses are for the identical 8.6% BDTA/4,4'-ODA solution cast directly onto the glass plate without a BTDA/4,4'-ODA base; they are presented for the sake of a direct comparison with the composite film.

Table 4. Reflectivity, Thermal, Mechanical, and Resistivity Data for Silver(I) Acetate–Hexafluoroacetylacetone Metallized BTDA/4,4'-ODA ($\eta = 2.2$ dL/g at 35 °C) Films (Base Layer ca. 1.5 mil after Thermal Imidization)

% silver (calc) ^a	% transmittance of silvered films (as a function of angle)			<i>T</i> _g (°C, DSC)	10 % wt loss °C (air)	10 % wt loss °C (N ₂)	tensile strength (Ksi) ^c	% elongation at break ^c	modulus (Ksi)
	20°	45°	70°						
control	na	na	na	276	506	532	19.9	25.1	391
3.9	67	56	29	278	437	543	19.0	11.7	449
6.7	72	63	38	279	420	542	19.4	20.0	415
8.0	71	62	37	276	424	542	18.7	17.1	424

^a Calculated for the silver acetate–HFAH dopant system decomposing completely to silver metal and volatile components which are lost from the film.

suggest that some diminution in reflectivity is due to the presence of a thin but significant layer of polymer covering the silver surface. This polymer layer increasingly absorbs the incident light as the optical path length through the overlayer increases with increasing angle of incidence. This partial overlayer, which does not give a flat surface but clearly follows the contour of the silver aggregates near the surface as shown from the AFM data presented later, is suggested by several data. First, the surface of all metallized films is not

electrically conductive. This lack of conductivity could be due to the island growth (similar to the Volmer–Weber growth mode in CVD)³⁵ in which small polymeric barriers keep the metallic islands from contact with one another and/or to polymer overlayer covering the entire surface. Second, the X-ray photoelectron spectral composition data presented in Table 7 for the 1.7 dL/g series of metallized films shows that there is a large amount of polymer at the surface of the film with carbon, oxygen, and nitrogen ratios which are reasonably similar to that for the neat BTDA/4,4'-ODA polyimide; silver atoms at the surface sampling depth are a distinct minority. Third, [AgHFA]-metallized BTDA/4,4'-ODA films show virtually no tendency to tarnish for periods up to 1 year. Finally, there is precedent for an overlayer with metallized polyimide films. Reports of overlayers on polyim-

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Table 5. Reflectivity, Surface Resistivity, and X-ray Data for Silver(I) Acetate–Hexafluoroacetylacetone Metallized BTDA/4,4'-ODA ($\eta = 1.7$ dL/g at 35 °C) Films as a Function of Thickness of the Silver-Doped Layer (Base Layer ca. 0.7 mil after Thermal Curing)

percent silver (calc) ^a	thickness of doped layer ^b (mil)	percent transmittance of silvered films ^c (as a function of angle)			X-ray <i>d</i> values (10 ⁻⁸ cm)
		20°	45°	70°	
7.4	4	74	64	45	2.38 (100), 2.05 (27), 1.45 (12), 1.24 (11)
7.4	8	73	62	43	2.35 (100), 2.04 (29), 1.44 (14), 1.23 (11)
7.4	12	69	57	39	2.40 (100), 2.02 (40), 1.46 (23), 1.24 (18),

^a Calculated for the silver acetate–HFAH dopant system decomposing completely to silver metal and volatile components which are lost from the film. ^b This is the thickness of the silver(I) resin before thermal curing. ^c Reflectivity are relative to a Perkin-Elmer polished aluminum mirror set at 100%. See Experimental Section.

Table 6. Reflectivity and Surface Conductivity Data for Silver(I) Acetate–Hexafluoroacetylacetone Metallized BTDA/4,4'-ODA ($\eta = 1.1$ dL/g at 35 °C) Films

% silver (calc) ^a	thickness of doped layer ^b (mil)	thickness of base after cure ^c (mil)	composite film thickness after cure ^c (mil)	thickness of doped layer after cure ^c (mil)	% transmittance of silvered films ^d (as a function of angle)			<i>T</i> _g , °C (DSC)	10 % wt loss °C (air)	10 % wt loss °C (N ₂)
					20°	45°	70°			
6.5	10	0.75	1.25	0.40	72	59	38	275	409	538
6.5	10	0.95	1.40	0.45	71	59	38	275	421	545
6.6	10	0.40	0.82	0.42	77	66	47	275	396	533

^a Calculated for the silver acetate–HFAH dopant system decomposing completely to silver metal and volatile components which are lost from the film. ^b This is the thickness at which the doped resin solution was cast on the BTDA/4,4'-ODA base. ^c Film thickness vary ca. \pm 10% around the film which due to irregularities in the glass plates. ^d Reflectivity values relative to a Perkin-Elmer polished aluminum mirror set at 100%. See Experimental Section.

Table 7. X-ray Photoelectron Spectral Data for the Silvered Surface of the Films of Table 1 (Relative Atomic Percent)

wt % silver in cured film	wt % silver in cured film				
	silver	fluorine	carbon	oxygen	nitrogen
4.3	15.7	2.75	63.7	12.7	5.14
6.6	17.8	2.24	61.3	13.9	4.86
8.6	20.4	1.62	59.2	12.5	6.22

ide films with gold,³⁶ copper,³⁷ and cobalt oxide³⁸ surfaces prepared via in situ metallization procedures have appeared. Also consistent with the presumption of an overlayer contributing to a diminution of reflected light is the fact that surface-conductive silver(0) films that we have prepared with other bidentate ligands do not show any decrease in reflectivity with increasing angle of incidence.³⁹ While some loss of reflectivity with an overlayer is undesirable, this may in part be balanced for selected applications by enhanced tarnish resistance of the surface or by the surface polymer providing a chemically compatible substrate to bind a more substantial protective polymeric topcoat.

In our previous work and for efforts reported herein, the TEM micrographs (Figure 2) show that the reflective silver layer is on the order of 60–70 nm in thickness. The majority of the silver metal resides in the bulk of the film. Thus, in the present work, where a doped film is cast onto a parent base, one should find that the reflectivity of the film-on-film mirror is not sensitive to the thickness of the doped poly(amic acid) layer placed on the base. Indeed, this is seen to be the case from the data in Table 5. This table displays data for three films where the doped (7.4% silver) layer was cast at 4, 8, and 12 mil onto a base that was 1.5 mil thick after

thermal imidization. The reflectivity of the two thinnest silver-containing resins (4 and 8 mil) was somewhat greater, although minimally, than that for the 12 mil resin. Table 6 displays data where the thickness of the base is varied with a constant thickness of the doped layer. There does not seem to be any strong correlation between base thickness of the observed reflectivity, although the thinnest base does have a somewhat higher reflectivity. Since there is no significant diffusion of silver into the base layer, one would not expect the thickness of the base to be a factor. Thus, the base can be adjusted to give whatever mechanical properties (relative to the parent BTDA/4,4'-ODA) are appropriate for a given application.

Thermal and Mechanical Properties. Thermal data for three sets of films prepared with resins of different viscosity are presented in Tables 2, 3, and 5. The glass transition temperatures of the metallized films are essentially the same as those of the parent BTDA/4,4'-ODA films sent through the same cure cycle. This is consistent with the passivity of the silver metal toward organic molecules in general and toward the BTDA/4,4'-ODA polymer functionalities in specific such that there is no cross-linking of chains via interaction with silver clusters or via anaerobic silver catalyzed organic cross-linking reactions which would elevate *T*_g. We have also observed virtually no change in *T*_g for films prepared with [AgHFA] in BTDA/4,4'-ODA which were cast directly onto the glass plates and for BTDA/4,4'-ODA films prepared with silver(I) acetate and trifluoroacetylacetone.³⁹

The linear coefficients of thermal expansion (CTE) for the [AgHFA] films prepared with the resin of 1.1 dL/g viscosity are displayed in Table 2. They are 33.2, 32.6, and 32.8 ppm/K for films with 4.3, 6.6, and 8.6% silver, respectively. These are significantly lower than the CTE for the parent polymer which is at 42.8 ppm/K and lower than those observed in the analogous [AgHFA] films cast directly onto glass at 42.7, 43.6, and 42.8 ppm/K for 5.0, 7.4, and 9.9% silver,^{2c} respectively. The lowered CTE values may be related to the polymer–

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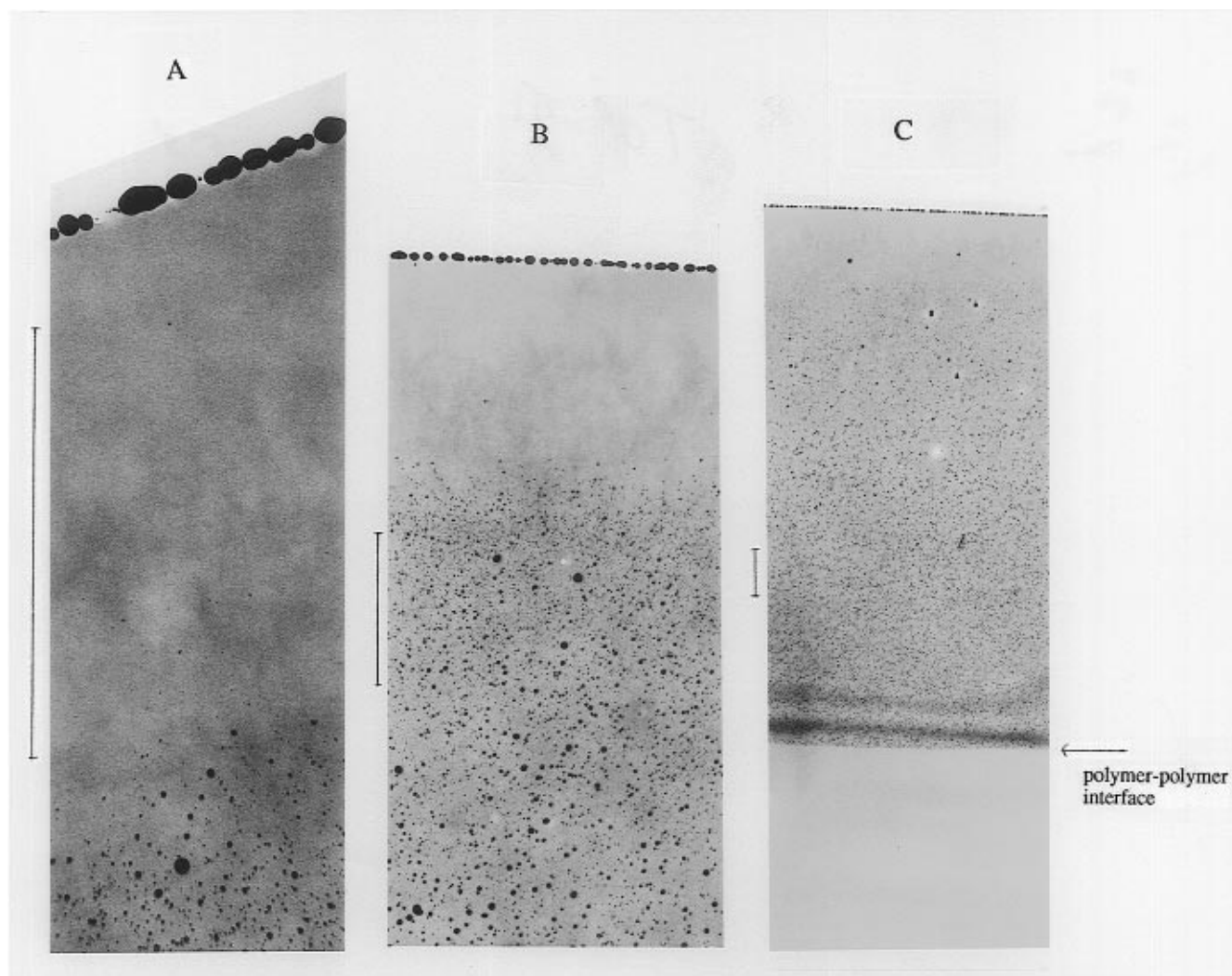


Figure 2. Transmission electron micrographs of the 8.6% silver(I)-hexafluoroacetylacetonate BTDA/4,4'-ODA film ($\eta = 1.1$ dL/g). Perspectives from the air-side surface. (The bars on the left side of each micrograph represent 1 μm .)

polymer interfacial bonding of the film-on-film composite. It is possible that there is metallic promoted cross-linking of the polymer which is giving a lowered CTE, although, as mentioned, we do not see any large increase in T_g values as might be expected for cross-linked films.^{40,41} Since BTDA/4,4'-ODA is a flexible polyimide and the metallized films are relatively thick, we do not attribute the lowered CTEs to any in-plane orientation effects. The films were cooled over a period of 2 h from 300 to 50 °C before removal from the oven.

TEM micrographs shown in Figure 2 clearly show that in addition to surface metallization there are silver clusters rather uniformly distributed throughout the bulk of the top half of the film. The formation of clusters throughout the polymer matrix as well as on the surface diminishes the thermal-oxidative stability of the polyimide in air such that the 10% weight loss temperature is in the range of 100–125 °C lower than that for the control. Nonetheless, the thermal stability of the mirrored films in air is more than adequate for most applications. In a nitrogen atmosphere 10% weight loss is essentially the same as that of the undoped parent polymer. This clearly implicates silver metal as playing

a catalytic role in the degradation of the polymer by oxygen.

Possible contributions to the lowering of thermal-oxidative stability of the BTDA/4,4'-ODA films containing metallic silver include:^{42,43} (1) metal(0) activation of the extended π -electron systems of the polymer to attack by dioxygen or monatomic oxygen and/or metal(0)-induced bond cleavage of the organic framework followed by oxidation, and (2) metal(0)-induced dissociation of dioxygen to surface-adsorbed monatomic oxygen, which then initiates and sustains polymer degradation. The first contribution should be of minimal importance since silver(0)-olefin or arene complexes are not known in stable isolable forms.^{44,45} It is most plausible that polymer degradation involves the second option, that is, metallic silver's well-established ability to bind and reversibly dissociate dioxygen⁴⁶ and generate a strong metal-based oxygen nucleophile.⁴⁷

Metals that form strong bonds with oxygen, such as cobalt, nickel, and copper, dissociate dioxygen readily

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but are usually ineffective oxygen-transfer agents since the oxygen prefers to be incorporated as a stable metal oxide network with a highly negative enthalpy of formation.⁴⁸ Platinum and palladium are sufficiently active to reversibly bind and dissociate dioxygen⁴² but do not form highly stable oxides;⁴⁸ they do, however, activate and cleave bonds in organic substrates.⁴² Thus, they are very useful for complete oxidation of organic species. How this influences polymer degradation is seen in an 8% palladium–BTDA/4,4'-ODA film which exhibited a 10% weight loss in air that was 223 °C lower than the control.⁴⁹ Silver has the weakest metal–oxygen bond ($\Delta H_f^\circ = -32.4$ kJ/mol)⁴⁸ except for gold and is used where selective organic oxidations are desired such as the oxidation of ethylene to ethylene oxide.⁵⁰ Thus, silver-filled BTDA/4,4'-ODA films are more stable than palladium-filled films and exhibit significantly higher polymer decomposition temperatures. Finally, the passivity of gold with a weakly exothermic heat of formation for the oxide ($\Delta H_f^\circ = -9.0$ kJ/mol)⁴⁸ is reflected in the fact that for a self-metallized BTDA/4,4'-ODA-gold film, 10% weight loss is only 23 °C lower than the control.⁵¹

Mechanical data for the three sets of metallized films with BTDA/4,4'-ODA resins of differing molecular weights show that in all cases the tensile strength, modulus, and elongation are not very different from those of the parent undoped films. There appears to be a slight tendency for the modulus to increase, but overall the mechanical properties of the metallized films are essentially those of the parent polyimide. All films remain flexible under a tight crease, and there is no tendency for the silver layer to crack or delaminate. This is consistent with microscopy, XPS, and conductivity data which show that silver aggregates grow at the surface as islands which are separated from one another by intervening polyimide. Thus, the metallized films are highly reflective and completely flexible with excellent adhesion at the polymer–polymer and polymer–metal interfaces. This flexibility with configurational change of the film may prove useful in the area of adaptive optics.^{12,13}

X-ray, Photoelectron Spectral, and Microscopy

Data. X-ray diffraction patterns (Figure 3) for three of the metallized films of Table 3 ($\eta = 1.1$ dL/g) show the four major lines characteristic of face-centered cubic silver. These diffraction patterns are typical for all films listed in the tables. In general the intensities increase modestly with increasing silver concentration, and although there are some variations in line widths, they are not large and suggest for all films prepared in this work that the major scattering is from particles that are greater than 10 nm. No additional reflections were ever observed, which precludes any significant amounts of silver(I) ionic structures such as silver(I) oxide or

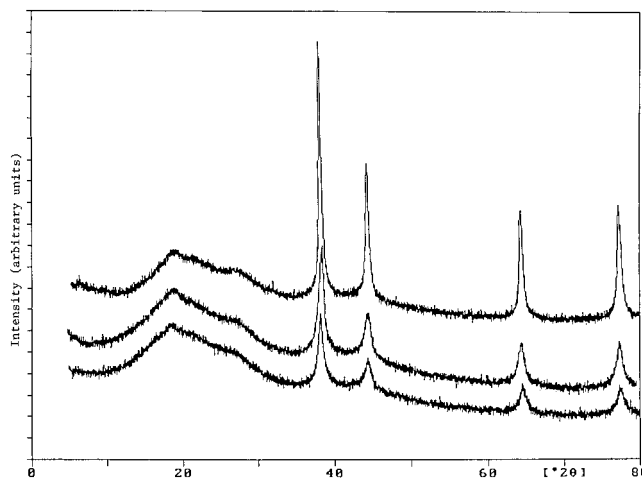


Figure 3. X-ray diffraction patterns for the 4.6, 6.3, and 10.8% silver(I)–hexafluoroacetylacetonate BTDA/4,4'-ODA ($\eta = 1.7$ dL/g) films of Table 5.

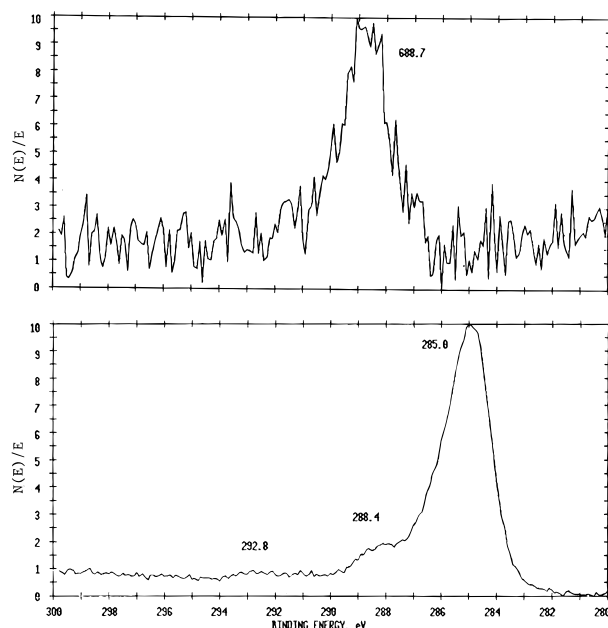


Figure 4. X-ray photoelectron spectra for the 6.6% silver(I)–hexafluoroacetylacetonate BTDA/4,4'-ODA film of Table 1. (Top spectrum: F 1s region; bottom: C 1s region.)

silver(I) fluoride, the fluoride salt arising from degradation of the ligand CF_3 groups. The absence of silver(I) fluoride is consistent with the X-ray photoelectron spectra shown in Figure 4, which displays the F 1s and C 1s regions for the 6.6% silver film of Table 4 (2.2 dL/g). A weak XPS peak for the air side is seen at 293 eV in the C 1s region, which is that expected for CF_3 groups;^{26b} the presence of CF_3 groups is also confirmed by the peak at 689 eV in the F 1s region. Inorganic fluoride, such as in silver(I) fluoride, is observed in the 684–685 eV range. The extent of fluorine incorporation in the polymer is seen from the XPS relative atomic percent data shown in Table 7. The percent fluorine near the reflective surface varies from ca. 1.6 to 2.8%. The $3d_{5/2}$ silver photopeaks in metallized BTDA/4,4'-ODA films occur at 368.4–368.5 eV and are very symmetrical. This is consistent with the absence of any significant amount of silver(I) oxide whose photopeak should appear at 0.5 eV lower in energy.^{3a,52} While silver(I) oxide has been reported as an intermediate product in the thermal decomposition of silver(I) acetate

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in an argon atmosphere, we have not found evidence for its formation in this work.⁵³

Figure 2 shows transmission electron micrographs for the highly reflective (81%) 8.6% film of Table 1. The reflective surface layer is ca. 50–60 nm thick; the bulk of the sample also contains silver particles which vary in size from a few nanometers to ca. 30 nm. It is interesting to observe that just beneath the reflective layer there is an apparent metal-free region of polymer matrix that extends for approximately 1 μm ; we do not know the origin of this effect. This depletion zone has been seen in other work with BTDA/4,4'-ODA with [AgHFA] prepared in situ² and with [AgHFA] introduced into the resin as the η^4 -1,5-cyclooctadiene adduct.³ Atomic force micrographs which we have run on BTDA/4,4'-ODA films have the general appearance of those shown in Figure 5 and are consistent with the relatively uniform undulating silver surface seen in the TEM. For the most reflective film of this study (81% – Table 1) the force micrograph (A) shows rather smooth pillowy islands of silver which are regular in appearance. For the 8.0% film of Table 4 (B), which has a reflectivity of 69%, the metallized surface is more undulating, and the pillowed silver aggregates are more distinct and well separated. The smoother surface of the 81% film is presumably related to higher reflectivity.

Conclusions

We have shown that flexible silvered BTDA/4,4'-ODA polyimide films, which have excellent reflectivity, outstanding metal-polymer and polymer-polymer adhesion, and the essential mechanical characteristics of the native polyimide, can be fabricated conveniently on a BTDA/4,4'-ODA parent polyimide base from a single phase homogeneous (hexafluoroacetylacetonato)silver(I)-poly(amic acid)-DMAc solution. This "film-on-film" approach minimizes the silver required for the formation of a reflective surface. Both silver(I) acetate and HFAH are readily available in high purity and are thermally and photochemically stable; a DMAc solution of [AgHFA], prepared in situ, along with the poly(amic acid) of BTDA/4,4'-ODA is stable with respect to phase separation of either metallic silver aggregates or silver-

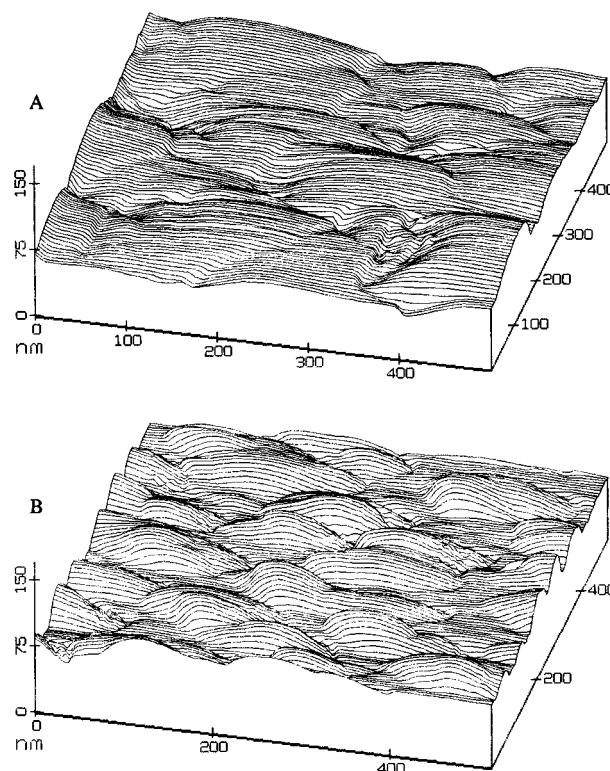


Figure 5. Atomic force micrographs of silver(I)-hexafluoroacetylacetonate BTDA/4,4'-ODA films: (A) the 8.6% film of Table 1; (B) the 8.0% film of Table 4.

(I) species for several days. The cast films do not have to be protected from light. The films prepared with silver(I) acetate and HFAH were not electrically conductive even after several hours of sintering at 300 °C. This is consistent with the islandlike growth of silver aggregates shown by microscopy, XPS, and conductivity data, where the silver aggregates remain separated from one another by intervening polymer. The in situ metallization of additional high performance polymers which exhibit both high reflectivity and surface conductivity is currently under investigation.

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