Synthesis of Reflective Polyimide Films via in Situ Silver(I) Reduction

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Optically reflective polyimide films have been prepared by the incorporation of silver(I) acetate and hexafluoroacetylacetone into a dimethylacetamide solution of the poly(amic acid) formed from 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride (BTDA) and 4,4′-oxydianiline (4,4′-ODA). Thermal curing of the silver(I)-containing poly(amic acid) leads to imidization with concomitant silver(I) reduction, yielding a reflective silver surface. The metallized BTDA/4,4′-ODA films retain the essential mechanical properties of undoped films and have good thermal stability particularly in nitrogen atmospheres. The surface and bulk are not electrically conducting. Several additional soluble silver(I) additive systems were examined, all of which underwent thermal reduction to metallic silver but gave widely varying degrees of reflectivity.

Introduction

Because of its singularly high reflection coefficient (0.93) and low coefficient of solar absorption (0.07), silver is a metal of choice for a reflecting material. The specular reflectance of silvered mirrors is unexcelled, and the hemispherical reflectance of a clean silver film is greater than 97% weighted over 250–2500 nm, the range of the solar spectrum.[1] Thus, silvered polymer films have been proposed and investigated for use in solar energy concentration/conversion devices for both space[2] and terrestrial applications.[3]

Metallized polymeric films are fabricated most often in two stages. First, the polymeric film is prepared, and second, the metal is deposited onto the film surface by external processes including sputtering, thermal and electron beam induced metal vapor deposition, thermal and photochemical induced chemical vapor deposition, electrodeposition, or electroless chemical reduction from solution. Unfortunately, adhesion of the more passive metals such as copper, silver, and gold to the polymer is a common problem even with polymer surface modification (plasma, ion beam, and chemical treatments) prior to metal depostition.[4-6] In this paper we report the preparation of silvered polymeric films via a convenient and efficacious in situ, self-metallization procedure involving thermal-initiated reduction of polymer-soluble silver(I) complexes to metallic silver. This single stage route to silvered polymeric reflectors has the potential to give improved adhesion at the metal–polymer interface as well as a highly reflecting surface over the visible and infrared regions of the electromagmetic spectrum.

Polyimides have outstanding thermal oxidative and chemical stability.[7-9] Thus, we chose to investigate the fabrication of reflective silvered surfaces on the polyimide film derived from 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride and 4,4′-oxydianiline (BDTA/4,4′-ODA). Solutions of BTDA/4,4′-ODA in dimethylacetamide (DMAc) were doped with silver(I) acetate and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone or HFAH). Silver(I) acetate is insoluble in DMAc but readily dissolves upon the addition of HFAH with formation of the silver–hexafluoroacetylacetonate, [AgHFA], coordination compound. A homogeneous single phase polymer–metal solution is essential for formation of a silver mirror. Thermal curing of the silver(I)-doped resins leads to metallized films which are strikingly reflective. We report the characterization of these silvered films with respect to reflectivity, composition, thermal properties, and conductivity. Our silver(I) acetate–HFAH system represents an improvement in efficiency and simplicity with enhanced reflectivity relative to the (1,5-cyclooctadiene)(hexafluoroacetylacetonato)silver(I)–polyimide systems recently reported by Rubira et al.[10] Metallization results using several additional soluble silver(I) additives in BTDA/4,4′-ODA are also reported. A preliminary account of a portion of this work has been reported.[11]

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Experimental Section

Materials. 4,4'-ODA and "ultrapure" BTDA were obtained from Wakayama Seika Kogyo Co., Ltd. (via Kennedy and Klim, Inc.) and Allco Chemical Corp., respectively. The 4,4'-ODA was used as received. BTDA was dried under vacuum at 150 °C for 5 h prior to use. The melting points of the monomers as determined by differential thermal analysis were 218 and 188 °C, respectively. DMAc (HPLC grade <0.03% water), silver(I) acetate (99.99%), silver(I) tetrafluoroborate (98%), tetrameric trimethylphosphine–silver(I) iodide, and AgFOD (99%), i.e., (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)silver(I), were purchased from Aldrich Chemical Co. and were used without further purification. Silver(I) carbonate was purchased form J. T. Baker, silver(I) oxide ("purified") from Fisher Scientific, and silver(I) nitrate (99.9995%) from Johnson Matthey. Hexafluoroacetylacetone (HFAH, Aldrich and Eastman Organic Chemicals), trifluoroacetic acid (TFAAH, Peninsular Chemresearch Inc.), trifluoroacetylacetone (TFAH, Lancaster), and 1,5-cyclooctadiene (COD, Aldrich) were redistilled under nitrogen before use. Dibenzoylmethane (DBM, Eastman) was sublimed under vacuum. Triphenylphosphine (99%) was purchased from Aldrich and used as received. Trimethylphosphine(hexafluoroacetylacetonato)silver(I) and triphenylphosphine(acetylacetonato)silver(I) were synthesized by Professor Robert K. Boggess, Radford University.

The BTDA/4,4'-ODA poly(amic acid) solution employed in this study was prepared with equimolar amounts of monomers at 12% solids (w/w) in DMAc. The resin preparation was performed by first dissolving the diamine[7] 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 viscosity was 1.4 dL/g at 35 °C.

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). However, if one or more equivalents of HFA is dissolved in DMAc followed by the addition of silver(I) acetate, dissolution occurs readily and completely with formation of the silver(I) hexafluoroacetylacetonate complex. Thus, silver-containing resins were prepared by first dissolving silver(I) acetate in a small volume of DMAc containing HFAH. (One gram of DMAc containing 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 were not light sensitive for at least a 24 h period. Thus, special precautions were not taken to protect the films in this study from light.

A series of films with varying concentrations of silver(I) acetate and HFAH were made as reported in Tables 1 and 2. Undoped and doped poly(amic acid) solutions were cast as films onto soda lime glass plates using a doctor blade set at 380–430 μm to obtain cured films approximately 25 μm in thickness. After remaining in an atmosphere of dry slowly flowing air (10% relative humidity) for 15 h, the tack-free films were thermally cured in a forced air oven. A typical cure cycle employed was 1 h at 100 °C followed by heating to 300 °C over 3 h and holding at 300 °C for 1 h. The films were removed from the glass plates by lifting the edges with a razor blade. Samples for reflectivity measurements were made by casting or affixing films onto 35 cm square glass plates.

The metallized films reported in Tables 7 and 8 were prepared in a similar manner except for the variation of the starting silver compound and secondary ligands. The cure cycle was 1 h at 100 °C and 1 h each at 100, 200, and 300 °C in a forced air oven. In a few cases the silver system was not soluble in the poly(amic acid) solution. These cases included (1) silver(I) oxide, (2) silver(I) carbonate–trifluoroacetylacetone, and (3) silver(I) acetate–dibenzoylmethane.

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Table 1. Reflectivity Data as a Function of Concentration for Silver Acetate/Hexafluoroacetylacetone-Doped BTDA/4,4'-ODA Films[a]

wt % silver[b]	polymer repeat unit/ metal ratio	HFAH/ Ag ratio	reflectivity[c] (angle and percent transmittance)		
			20°	45°	70°
2.5	8.7/1	1.2	43	32	12
5.0	4.3/1	1.2	68	59	33
7.4	2.8/1	1.1	75	64	46
9.9	2.0/1	1.1	79	69	49
12.1	1.6/1	1.2	82	65	52
17.9	1.0/1	1.1	76	54	36

[a] Cure cycle: 100 °C for 1 h; 100–300 °C over 3 h; 300 °C for 1 h. Forced air oven. [b] Percent silver calculated only on the basis of poly(amic acid) and silver metal. Other added components were assumed to be thermally degraded to volatile products. [c] Data are for the air-side only of the cured polymer films. Relative to a Perkin-Elmer front-aluminized glass mirror with 92% reflectivity at 531 nm.

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 0.42% (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. Surface and volume resistivities of selected films were measured with a Keithley 617 electrometer and 6105 resistivity chamber. 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. Elemental analyses were done by Galbraith Laboratories, Inc.

Results and Discussion

Synthetic Considerations. As summarized in Tables 1 and 2 thermal imidization and curing of BTDA/4,4'-ODA poly(amic acid) solutions in DMAc containing soluble silver(I) as the (hexafluoroacetylacetonato)silver-(I) complex species leads to polyimide films with lustrous metallized surfaces. These films have excellent specular reflectivity. They also sustain the mechanical properties of imidized BTDA/4,4'-ODA control films as seen from the data presented in Table 3. All films are flexible and can be creased without breaking. To obtain even modest levels of reflectivity upon thermal treatment, it is essential that the silver(I) dopant system be soluble in the poly(amic acid)–DMAc solution and in the solvent free poly(amic acid) film that results during the cure cycle. That is, the silver(I) species must remain unaggregated and homogeneously dispersed through-

**Table 2. Reflectivity Data as a Function of Additive Concentration, Atmosphere, and Cure Cycle for Silver Acetate/
Hexafluoroacetylacetone-Doped BTDA/4,4'-ODA Films[a]**

section designation	cure cycle	wt % silver[b]	polymer repeat unit/ metal ratio	HFAH/Ag ratio	reflectivity angle and percent transmittance		
					20°	45°	70°
A	60, 100, 200, 300, 1 h each	9.6	2.1/1	1.0/1	72	63	49
	100 1 h; 100–300 3 h; 300 1 h	10.0	2.0/1	1.0/1	70	60	47
B	60, 100, 200, 300, 1 h each	8.7	2.3/1	1.1/1	71	61	47
	60, 100, 200, 300, 1 h each	8.8	2.3/1	1.9/1	72	52	27
	60 1 h; 100–300 5 h, 300 1 h	8.6	2.3/1	1.1/1	73	58	48
	100 1 h; 100–300 3 h; 300 1 h	8.6	2.4/1	1.1/1	74	63	46
	100, 150 1 h each; 150–200 1.5 h; 200–300 0.7 h; 300 1 h	8.6	2.4/1	1.1/1	67	57	45
C	60, 100, 200, 300, 1 h each	7.8	2.6/1	1.1/1	72	62	40
	100 1 h; 100–300 3 h; 300 1 h	7.6	2.7/1	1.1/1	72	62	47
D	100 1 h; 100–300 3 h; 300 1 h	5.0	4.3/1	1.3/1	67	58	36
	100 1 h, 210 3 h, 300 1 h	5.0	4.2/1	1.1/1	69	55	32
E	Cured in nitrogen 60, 100, 200, 300 1 h each	7.7	2.6/1	1.1/1	69	56	30
	postcured 300 1 h in air				64	52	29

[a] Cure cycle: 100–300 °C over 3 h; 300 °C for 1 h in a forced air oven. [b] Percent silver calculated only on the basis of poly(amic acid) and silver metal. Other added components were assumed to be thermally degraded to volatile products. [c] Relative to a Perkin-Elmer front-surfaced aluminum optical mirror.

**Table 3. Mechanical and Resistivity Data for Silver(I)
Acetate-Hexafluoroacetylacetonate Doped
BTDA-4,4'-ODA Films**

wt % silver	modulus (Ksi)	tensile strength (Ksi)	surface resistivity/ volume resistivity
0[a]	449	21	6.5×10^{15} Ω (air-side) 1.5×10^{17} Ω (glass-side) 9.2×10^{17} Ω cm (volume)
5.0[a]	497	22	8.4×10^{16} Ω (air-side) 7.1×10^{16} Ω (glass-side) 7.8×10^{16} Ω cm (volume)
7.4[a]	504	23	1.7×10^{17} Ω (air-side) 9.9×10^{16} Ω (glass- side) 6.8×10^{17} Ω cm (volume)
9.8	402	17	6.5×10^{16} Ω (air-side) 6.7×10^{14} Ω (glass-side) 3.1×10^{17} Ω cm (volume)

[a] The densities of the first three films, top to bottom, are 1.429, 1.451, and 1.487 g/cm^3. The density of bulk silver (ffc) is 10.5 g/cm^3.

out the polymer until reduction of silver(I) occurs. This facilitates the formation of single silver(0) atoms or very small clusters of silver(0) which are necesary for migration of metallic silver to the polymer surface to form an acceptably smooth and uniform reflective layer. Faupel et al.[12] have demonstrated in vapor deposition studies that only single atoms or small clusters of silver can diffuse within a polyimide matrix.

Common simple silver(I) salts such as silver(I) nitrate and tetrafluoroborate, which are soluble in DMAc, do not give metallized films of acceptable quality as will be discussed later. Many other uncomplicated silver(I) compounds such as the halides, cyanide, sulfate, and oxide are insoluble in DMAc and similar solvents useful for polymer dissolution. Thus, it was necessary to search for more complex soluble silver(I) species which are easily prepared at reasonable cost and are thermally and photochemically stable. We chose the silver(I) acetate–hexafluoroacetylacetone system. Silver(I) acetate is readily available in excellent purity (99.99%), is thermally and photochemically stable, and is not

hygroscopic. However, it is insoluble in common poly-(amic acid) solvents such as DMAc. Solubilization of silver(I) acetate can be accomplished readily as illustrated in the following reaction where hexafluoroacetylacetone undergoes proton transfer to the acetate ion of silver(I) acetate yielding the β-diketonate complex and acetic acid. Both products are soluble in the BTDA/4,4'-ODA-DMAc poly(amic acid) solution.
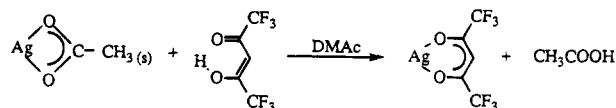
The equilibrium constant for this dissolution reaction is large due to the enhanced acidity of the fluorinated β-diketone, HFAH (pK_a = 4.35),[13] coupled with the significant basicity of the acetate ion (pK_b = 9.3) and due to the much larger stability constants for metal–β-diketonate complexes relative to metal–acetate complexes.[14] Under similar conditions, i.e., a 1:1 metal-to-ligand stoichiometry, less acidic β-diketones such as acetylacetone (pK_a = 8.93),[15] trifluoroacetylacetone (pK_a = 6.3),[16a] benzoylacetone (pK_a ~ 8),[16b] and dibenzoylmethane (pK_a ~ 8),[16b] do not bring silver(I) acetate into solution in DMAc. However, excess trifluoroacetylacetone coupled with the poly(amic acid) of BTDA/4,4'-ODA does dissolve silver(I) acetate. Solid acetylacetonate and trifluoroacetylacetonate complexes of silver(I) have been isolated, albeit in somewhat less than pure and/or stable forms. However, the (hexafluoroacetylacetonato)silver(I) complex, although reported once in the literature as a dark solid which did not melt below 300 °C,[17] is stable only with the inclusion in the metal coordination sphere of soft ligands such as dienes and phosphines.[18,19] (Acetylacetonato)silver(I) is not soluble

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2174 *Chem. Mater., Vol. 7, No. 11, 1995*

Southward et al.

in DMAc and similar polar solvents necessary for the dissolution of poly(amic acids), and (trifluoroacetylacetonato)silver(I) is difficult to prepare reproducibly and does not give metallized BTDA/4,4'-ODA films of reproducible quality.[20] Thus, hexafluoroacetylacetone is rather singular in rendering silver(I) acetate soluble to give a stable silver(I)-β-diketonate complex in solution. The silver(I) in this complex then undergoes reduction to give metallized polymer surfaces.

From magnified observation of the silver(I)–HFA metallization of BTDA/4,4'-ODA poly(amic acid) films (dried 18 h in slowly flowing air at 10% relative humidity) using a hot stage (3 °C/min temperature rise), one observes that the films begin to darken (orange-brown) near 160 °C, to exhibit a definite sheen near 190 °C, and to show a distinctly silvered surface near 220 °C. If the doped film is heated slowly to and held constant at 200 °C, the film surface is distinctly silvered after 30 min. The formation of metallic silver is reasonably related to thermal decomposition of the in situ formed silver(I)–HFA complex which is accompanied by silver(I) reduction. It is interesting to observe that the TGA curve for the hexafluoroacetylacetonate complex of silver(I) stabilized with COD, [(COD)(HFA)-Ag], loses COD (bp 150 °C/760 Torr) over the temperature range 100–160 °C and then decomposes rapidly in the range 160–220 °C to predominately metallic silver.[20]

However, we do not know the detailed mechanism for reduction to silver(0). Silver(I) oxide may be involved. It is reported that this oxide slowly begins to liberate oxygen with decomposition to metallic silver at 160 °C with rapid oxygen evolution occurring at 250–300 °C; the partial pressure of oxygen reaches 1 atm at 184 °C.[21] Kirshenbaum et al.[22] have presented evidence that silver(I) oxide is involved in the sealed tube thermal decomposition of silver(I) perfluorobutyrate in the temperature range 260–275 °C. The silver(I) oxide was then thought to be reduced by carbon monoxide which is a product of the decomposition. However, in limited amounts of carbon monoxide, which is the case in our forced air oven, silver(I) oxide may simply thermally liberate metallic silver. As presented in Table 7 silver(I) oxide is reduced to metallic silver when suspended heterogeneously in BTDA/4,4'-ODA poly(amic acid) film which is thermally cured to 300 °C. This film is not reflective due to large irregularly spaced silver(0) aggregates. The X-ray pattern for this silver(I) oxide film showed only the characteristic reflections for crystalline face-centered cubic silver. All reflections of cubic silver oxide, including the intense peak at 2.73 Å (111), were absent. On the other hand, silver(I) reduction may occur via a straightforward homolytic metal–oxygen bond cleavage to give silver(0) and the neutral organic radical derived from HFA. The conjugation of HFA and the electron withdrawing fluorine groups should stabilize this radical intermediate. Fetizon and co-workers[23a] have presented substantial evidence for such a mech-
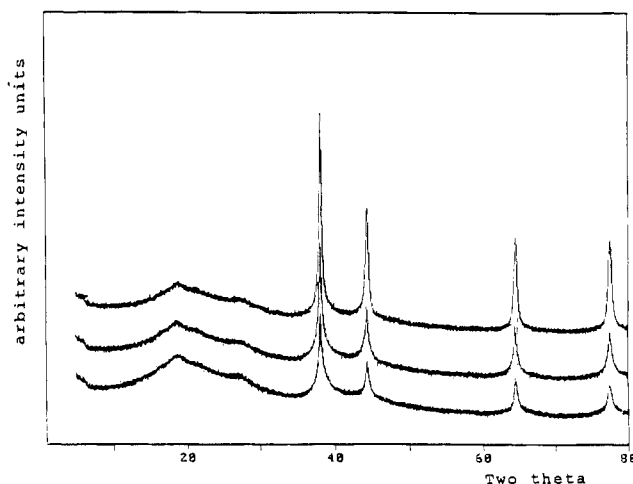

Figure 1. X-ray diffraction patterns for 5.0, 7.4, and 12.1% silver(0) BTDA/4,4'-ODA films of Table 1. The films are all at a thickness of 0.91 mil and scaled to the same ordinate.

Table 4. Elemental Analyses of Silver Acetate/Hexafluoroacetylacetone-Doped BTDA/4,4'ODA Films

	calcd (wt %)				found (wt %)				
Ag	F	C	H	N	Ag	F	C	H	N
0 (control)	0	71.6	2.90	5.76	0	0.065	70.4	3.05	5.58
5.32	0	67.8	2.75	5.45	4.82	1.45	66.1	2.77	4.93
7.86	0	66.0	2.67	5.31	7.34	1.95	64.5	2.80	5.06
10.5	0	64.1	2.60	5.15	11.2	2.05	62.3	2.77	4.70
12.8	0	62.4	2.53	5.02	11.6	2.44	60.9	2.23	4.90

anism in the synthetically important reduction of alcohols by silver(I) carbonate supported on Celite, and Yang and Kutal[23b] have suggested a similar pathway of ligand–metal electron transfer in the photochemical-initiated reduction of *trans*-tris(trifluoroacetylacetonato)-rhodium(III) to a rhodium(II) species and free trifluoroacetylacetone.

Elemental analysis data are presented in Table 4 for four films prepared to have 5–12% silver after thermal curing. The elemental percentages found are in reasonable agreement with that expected if the organic moieties of the silver(I) acetate–HFAH dopant are predominately decomposed and volatilized from the system and if the silver metal in the films does not cause significant oxidative degradation of the polyimide to volatile products. For all the films in Table 1 the X-ray diffraction patterns are consistent with all of the silver both in the bulk and at the surface having been reduced to silver(0). Figure 1 shows a regular increase in the intensity of the silver(0) reflections with increasing dopant concentration for films of the same thickness, while transmission electron microscopy (e.g., Figure 2) shows a relatively constant surface layer of silver(0) at ca. 60–70 nm in thickness. The reduction of silver(I) both in the bulk and at the surface of the polymer is not surprising as cure studies in nitrogen (Table 2) show that there is no significant role for either atmospheric oxygen or moisture in the formation of a reflective surface. Thus, it is not necessary for oxygen or water to diffuse into the polymer, and the chemistry in the bulk should be similar to that at the surface. Finally, it is notable that there is a gradual increase in the

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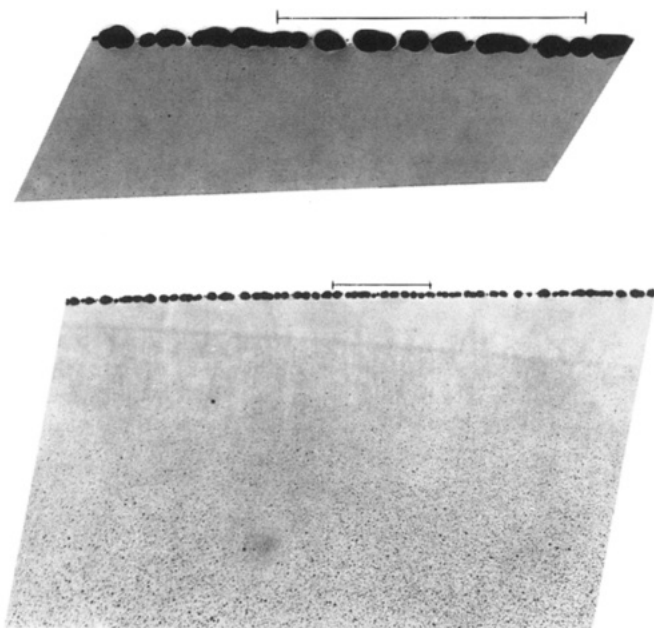
Figure 2. Transmission electron micrographs (different magnifications) of the 9.9% silver(0)-BTDA/4,4′-ODA film of Table 1. The bars represent 1 μm.

fluorine content with increasing dopant concentration. Our analytical results parallel those obtained with [(COD)(HFA)Ag]-doped BTDA/4,4′-ODA by Rubira et al.[10]

Reflectivity and Surface Characterization. Table 1 displays specular reflectivity data for a series of BTDA/4,4′-ODA films with varying mole ratios of polymer repeat unit to metallic silver from 8.7:1 (2.5% Ag^0) to 1.0:1 (17.9% Ag^0). The air side of each film is distinctly metallic and bright while the glass side is metallic gray in appearance without luster and minimal (<5%) measured reflectivity. The scanning electron micrographs presented in Figure 3 show an air-side deposition of globular silver clusters which are relatively uniform in size and evenly spread over the surface of the film; the glass-side surface is much less homogeneous. The air-side reflectivity at a 20° angle of incidence increases rapidly (43−68%) in going from 2.5 to 5.0% silver and, thereafter, increases only slowly, reaching a maximum 82% at the 12.1% silvered film. Reflectivity falls as a function of increasing angle of incidence due to an irregular and discontinuous silver surface. No attempt was made to polish the surfaces. For the 17.9% film the reflectivity is modestly, but reproducibly, diminished at the larger reflectivity angles of 45° and 70°, relative to the 7−12% films. This may be due to greater irregularity of the silver clusters at the surface with high silver(I) dopant concentrations.

The films have strongly adhered surface layers and are completely stable to removal of silver by a variety of adhesive tapes. The mechanism for this strong adhesion may be 2-fold. A significant contribution to the metal−polymer adhesion may involve mechanical interlocking. This is supported by the surface composition data from XPS (Table 5) which shows that there is only ca. 20 atom % silver on the reflective air-side surface. Carbon is abundant, which indicates that substantial polymer surrounds and separates the silver clusters. Adhesion may also be due to the interfacial interaction of silver with carboxylate groups. Boerio
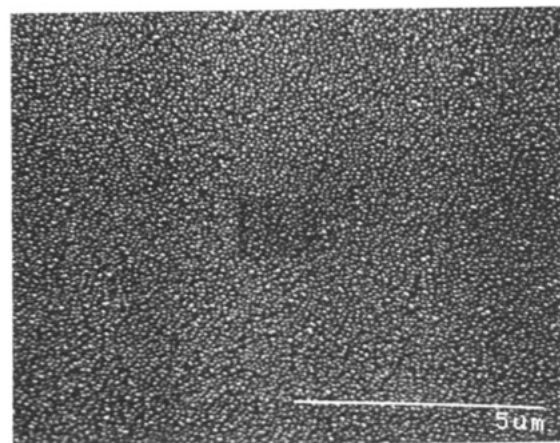
AIR SIDE
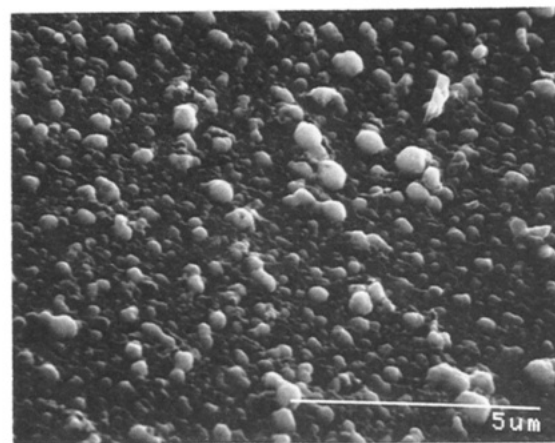
GLASS SIDE

Figure 3. Scanning electron micrographs of the air and glass sides of an 8.8% silver(0)-BTDA/4,4′-ODA film prepared as those in Table 1.

Table 5. X-ray Photoelectron Spectroscopy Surface Composition for Silver Acetate/ Hexafluoroacetylacetonedoped BTDA/4,4′-ODA Films (Relative Atomic Percent[a])

wt % silver	film surface	silver	fluorine	carbon	oxygen	nitrogen
5.0	air	20.3	2.0	58.5	15.95	3.3
	glass	2.1	22.2	56.3	11.58	7.8
7.4	air	16.5	3.4	63.6	12.7	3.8
	glass	3.9	24.7	57.1	9.9	4.4
9.9	air	17.5	3.2	63.1	12.3	3.9
	glass	0.8	18.3	61.1	12.2	7.6

[a] Same film samples as reported in Table 1.

and co-workers[24] have concluded from surface enhanced Raman scattering and X-ray photoelectron spectroscopy of polyimides cured on silver substrates that imidization is inhibited by the formation of silver carboxylate complexes by way of the amic acid carboxyl groups. The films studied, however, were only thermally cured to a temperature of 200 °C. Meyer et al.[25] have also reported XPS evidence for the formation of silver carboxylate

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(25) Meyer, W.; Grunze, M.; Lamb, R.; Oretga-Vilamil, A.; Schrepp, W.; and Braun, W. *Surf. Sci.* **1992**, *273*, 205.

complexes with alkylammonium salts of the poly(amic acid) of PMDA/4,4'-ODA cast on a clean silver surface. While carboxylate complexes may be formed at some early point in the poly(amic acid) cure cycle, it is unclear that the polyimide film cured for an hour at 300 °C would allow the metal–carboxylate interaction to persist. TGA measurement shows that solid bulk silver(I) acetate is completely decomposed in air to silver metal by 280 °C at a heating rate of 2.5 °C/min.[20] On the other hand, Madix and co-workers[26] found that for an isolated acetate ion adsorbed on the silver (110) surface, the acetate decomposition temperature to carbon dioxide, acetic acid, methane, and ketene and adsorbed carbon was 367 °C. Thus, carboxylate groups bound to silver clusters, Ag_n^+,[27] may well survive the 300 °C cure temperature and exhibit a different thermal chemistry than bulk silver(I) acetate. While imidization may be inhibited by the formation of silver carboxylate complexes, this same interaction may enhance adhesion after thermally curing the polyimide at 300 °C. Indeed, Rubira et al.[10] found for metallized BTDA/4,4'-ODA films formed using [AgHFA(COD)] that the photoelectron spectrum had carbon and oxygen photopeaks that matched well with those from silver benzoate and acetate. Finally, Gerenser[5b] found significantly improved adhesion for silver which was vapor deposited on oxygen-plasma treated poly(ethylene terephthalate) as opposed to argon-treated or untreated polymer. XPS data with an observed photopeak at 531.2 eV (O 1s) were consistent with the formation of a silver(I) carboxylate species in this polyester.

Table 5 presents surface composition as determined by XPS for three of the reflective films presented in Table 1. As mentioned, it is striking to note the large amount of polymer that is still in the surface region of the film on both the air and glass sides. While there is migration of silver to the air-side surface of the film, the migrating silver atoms and/or small clusters aggregrate to give surface islands which appear from microscopy data to be roughly 60–70 nm in thickness. Interestingly, TEM data (Figure 2) suggest that the adjacent several hundred nanometers are substantially free of silver(0) particles; this "depletion zone", for which we have no explanation at present, was also observed in [(COD)(HFA)Ag] metallized BTDA/4,4'-ODA films reported by Rubira et al.[10] The TEM micrograph clearly indicates that there is no continuity of the metal surface. This is also clear from the fact that none of the films of this study were surface conductive (Table 3). Clearly, there must be substantial amounts of polymer surrounding the silver globules. This does not seem to be the case for surface conducting palladium-doped BDTA–4,4'ODA films using a self-metallizing procedure involving thermal decomposition of dichlorobis(dimethyl sulfide)palladium(II).[28] The difference may well be due to the much greater catalytic activity of palladium(0) over silver(0) for the oxidation of organic substrates, as will be discussed later. The glass-side of the film has much less metal and is strikingly rich in fluorine. It may be

that organofluorine species liberated in the thermal decomposition of the silver–HFA complex undergo glass catalyzed/promoted or simply thermal reactions with the polymer backbone such as acylations via the very reactive trifluoromethylacylium ion. Indeed, as seen in Figure 4a, a prominent C(1s) XPS peak for the glass-side only is centered at 292.5 eV, which is that expected for CF_3 groups.[24b] This peak is virtually absent for the air-side surface. The bulk fluorine content of the film is also enhanced but to a much lesser degree. The presence of fluorine does not seem to be due to silver(I) fluoride which might be formed by thermal decomposition. Silver(I) fluoride is soluble in water. Refluxing finely cut metallized BDTA/4,4'ODA films for several hours in water gave solutions which did not precipitate any silver(I) iodide on the addition of aqueous potassium iodide. Furthermore, no X-ray reflections were observed in any films corresponding to crystalline AgF. Finally, the F(1s) XPS spectrum, displayed in Figure 4b, shows only a single symmetric peak centered at 688.3 eV which is consistent with fluorine covalently bound to carbon.[24c] The F(1s) photopeak in nickel(II) trifluoroacetate appears at 688.4 eV. Inorganic fluorides such as those of lithium, sodium, potassium, calcium, show a F(1s) peak in the range 684–685 eV.[24c] Thus, there is no indication of ionic inorganic fluoride at the glass or air surface.

Table 2 presents reflectivity data for the second set of BTDA/4,4'-ODA–silver(I) acetate/HFAH silvered films which primarily vary with regard to the thermal cure program employed. Sections A–C of the Table 2 demonstrate that there is virtually no effect on reflectivity at silver concentrations in the range 7.6–10% by varying the thermal cure cycle stages as long as a final temperature of 300 °C is attained for a duration 1 h. Of particular interest were the slower cure cycles listed in section B. Since it is well-known that the slow deposition of silver onto glass from Tollen's type silver(I) reductions of aldehydes gives mirrors of high quality, it was of interest to see if slower heating, with slower formation of silver(0) atoms, of the doped BTDA/4,4'-ODA solutions would give more highly reflecting surfaces. Visual observation of the curing silver(I) acetate/HFAH doped film makes it clear that the reduction process begins below 200 °C when the film is cured at a rate of ca. 3 °C/min. The data of section B show that lingering in the region of silver reduction (150–200 °C) has no significant effect on observed reflectivity. Furthermore, the addition of 2 equiv of HFA does not change reflectivity. Again, as the concentration of silver is lowered to 5.0% (section D) a small decrease in reflectivity is observed. Section E shows that there is not a major role for air or atmospheric moisture in reduction of silver(I) and generating the mirror during the cure cycle as films cured in dry nitrogen have similar reflectivities to those cured in air. Since metallic silver is known to activate molecular oxygen[29] and silver(I) coordinates to arenes,[30] it would not have been surprising to see a difference in film properties between air- and nitrogen-cured systems. It also appears that the water liberated in the imidization of the BTDA/4,4'-ODA poly(amic acid) is not intimately involved in the reduction and migration of silver. This was demonstrated

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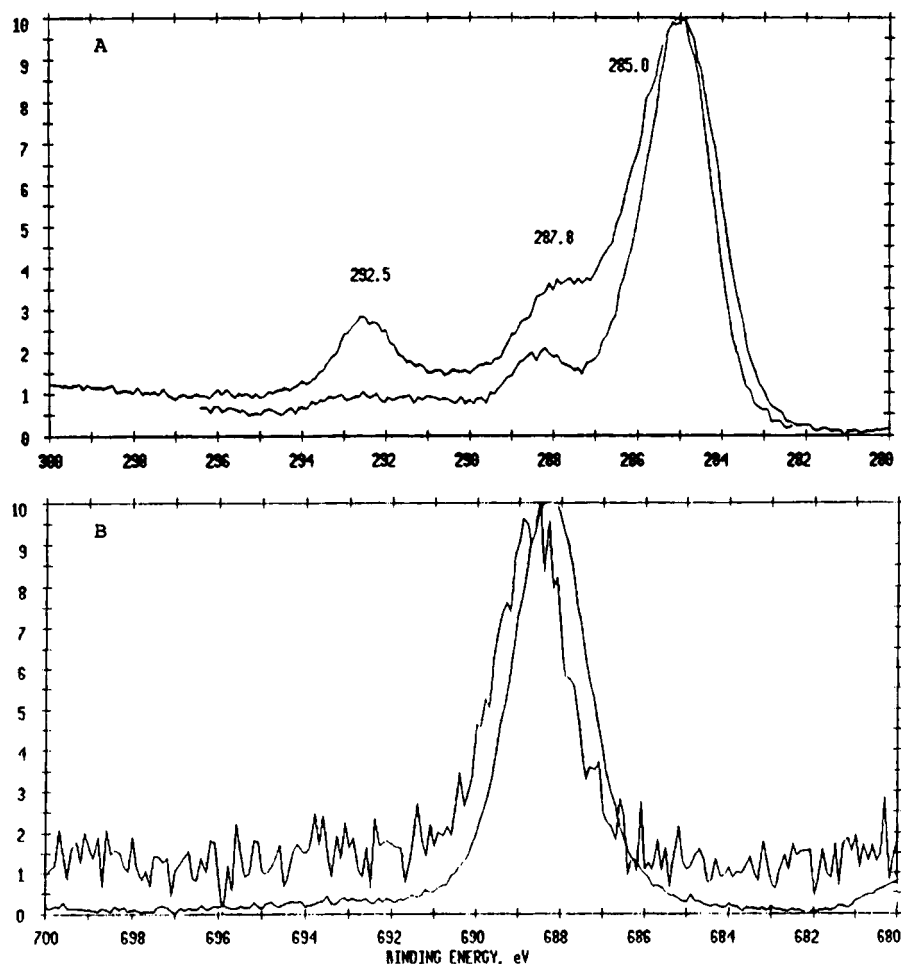(30) Hartley, F. M. *Chem. Rev.* **1973**, 163.

Figure 4. (a) C(1s) photoelectron spectra for the air and glass sides of the 9.9% silver(0)—BTDA/4,4'-ODA reported in Table 1. Upper trace, glass side; lower trace, air side. (b) F(1s) photoelectron spectra for the air and glass sides of the same film. Smooth trace, glass side; jagged trace, air side.

Table 6. Thermal Data for Silver Acetate/Hexafluoroacetylacetone-Doped BTDA—4,4'-ODA Films

wt % silver	T_g by DSC (°C)	TGA 10 wt % loss in air (°C)	TGA 10 wt % loss in N_2 (°C)	CTE (ppm/°C)
control	275	524	540	42.8[b]
2.5	269	361	531	a
5.0	268	379	489	42.7
7.4	270	372	488	43.6
9.9	272	376	491	42.8
12.1	269	361	531	a
17.9	272	361	477	a

[a] CTE not measured. [b] Numata, S.; Fujisaki, K.; Makino, D.; Kinjo, N. *Recent Advances in Polyimide Science and Technology*, Weber, W. D., Gupta, M. R., Eds.; Society of Plastics Engineers: New York, 1987; p 164.

by the fact that the soluble polyimide derived from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, 6FDA, and 1,3-bis(3-aminophenoxy)benzene, APB, when doped with the same silver(I) acetate—HFAH couple used in this study, gives films with reflectivity similar to those reported herein.[11] Since 6FDA/APB is already in the imidized form when the silver(I) dopant is added, no water is generated during thermal heating cycle.

Thermal Properties. Thermal data for films of Table 1 are presented in Table 6. The glass transition temperatures (run on sealed samples) of the metallized films are only slightly different from that of undoped BTDA/4,4'-ODA. This is consistent with the passivity of the silver metal toward organic molecules in general and toward the polymer functionalities in specific such

that there is no cross-linking of chains via interaction with silver(0) clusters or via silver(0) catalyzed organic cross-linking reactions which would elevate T_g. However, the formation of metallic silver clusters in the bulk of the polymer as well as on the surface diminishes the thermal oxidative stability of the polyimide. In a nitrogen atmosphere the temperature at which there is 10% weight loss is 10—50 °C lower than that of the undoped polymer. In air there is a dramatic reduction of thermal oxidative stability with a 10% weight loss temperature that is ca. 150 °C lower than the control. Nonetheless, the thermal stability of the mirrored films in air is more than adequate for most purposes.

Two possible contributions to the lowering of thermal oxidative stability of the BTDA/4,4'-ODA films containing metallic silver include:[31,32] (1) metal activation of the π-systems of the polymer to attack by dioxygen or monoatomic oxygen and/or metal-induced bond cleavage of the organic framework followed by oxidation; (2) metal(0)-induced dissociation of dioxygen to surface-adsorbed monoatomic 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[32] unlike palladium(0) which forms numerous

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Table 7. Metallized Films Prepared from Miscellaneous Silver(I) Compounds in DMAc BTDA/4,4′-ODA Resin Solutions

silver(I) additive[a]	% metal	reflectivity (% at 20°)	X-ray d spacings (Å)	appearance (air/glass)	conductive (four-point probe)
(Me$_3$P)Ag(HFA)	10	9.4 8.0	2.36 (100), 2.04 (31), 1.44 (13), 1.23 (17)	purplish sheen/gray	no
(Ph$_3$P)Ag(HFA)	10	16.7 17.4	2.35 (100), 2.04 (25), 1.44(11), 1.23(15)	metallic blue/pewter	no
Ag(FOD)	10	36.7 33.7	2.38(100), 2.05(23), 1.45(12), 1.23(11)[c]	metallic green/beige	no
(Me$_3$P)AgI	10	7.2 7.0	3.98 (78), 3.75 (78), 3.63 (42), 3.41 (4.9), 2.30 (100), 2.18 (5.7), 2.05 (3.5), 1.99(7.3), 1.96 (31), 1.50 (2.7), 1.48 (2.6), 1.33 (2.4)	heterogeneous, brown (air and glass)	no
AgNO$_3$[b]	5.4	20	2.35 (100), 2.03 (26), 1.43(12), 1.23(14)	metallic green/brown	no
AgBF$_4$	10	48	2.77 (33), 2.36 (100), 2.04 (29), 1.44 (13), 1.23 (11)	metallic green/pewter	no
Ag$_2$O (insoluble)	10	4.9	2.35 (100), 2.04 (34), 1.44 (15), 1.23 (14)	heterogeneous brown (air and glass)	no

[a] Ligand abbreviations: HFA = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato; ACAC = 2,4-pentanedionato; FOD = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato. [b] This sample is reported as 5.4% silver since concentrations near 10% give severely brittle and broken films. [c] Reflections are broad.

zerovalent metal complexes with unsaturated organic species.[33] It is silver(I) which is isoelectronic with palladium(0) and forms olefin and arene complexes. The X-ray data for the films of Table 1 do not suggest any silver(I), which could catalyze organic degradation, remaining in the films, e.g., no crystalline silver(I) oxide or silver(I) fluoride; only reflections due to crystalline metallic silver are observed as previously mentioned. Also, dissolution of a silver-metallized 6FDA/APB (a soluble polyimide) film in DMAc[11] or refluxing this film in water for 12 h did not result in any soluble silver(I) species which could be precipitated with aqueous sodium bromide. Similar extraction of metallized BTDA/4,4′-ODA films with boiling ammonia did not give observable silver halide when neutralized with hydrochloric acid; this is consistent with no residual silver(I) fluoride, silver(I) acetate, silver(I) oxide, or ionic silver(I) in the metallized film. It is most plausible that the degradation efficacy of metallic silver involves the second option, that is, the well-established ability of metallic silver to bind and reversibly dissociate dioxygen[37] and thus produce a continuous supply of absorbed atomic oxygen which can degrade the polymer by its ability to abstract protons and to serve as a strong nucleophile.[38]

The linear coefficients of thermal expansion (Table 6) of silver-doped BTDA/4,4′-ODA films are essentially unchanged relative to an undoped film. We interpret this constancy of the CTE to be consistent with essentially all of the silver having undergone reduction to the metallic state, and in the native state silver would not bind strongly to functionalities in polymer chains. This lack of silver(0) interaction would not generate any effective cross-linking which is commonly responsible for a lowering of the CTE in doped systems. Since the CTE for silver is 19 ppm, there is no continuous layer

of silver at the film surface as the TEM and surface conductivity data show.

Additional Silver(I) Dopant–BTDA/4,4′-ODA Systems. The mechanism for the reduction of silver(I) to the metallic state is uncertain. We do know from data displayed in Tables 7 and 8 that the silver(I) dopant must be soluble with the poly(amic acid) in DMAc in order to obtain reflective films. For example, cured BTDA/4,4′-ODA films prepared with the insoluble dopants, silver(I) oxide, silver(I) acetate–dibenzoylmethane, and silver(I) carbonate-1,1,1-trifluoro-2,4-pentanedione (Tables 7 and 8) are distinctly (visually) heterogeneous and have reflectivities at 20° of 10 % or less. The question remains as to whether it is only necessary to have a soluble silver(I) species in any form, complexed or ionic, coupled with the amic acid of BTDA/4,4′-ODA in DMAc to undergo reduction and produce a mirrored surface. Table 7 contains reflectivity data for six silver compounds which are soluble with the amic acid of BTDA/4,4′-ODA in DMAc. None of the six soluble silver compounds gave highly reflective films under similar cure conditions used with silver(I) acetate–HFAH even though X-ray diffraction data show that all of the additives generate crystalline metallic silver except for the tetrameric iodo(trimethylphosphine)-silver(I). With this latter additive trimethylphosphine is liberated with heating (ca. 200 °C) to leave insoluble silver(I) iodide heterogeneously dispersed throughout the film. X-ray data support the presence of silver(I) iodide and show that no metallic silver is produced in this system. Surprisingly, the trimethylphosphine adduct of AgHFA gives films that are less than 10% reflective. This is puzzling since this complex is an adduct stabilized [AgHFA] complex[19] similar to [COD(HFA)Ag] which gives films with reflectivities of ca. 65%.[10] The partially fluorinated Ag(FOD) gives modestly reflective films. The best reflectivity, 48% at 20°, reported in Table 7 was obtained with silver(I) tetrafluoroborate, a simple silver(I) compound with a stable and chemically benign anion. The mechanical properties of this AgBF$_4$ film were similar to those for the films of Table 1. This suggests that the brittleness seen with the silver(I) nitrate doped films is due to the nitrate anion which at elevated temperatures is a proficient oxidizing agent. It is not clear what functions as the reducing agent toward silver(I) in the AgBF$_4$–BTDA/

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Table 8. Additional Metallized Films Prepared from Silver(I) Acetate with a Variety of Solubilizing Ligands in DMAc BTDA/4,4'-ODA Solution

additive	% metal	reflectivity (% at 20°)	X-ray d spacings (Å)	appearance air/glass	conductive (four-point probe)
Ag(C₂H₃O₂)/HFAH	9.9	79	2.37 (100), 2.05 (32), 1.45 (14), 1.23 (12)	bright metallic/pewter	no
Ag(C₂H₃O₂)/HFAH−PPh₃	8.2	34/24/9	2.34 (100), 2.03 (23), 1.44 (9), 1.23 (8)	brown metallic/pewter	no
Ag(C₂H₃O₂)/TFAAH	7.1	57/46/44	4.41 (16), 2.36 (100), 2.04 (16), 1.475 (1.4), 1.44 (10), 1.23 (9)	bright metallic/pewter	no
Ag(C₂H₃O₂)/₂TFAH	8.5	38/27/11	2.34 (100), 2.02 (17), 1.44 (9), 1.23 (9)	metallic green/dark	no
Ag(C₂H₃O₂)/₂TFAH	10.8	46/36/15	2.36 (100), 2.05 (15), 1.44 (8), 1.23 (7)	metallic green/dark	no
Ag(C₂H₃O₂)/₂TFAH−COD	8.4	36/26/10	2.36 (100), 2.03 (13), 1.44 (7), 1.23 (7)	metallic green/dark	no
Ag(C₂H₃O₂)/₂TFAH−PPh₃	8.3	31/21/9 [53/42/18, −2 h sinter 300 °C]	2.35 (100), 2.05 (18), 1.43 (7), 1.23 (8) [2.36 (100), 2.03 (16), 1.45 (9), 1.23 (8)]	metallic green/dark	no
Ag(C₂H₃O₂)/TFAH−PPh₃	8.2	30/21/8 [42/32/12, −2 h sinter 300 °C]	2.36 (100), 2.04 (19), 1.44 (11), 1.23 (8) [2.35 (100), 2.04 (16), 1.44 (7), 1.23 (7)]	metallic green/dark	no
Ag(C₂H₃O₂)/DBM (insoluble)	8.3	11/7/7	2.34 (100), 2.03 (16), 1.44 (7),1.23 (8)[b]	heterogeneous silver globules	no
Ag₂(CO₃)/2 TFAH (partially soluble)	9.4	6.8 5.7	2.35 (100), 2.04 (36), 1.44 (16), 1.23 (14)	heterogeneous brown/same	no

[a] Solubilizing ligand abbreviations: TFAAH = trifluoroacetic acid; TFAH = 1,1,1-trifluoroacetylacetone; DBM = dibenzoylmethane; COD = 1,5-cyclooctadiene; PPh₃ = triphenylphosphine. [b] Peaks are very broad and of low intensity relative to the amorphous polymer halo.

4,4'-ODA system since neither boron nor fluorine in the tetrafluoroborate anion can be reasonably oxidized; the polymer itself may function as the reducing agent. Thus we can see from Table 7 that the reduction of silver(I) in a curing polymer film in such manner so as to generate highly reflective films is subtle and requires much more than simply having a soluble silver(I) additive.

Table 8 reports data for the preparation of silvered films using silver(I) acetate coupled with coordinating ligands other than HFAH by itself as reported earlier in Tables 1 and 2. As discussed above the trimethylphosphine complex of [AgHFA] gave films with poor reflectivity and, consistent with this observation, the addition of 1 equiv of triphenylphosphine to silver(I) acetate and HFAH gave films which were only modestly reflective even though the X-ray data demonstrated that reduction to metallic silver had occurred. The addition of trifluoroacetic acid (pK_a = 0.6) readily dissolves silver-(I) acetate to form silver(I) trifluoroacetate in solution. This dopant system gave the most reflective films (57%) except for those of the silver(I) acetate−HFAH systems reported in Table 1. Trifluoroacetylacetone (TFAH) is similar to HFAH but is less acidic as mentioned earlier. One equivalent of TFAH would not dissolve silver(I) acetate in DMAc; however, a 2 equiv did render the dopant system soluble. Upon thermal curing the reflectivies of 8.5 and 10.8% silver(0) films were only 38 and 46%. Metallized polyimide films that were conducting have been prepared with the isolated complex (trifluoroacetylacetonato)silver(I) have been claimed.[40] Again, the X-ray data indicated that the additive was reduced to crystalline metallic silver. Adding triphenylphosphine and 1,5-cyclooctadiene to the silver(I) acetate−TFAH system did not give any significant variation in reflectivity. In the TFAH−triphenylphosphine systems it was interesting to note that sintering the metallized films for 2 h at 300 °C improved reflectivity

notably, e.g., from 31 to 53% but did not give conductive films. Such a favorable sintering effect has been observed by Manning[41] and Reich et al.[42] for pyromellitic dianhydride/4,4'-ODA polyimide films which were fabricated electrochemically and electrolessly with an ca. 500 nm silver(0) interlayer. Reflectivity (at 1000 nm) was increased from "32 to 95%" after sintering for 5−10 h at 300−350 °C. Microscopy demonstrated that the annealing process led to a smoothing of the silver boundary layer, to larger particles and to a larger average radius of curvature of surface irregularities. With regard to our silver(I) acetate−HFAH film samples presented in Table 1, we did not observe that sintering at temperatures between 300 and 340 °C gave any improvement in reflectivity or conductivity.

Conclusions. We have demonstrated that BTDA/4,4'-ODA silvered polyimide films can be prepared from a single phase homogeneous silver(I)−poly(amic acid) solution which have excellent reflectivity, outstanding metal−polymer adhesion, and the essential mechanical characteristics of the native polyimide. 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 silver(I) reduction for several days, and the cast films do not have to be protected from light. Our approach to silvered BTDA/4,4'-ODA films gives a 20−25% improvement in reflectivity relative to the use of the rather similar [COD(HFA)Ag] complex. Furthermore, neither silver(I) acetate nor HFAH require special precautions while [COD(HFA)Ag] is reported by Partenheimer and Johnson,[18] who first synthesized the complex, to "lose olefin slowly when exposed to air" and to require refrigeration. The silver(I) acetate−HFAH films reported herein are ca. 7% more reflective than similar films prepared with silver(I) fluoride and HFAH.[43]

The films prepared with silver(I) acetate and HFAH were not found to exhibit surface conductivity signifi-

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cantly different from that of control BTDA/4,4'-ODA control films even after additional sintering. Thus, the silver aggregates at the surface are not in contact with one another. That they are separated by intervening polymer is clear from the high concentration of C, O, and N at the surface found by XPS and surface microscopy. However, BTDA/4,4'-ODA films prepared with silver(I) acetate and TFAH which were sintered for 1 h at 340 °C in air were surface conductive, although of lower reflectivity. Attempts to maximize both reflectivity and conductivity will be described in subsequent publications.[44]

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